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Bulky Ytterbium Formamidinates Stabilise Complexes with Radical Ligands, and Related Samarium "Tetracyclone" Chemistry

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Abstract: *Divalent* [Yb(DippForm)$_2$(thf)$_n$] (n = 2 (**1a**), or 1 (**1b**); DippForm = *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate) complexes were treated with the ketones: 9-fluorenone (fn), or 2,3,4,5-tetraphenylcyclopentadienone (tpc, tetracyclone), giving *ketyl*[†] complexes: [Yb(DippForm)$_2$(fn˙-*O*)(thf)] (**2**), and [Yb(DippForm)$_2$(tpc˙-*O*)] (**3**) respectively. By contrast, when perfluorobenzophenone (pfb) was treated with either **1a** or **1b**, transitory *ketyl* formation was followed by rapid decomposition via a C–F activation pathway, giving [YbF(DippForm)$_2$(thf)] (**4a**) and a highly unusual fluoride/oxide bridged species: [Yb$_5$F$_6$O$_2$(DippForm)$_5$] (**4b**). The reduction of diketones: 3,5-di-*tert*-butyl-benzo-1,2-quinone (tbbq), phenanthrene-9,10-dione (phen), or acenaphthalene-1,2-dione (acen), was also examined giving *ketyl* complexes: [Yb(DippForm)$_2$(tbbq˙-*O*$_2$)] (**5**), [Yb(DippForm)$_2$(phen˙-*O*$_2$)] (**6**), and [Yb(DippForm)$_2$(acen˙-*O*$_2$)(thf)] (**7**). An unsolvated derivative of **7**, namely [Yb(DippForm)$_2$(acen˙-*O*$_2$)] (**8**) was obtained from PhMe All *ketyl* complexes had suitably elongated C˙–O bonds, were stable in both polar and non-polar solvents - an uncommon trait for rare-earth *ketyl* complexes – and, with the exception of **3.** showed radical signals in ESR spectra. To investigate the reactivity of the tpc˙-*O ketyl* complex, **3** was treated with oxidants (CS_2, Se), reducing agents (Mg^0, KH, or [SmI_2(thf)$_2$]). Thus **3** was oxidised to tpc by Se, treatment of **3** with KH led to a ligand exchange process giving an unusual di-*ketyl* species [Yb(DippForm)(tpc˙-*O*)$_2$(thf)$_2$] (**10**), which has two *cisoid* tpc˙-*O*$^-$ ligands in very close proximity. When treated with [SmI_2(thf)$_2$], the tpc˙-*O ketyl* was further reduced to a di-anion (1-oxido-2,3,4,5-tetraphenyl-cyclopentadianide(2-), ({C_5Ph_4}–*O*)$^{2-}$ by [SmI_2(thf)$_2$], giving dimeric [{SmI({C_5Ph_4}-*O*)(thf)$_2$}$_2$] (**Sm11**) and monomeric complexes [YbI(DippForm)$_2$(thf)] (**11b**) and [YbI$_2$(DippForm)(thf)$_2$] (**11c**). Activated Sm metal reduced neutral tetracyclone to the dianion, ({C_5Ph_4}–*O*)$^{2-}$, in THF, giving tetranuclear [{Sm^{II}$_2$({C_5Ph_4}–*O*)$_2$(thf)$_3$}$_2$] (**Sm13**). Treatment of **Sm13** with iodine in situ provided access to [{SmI({C_5Ph_4}-*O*)(thf)$_2$}$_2$] **(Sm11)**, in good yield.

[†]*Ketyl:* A radical anion containing a C˙-O$^{(-)}$ group. *Abbreviations: fn: 9-fluorenone; fn˙-*O*$^-$: 9-Fluorenone *ketyl*; pfb: perfluorobenzophenone; tpc: 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone), tpc˙-*O*$^-$: 2,3,4,5-tetraphenylcyclopentadienone *ketyl*; ({C_5Ph_4}-*O*)$^{2-}$: 1-oxido-2,3,4,5-tetraphenyl-cyclopentadienide(2$^-$). tbbq: 3,5-di-*tert*-butyl-benzo-1,2-quinone; tbbq˙-*O*$_2^-$: 3,5-di-*tert*-butyl-benzo-1,2-quinone *ketyl*; phen: phenanthrene-9,10-dione, phen˙-*O*$_2^-$: phenanthrene-9,10-dione *ketyl*; acen: acenaphthalene-1,2-dione; acen˙-*O*$_2^-$*:* acenaphthalene-1,2-dione *ketyl.*

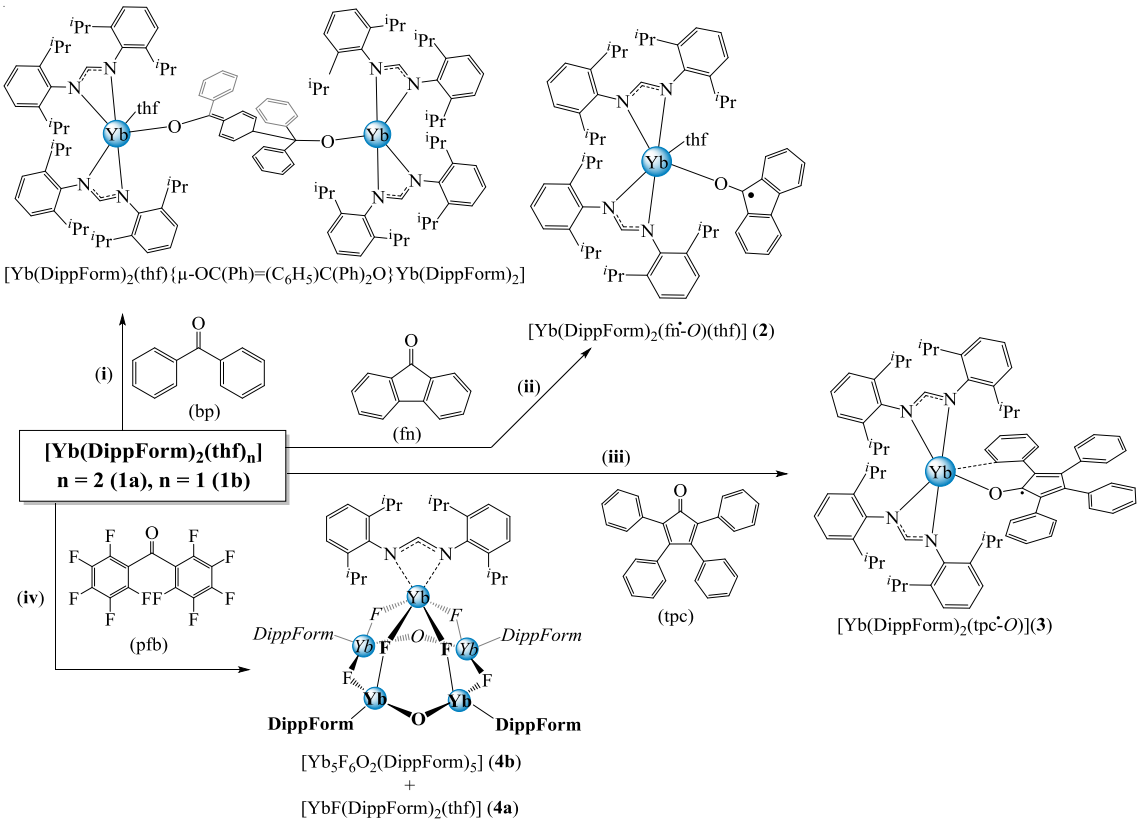
Introduction:

First reported over 100 years ago,[1] metal *ketyl* complexes have become highly important in organic chemistry, especially transient samarium ketyls in SmI_2/ketone promoted organic syntheses,[2] in addition to their ubiquitous role

in drying organic solvents. Given their highly reactive nature, isolating *ketyl* complexes is difficult, as they may have only transient existence,[3] or rapidly undergo radical C–C coupling resulting in pinacolate-type complexes.[4] Stabilisation of metal-*ketyls* is an arduous task, that requires careful consideration of co-ligands (typically of high steric demand),[5] and solvents[4b, 6] to avoid decomposition. The first crystallographically characterised metal *ketyl* complex, $[Sm^{III}(OAr)_2(thf)_2(fn^{\cdot}\text{-}O)]$ (OAr = 2,6-^{t}Bu-4-MeC_6H_2O, fn$^{\cdot}$-O^- = 9-fluorenone *ketyl*), was synthesised by the single-electron reduction (SER) of 9-fluorenone by $[Sm^{II}(OAr)_2(thf)_3]$.[4a] However, the resulting *ketyl* complex underwent pinacol coupling upon dissolution in Et_2O.[4a] Since then, there have been several other metal fn$^{\cdot}$-*O* or metal benzophenone *ketyl* (bp$^{\cdot}$-*O*) complexes crystallographically characterised across a variety of different metal[7] and co-ligand classes.[4, 7d, 8] Of the ligand classes used, simple amide based ligands (including amidinates and formamidinates) have been virtually neglected, with only a few known examples crystallographically characterised,[4b, 9] namely $[Sm\{N(SiMe_3)_2\}_2(fn^{\cdot}\text{-}O)(hmpa)]$ (hmpa = hexamethylphosphoramide),[4b] $[Mg([\{N(R)C(Me)\}_2CH)(bp^{\cdot}\text{-}O)(dmap)]$ (R = 2,6-(*i*Pr)$_2C_6H_3$, dmap = 4-(dimethylamino)pyridine),[9b] and a Zr-Co bimetallic.[9a] To extend our studies of compounds with *N*-donor alternatives to the cyclopentadienyl ligand class,[10] we are developing rare-earth based *ketyl* complexes bearing sterically bulky *N*,*N*′-bis(aryl)formamidinate co-ligands, namely *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate (DippForm). However, initial attempts failed to yield a stable ketyl complex.[11] Thus, the reaction of benzophenone (bp) with divalent formamidinate complexes: $[Ln^{II}(DippForm)_2(thf)_2]$ (Ln = Sm, Yb), or $[Yb(DFForm)_2(thf)_3]$ (DFForm = *N*,*N*′-bis(2,6-difluorophenyl)formamidinate) yielded only transient *ketyl* species. In the case of the DippForm complexes, there was rapid conversion into a highly unusual head to tail C–C coupled product (Scheme 1(i)) in good yield.[11a] Such coupling of bp has otherwise only been observed twice, namely as a minor product from the treatment of bp with a U^{III} compound,[6b] or more recently with a Co-Zr bimetallic.[12] To establish that the Yb(DippForm)$_2$ moiety can be a suitable scaffold for *stable ketyl* complexes, reactions of $[Yb(DippForm)_2(thf)_n]$ (n = 2 (**1a**), 1 (**1b**)) with a range of ketones, mainly more rigid or bulkier than bp, have been undertaken. Thus we report the first crystallographically characterised rare-earth amidinate *ketyl* complexes $[Yb(DippForm)_2(fn^{\cdot}\text{-}O)(thf)]$ (fn$^{\cdot}$-O^-: 9-fluorenone *ketyl*) and $[Yb(DippForm)_2(tpc^{\cdot}\text{-}O)]$ (tpc$^{\cdot}$-*O*: 2,3,4,5-tetraphenylcyclopentadienone *ketyl*). On the other hand, perfluorobenzophenone (pfb), gave C–F activation products. Ytterbium/ketone redox chemistry was further expanded by reactions of **1a** or **1b** with bulky/rigid di-ketones 3,5-di-*tert*-butyl-benzo-1,2-quinone (tbbq), phenanthrene-9,10-dione (phen), or acenaphthalene-1,2-dione (acen), generating three new rare-earth *ketyls*: $[Yb(DippForm)_2(tbbq^{\cdot}\text{-}O_2)]$ (**5**), $[Yb(DippForm)_2(phen^{\cdot}\text{-}O_2)]$ (**6**), and $[Yb(DippForm)_2(acen^{\cdot}\text{-}O_2)(thf)]$ (**7**). Currently, there are only a few previous rare-earth tbbq complexes reported,[8b, 13] with only some crystallographically characterised,[13d-g] and no crystallographically characterised examples from the phen and acen di-ketones. The reactivity of the representative *ketyl* complex, $[Yb(DippForm)_2(tpc^{\cdot}\text{-}O)]$ (**3**), was examined with oxidants and reducing agents. Of particular interest was the reaction between **3** with $SmI_2(thf)_2$, which led to the formation of a dimeric half-sandwich samarium complex containing two dianionic 1-oxido-2,3,4,5-tetraphenylcyclopentadienide(2$^-$) ligands ($(\{C_5Ph_4\}\text{-}O)^2$), and a terminal iodide, namely $[\{SmI(\{C_5Ph_4\}\text{-}O)(thf)_2\}_2]$ (**Sm11**) in low yield. A better route to this compound was treatment of activated Sm metal with TPC in THF, giving divalent $[\{Sm^{II}{}_2(\{C_5Ph_4\}\text{–}O)_2(thf)_3\}_2]$ (**Sm13**), which was oxidised with iodine to give trivalent **Sm11**. A theoretical study of the reactions of $[Ln(DippForm)_2(thf)_2]$ (Ln = Sm, Yb), with benzophenone shows a plausible path via $[Ln(DippForm)_2(O\text{-}C^{\cdot}Ph_2)]$ to the head to tail coupled complex shown in Scheme 1(i).

Results and discussion:

Reduction of ketones by a divalent ytterbium formamidinate: When the *divalent* ytterbium compounds [Yb(DippForm)$_2$(thf)$_2$] (**1a**)[10d] and the mono-solvated [Yb(DippForm)$_2$(thf)] (**1b**),[11b] were treated with 9-fluorenone (fn), tetraphenylcyclopentadienone (tpc), or perfluorobenzophenone (pfb) in C_6D_6, the orange/red solution of **1a**/**1b** changed immediately to dark maroon, orange/gold, and royal blue respectively. ^{1}H NMR spectroscopic analysis of each solution showed immediate and quantitative oxidation of divalent, diamagnetic **1a**/**1b**, by the observation of paramagnetically broadened resonances which could not be assigned (see supplementary information). Free THF could be identified in each spectrum. In the cases where *complexes of ketyl ligands* were obtained, the species were highly air and moisture sensitive, decomposing immediately on even slight exposure to air. Supplementary information has Chemdraw schematics and ID numbers of each presented complex (Chart S1).



Scheme 1. Reactions of [Yb(DippForm)$_2$(thf)$_n$] (n = 2 (**1a**), or n = 1 (**1b**)) with (i) benzophenone, giving the head to tail coupled species,[11a] (ii) 9-fluorenone; (iii) 2,3,4,5-tetraphenylcyclopentadienone; (iv) perfluorobenzophenone;.

Reaction with 9-fluorenone (fn): Addition of fn to **1a** immediately produced a dark maroon/brown colour, consistent with aryloxide supported 9-fluorenone *ketyl* complexes.[4a] Single yellow/pink crystals were obtained from a THF/hexane solution, and X-ray crystallography established the formation of an amidinatolanthanoid *ketyl* complex: [Yb(DippForm)$_2$(fn$^{\bullet}$-*O*)(thf)]·THF (**2**·THF) (Figure 1). The X-ray data for **2**·THF were modelled and refined in the triclinic space group *P*-1, with one molecule and one THF of crystallisation within the asymmetric unit. The ytterbium atom is coordinated by two terminal κ(*N*,*N*′) DippForm ligands, and a thf donor which is *cisoid* to an oxygen bound fluorenone-*ketyl*. Successful reduction of fn to fn$^{\bullet}$-*O* is supported by the following crystallographic features. The short Yb1–O1 bond length of 2.070(4) Å, is indicative of a Yb alkoxide bond, *c.f.* Yb1-O2$_{(thf)}$: 2.350(4) Å, and the C51–O1 bond is elongated to 1.314(7) Å, (from 1.22 Å of fn).[14] In addition the bond angles between C51 and its connected atoms (O1, C52, C63) indicate sp^2 hybridisation (average angle: 120.0°). These features have also been observed in other fn$^{\bullet}$-*O* complexes.[4, 15] The Yb–N bond lengths in **2**·THF (Yb–N range = 2.339(4)-2.358(4) Å) are comparable

with Yb–N bond lengths in other *trivalent* ytterbium formamidinate complexes,[10b, 16] (e.g. [Yb(DippForm)$_2$Br(thf)]: Yb–N range: 2.330(3)-2.366(3) Å).[10d] The fn˙-*O ketyl* coordinates to ytterbium in a near linear fashion, with a Yb1-O1-C51 angle of 168.6(3)º. There was also an additional disordered THF molecule (approximately $^1/_3$ occupancy) within the lattice that was omitted during the refinement process (see X-ray experimental). Elemental analysis performed on vacuum dried crystals were consistent with the composition: [Yb(DippForm)$_2$(fn˙-*O*)(thf)]·THF (**2**·THF), that is loss of the disordered solvent of crystallisation.

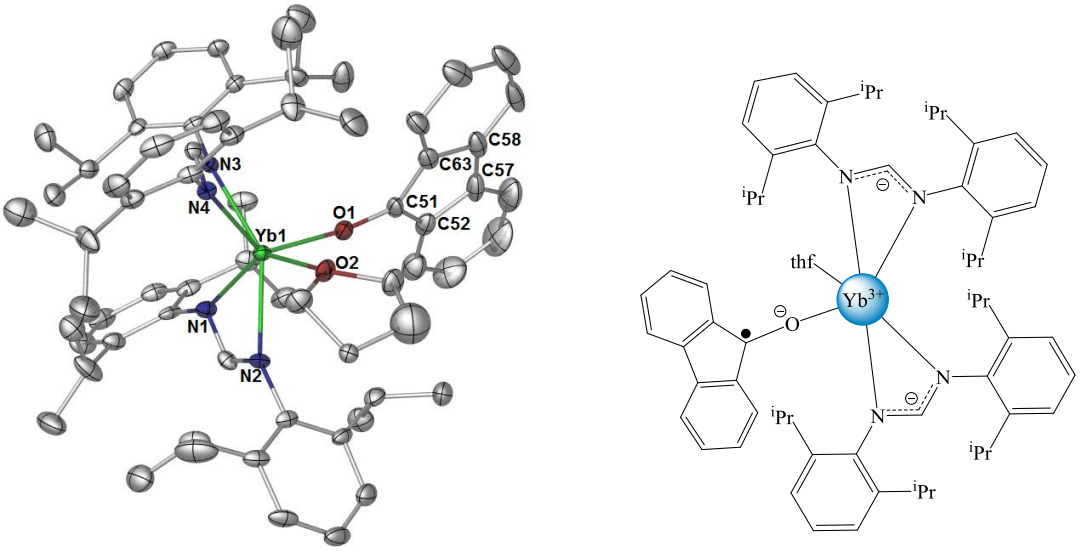


Figure 1. *Left*: Molecular structure of [Yb(Dippform)$_2$(fn˙-*O*)(thf)]·THF (**2**·THF). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvents removed for clarity. *Right*: simplified diagram of **2**·THF. Selected bond lengths (Å) and angles (º) for **2**·THF: Yb1-N1: 2.354(5), Yb1-N2: 2.358(4), Yb1-N3: 2.362(5), Yb1-N4: 2.339(4), Yb1-O1: 2.070(4), Yb1-O2: 2.350(4), O1-C51: 1.314(7), C51-C52: 1.417(17), C51-C63: 1.433(7), O1-C51-C52: 125.7(6), C63-C51-C52: 107.5(6), C63-C51-O1: 126.7(6).

A feature of compound **2**·THF is its stability in non-polar solvents. Solutions of pure **2**·THF gave no observable evidence of decomposition upon heating (25-70°C) in C_6D_6 as determined by ^{1}H NMR spectroscopy, and it retained its maroon colour in hexane. EPR analysis of **2**·THF in PhMe gave a single broad signal at g = 2.0076, a value indicative of an organic radical and almost identical with those of other fn˙-*O* complexes.[4b, 7c] Complex **2** shows λ_{max} values of 415 and 440 nm and broad absorptions at 500-640 nm were also observed, as reported for other fn˙-*O* complexes, such as [Yb(OAr)$_2$(fn˙-*O*)(thf)$_3$] (OAr = 2,6-di-*tert*-butyl-4-methylphenolate), which gives a maximum at 440nm, and broad absorptions between 500-640 nm.[4b] The λ_{max} value of 415 nm is close to that of the deep brown transition metal fn˙-*O* complex: [Zr(C_5Me_5)$_2$Cl(fn˙-*O*)] (λ_{max} 417 nm).[7c] Upon exposure of a solution or crystals of **2**·THF to air, the maroon colour vanished immediately, and IR spectroscopy showed the presence of a ν(C=O) band attributable to fn at 1723 cm^{-1} indicative of oxidation.

Reaction with 2,3,4,5-tetraphenylcyclopentadienone (tpc): When tpc ("tetracyclone") was treated with **1b** in C_6D_6, the solution did not turn a deep purple colour as for bp[11a] or fn. Instead a deep orange colour was observed. Large orange block crystals were obtained from a PhMe solution. X-ray crystallographic examination of the crystals revealed the formation of a tpc˙-*O*$^-$ *ketyl*, bound to ytterbium in [Yb(DippForm)$_2$(tpc˙-*O*)]·PhMe (**3**·PhMe) (Figure 2).

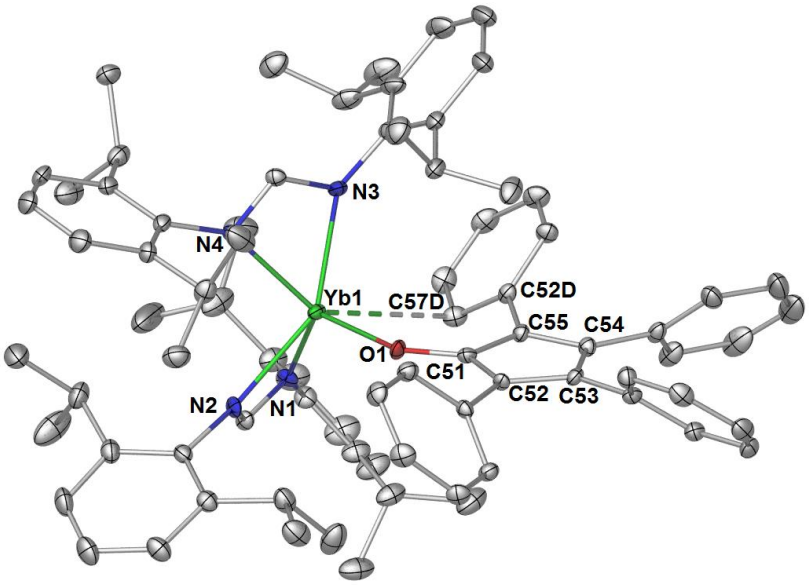


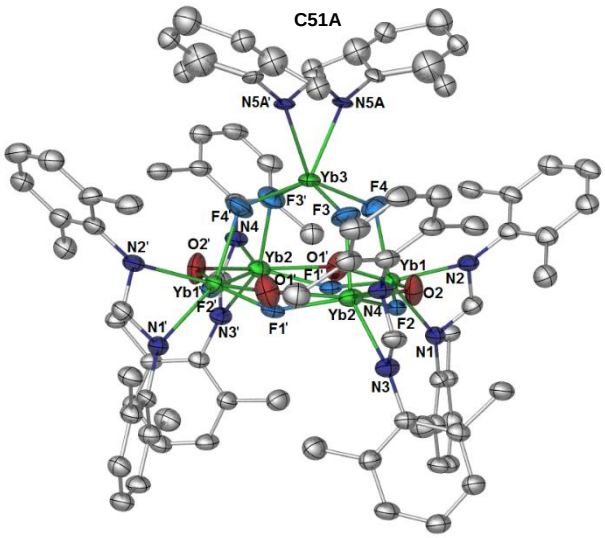
Figure 2. Molecular structure of [Yb(DippForm)$_2$(tpc˙-*O*)]·PhMe (**3**·PhMe). Ellipsoids shown at 50% probability, hydrogen atoms, isopropyl groups, and lattice solvents removed for clarity. Selected bond lengths (Å) and angles (º) for **3**·PhMe: Yb1-N1: 2.294(4), Yb1-N2: 2.367(4), Yb1-N3: 2.341(4), Yb1-N4: 2.303(4), Yb1-O1: 2.090(3), Yb1-C57D: 3.077(6), O1-C51: 1.313(6), C51-C52: 1.450(7), C52-C53: 1.394(7), C53-C54: 1.487(7), C54-C55: 1.396(7), C51-C55: 1.442(7), Yb1-O1-C51: 146.1(3).

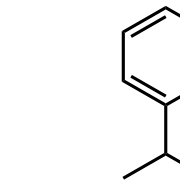
The X-ray data for **3**·PhMe were solved and refined in the monoclinic space group $P2_1/n$, with the entire molecule and one lattice PhMe occupying the asymmetric unit. The tpc˙-*O ketyl* has similarities with the fn˙-*O ketyl* in **2**·THF, i.e. a short Yb–O bond length, and an elongated C–O bond (1.313 (6) Å, *c.f.* C–O in tpc = 1.208 Å).[17] Intriguingly, the tpc˙-*O* ketyl does not coordinate in a near linear fashion as observed with fn˙-*O* in **2**·THF (168.6(3)º), but rather on a tilted angle of 146.1(3)º. Such an arrangement brings the *ortho*-carbon atom of the 2-phenyl group of tpc˙-*O* into the coordination sphere of ytterbium. At a distance of 3.077(6) Å, Yb-C57D is comparable with the longer π-Yb-C(Ph) interactions of [Yb(OC$_6$H$_3$Ph$_2$-2,6)$_3$] (3.038(6), 3.148(6), 3.085 (5) Å).[18] It is likely that the combined steric pressure of both coordinating DippForm and tpc˙-*O* ligands inhibits the ability of the initial thf ligand of **1b** to remain coordinated, and coordination saturation is satisfied by π-binding C57D. Vacuum drying **3**·PhMe and subsequent micro-analysis indicated a bulk sample composition of [Yb(DippForm)$_2$(tpc˙-*O*)] (**3**). Despite evidence for a *trivalent* species by both ^{1}H NMR spectroscopy and X-ray crystallography, EPR analysis of **3** in PhMe did not give an observable signal, plausibly owing to rapid relaxation associated with the delocalisation of the unpaired electron onto the phenyl substituents. Exposure of solutions of **3** to air rapidly changed the colour of the solution to deep purple indicating the formation of free tpc.

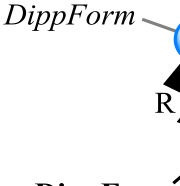
Reaction with perfluorobenzophenone (pfb): With the successful stabilisation of the fn˙-*O* and tpc˙-*O ketyls*, it was of interest to determine whether perfluorobenzophenone would follow a similar reaction pathway to benzophenone (Scheme 1i), or if the electron withdrawing fluorine atoms would stabilise the radical species, giving pfb˙-*O*. When complex **1a** was treated with perfluorobenzophenone (pfb) in THF, a transitory deep purple colour was observed

before a rapid change to deep blue. A broad absorption at λ_{max} = 614 nm was observed, which is near to that of the deep blue $[Na_3(bp^{\cdot}\text{-}O)_3(hmpa)_4]$ *ketyl* (675 nm),[7a] and the deep blue potassium benzophenone polymer $[K(bp^{\cdot}\text{-}O)]_\infty$ (656 nm),[7b] suggesting the initial formation of a *ketyl* species**.** On standing, the deep blue colour faded to a light green, and crystallisation from hexane/THF mixtures gave colourless crystals of $[YbF(DippForm)_2(thf)]$ (**4a**) in moderate yield (30%). Complex **4a** is isostructural with other $[LnF(DippForm)_2(thf)]$ (Ln = La, Ce, Nd, Sm, Tm) compounds,[10b] which were previously obtained by C–F activation of coordinated C_6F_5 of a putative $[Ln(DippForm)_2(C_6F_5)]$ intermediate in redox transmetalation protolysis (RTP) reactions. Previous attempts to synthesise **4a** by a similar RTP/ C–F activation reaction were unsuccessful,[19] with only divalent **1a** obtained. Therefore, the addition of pfb to **1a** is currently the only viable synthesis of the terminal fluorido complex. The Yb–F bond length of 2.016(3) Å in **4a** is consistent with those of the other $[LnF(DippForm)_2(thf)]$ complexes,[10b] after allowing for the difference in the Ln^{3+} ionic radii.[20] No observable OH stretching band was identified in the IR spectrum, as expected for the presence of fluoride rather than OH. Isolation of the intermediate "$[Yb(DippForm)_2(pfb^{\cdot}\text{-}O)]$" *ketyl* complex could not be achieved. Both the ^1H and ^{19}F NMR spectra of **4a** were uninterpretable. The elemental analysis of **4a** repeatedly gave poor results, even when the sample was uniform crystals. However, a satisfactory metal analysis was obtained from the same crystalline sample. In addition to **4a**, from one experiment small yellow pink crystals were also obtained from a hot hexane solution. Analysis of the yellow/pink crystals by X-ray crystallography revealed the formation of a pentanuclear, square pyramidal, fluoride/oxide cage, $[Yb_5F_6O_2(DippForm)_5]$ (**4b**) (Figure 3).

The X-ray data for **4b** were solved and refined in the orthorhombic space group *Pccn*, giving three ytterbium atoms within the asymmetric unit and two distinct ytterbium coordination environments. Four ytterbium atoms are positioned at the corners of a square plane (Yb1/Yb2 and their symmetry equivalents Yb1′/Yb2′). Each metal is coordinated by one terminal κ(*N*,*N*′) DippForm ligand, two bridging fluorides and one bridging oxide, giving each Yb atom a coordination number of five. The bridging oxide/fluoride ligands at the base of the cage are disordered over two positions, with a total of two fluorides and two oxides around the base. The second ytterbium environment, Yb3, caps the square pyramid with one terminal κ(*N*,*N*′) DippForm ligand, and is connected to the base by four bridging fluoride ligands, giving Yb3 a coordination number of six. The overall shape of the cage can be considered to be square pyramidal (Yb1-Yb2-Yb1′ = 90.017(13)°, Yb2-Yb3-Yb2′ = 87.27(2)°). The terminal DippForm ligand on Yb3 is disordered equally across two positions, with the second position being perpendicular to that shown in Figure 3, pivoting 90º at C51A (See Supporting Information Figure S1). The source of both oxide and fluoride in **4b** is likely to originate from the decomposition of pfb caused during the C–F and apparent C=O activation process. A search of the Cambridge structural database indicates that there are many square-pyramidal, pentanuclear rare-earth cages, but they typically surround a central oxide or hydroxide ligand.[21] This feature is absent in the structure of **4b**. In addition, there appears to be only one other reported example of the C–F activation of pfb, although it does not involve such dramatic rearrangement as in formation of **4b**, or proceed through a *ketyl* intermediate. A hexahydridoosmium complex $[OsH_6(iPr_3P)_2]$ selectively removed one *ortho* fluorine atom of coordinated pfb, forming HF and an Os–C bond.[22] Because of the complexity of the reaction between **1a**/**1b** and pfb, further studies are in progress.





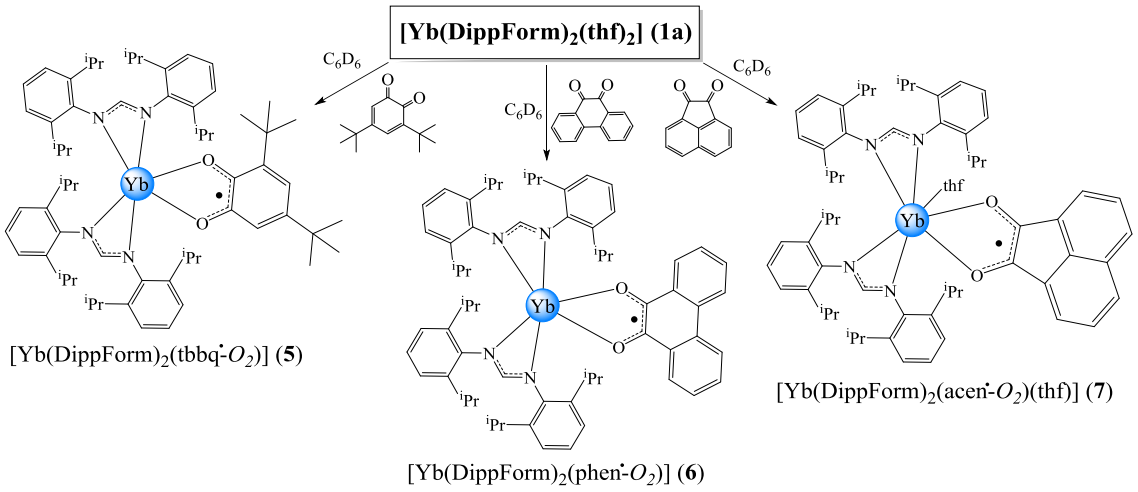


DippForm

Figure 3. *Left*: Molecular structure of $[Yb_5F_6O_2(DippForm)_5]$ (**4b**). Ellipsoids shown at 30% probability; disordered DippForm, hydrogen atoms, and methyl groups on the isopropyl groups have been removed for clarity. *Right*: Simplified diagram of **4b**, representing the O/F disorder if R = F then X = O and when R = O then X = F. Disordered DippForm ligand (N5A/N5A′) shown in only one orientation (at C51A). Selected bond lengths (Å) of **4b**: Yb1-N1: 2.322(8), Yb1-N2: 2.320(8), Yb1-F1′: 2.080 (17), Yb1-O1′: 2.20(2), Yb1-F2: 2.036(17), Yb1-F4:2.134(7), Yb1-O2: 2.26(2), Yb2-N3: 2.322(8), Yb2-N4: 2.322(8), Yb2-F1: 2.061(18), Yb2-O1: 2.26(2), Yb2-F2: 2.087(17), Yb2-O2: 2.19(2), Yb2-F3:2.136(7), Yb3-N5A: 2.347(12). Yb3-F3: 2.193(7), Yb3-F4: 2.193(7).

Reduction of 1,2-diketones by a divalent ytterbium formamidinate:

Three 1,2-diketones, namely: 3,5-di-*tert*-butyl-benzo-1,2-quinone (tbbq), phenanthrene-9,10-dione (phen), or acenaphthalene-1,2-dione (acen), were examined for SET reactions with the *divalent* ytterbium complex $[Yb(DippForm)_2(thf)_2]$ (**1a**), generating three new rare-earth *ketyls*, $[Yb(DippForm)_2(tbbq^{\cdot}\text{-}O_2)]$ (**5**), $[Yb(DippForm)_2(phen^{\cdot}\text{-}O_2)]$ (**6**), and $[Yb(DippForm)_2(acen^{\cdot}\text{-}O_2)(thf)]$ (**7**) (Scheme 2). Interestingly, upon exposure to air, the 1,2-diketone *ketyl* complexes showed dramatic colour changes, but colourless solutions eventually formed along with the respective 1,2-diketone.



Scheme 2. Single electron transfer reactions of [Yb(DippForm)$_2$(thf)$_2$] (**1a**) with 1,2-diketones: tbbq, phen, and acen.

Treatment of 1a with 3,5-di-tert-butyl-benzo-1,2-quinone (tbbq) or phenanthrene-9,10-dione (phen): Addition either tbbq or phen to **1a** in C_6D_6 resulted in an immediate colour change to brown/olive green and yellow/green respectively. Oxidation of **1a** by either ketone was immediate and quantitative, as indicated by ^{1}H NMR spectroscopy showing large broadened peaks, and the liberation of THF (*cf.* fn and tpc reactions). Two unsolvated *ketyl* complexes, [Yb(DippForm)$_2$(tbbq˙-O_2)] (**5**) and [Yb(DippForm)$_2$(phen˙-O_2)] (**6**), were obtained as analytically pure, crystalline species from either THF/Hexane (**5**) or PhMe (**6**). The *ketyl* species were stable in PhMe. EPR analysis of the complexes gave *g* values of 2.0081 and 2.0036 respectively, supporting the formation of organic radicals. The crystal structures of complexes **5** and **6** are similar (Figure 4), both showing near symmetric coordination of the *ketyl* ligand.

Complex **5** crystallises as small blue/yellow dichroic crystals, suitable for diffraction at the Australian Synchrotron, with X-ray data modelled and refined in the triclinic space group *P*-1. The ytterbium atom is coordinated by two terminal κ(*N*,*N*′) DippForm ligands with an average Yb1–N bond length of 2.334 (4) Å and the tbbq˙-O_2 ligand shows near symmetrical chelation (Yb-O1 = 2.233(3), Yb1-O2 = 2.209(3) Å). Therefore the ytterbium atom is six-coordinate.

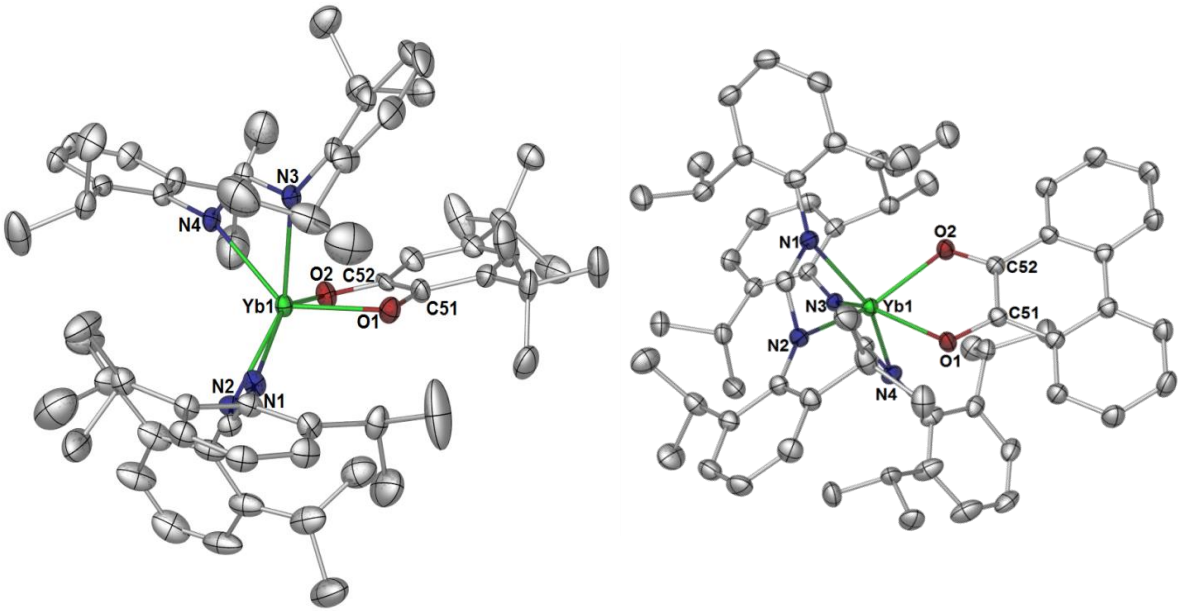


Figure 4. Molecular structures of [Yb(DippForm)$_2$(tbbq˙-O_2)] (**5**) (*left*) and [Yb(DippForm)$_2$(phen˙-O_2)] (**6**) (*right*). Ellipsoids shown at 50% probability, hydrogen atoms removed for clarity. Selected bond lengths (Å) for **5**: Yb1-O1: 2.233(3), Yb1-O2: 2.209(3), Yb1-N1: 2.341(4), Yb1-N2: 2.324(4), Yb1-N3: 2.317(4), Yb1-N4: 2.355(4), O1-C51: 1.288(5), C51-C52: 1.452(6), C52-O2: 1.308(5). Selected bond lengths (Å) for **6:** Yb1-O1: 2.2337(17), Yb1-O2: 2.2289(18), Yb1-N1: 2.306(2), Yb1-N2: 2.328(2), Yb1-N3: 2.327(2), Yb1-N4: 2.303(2), O1-C51: 1.288(4), C51-C52: 1.449(4), C52-O2: 1.285(4).

The phen˙-O_2 analogue, **6**, crystallises as dichroic green/yellow plates with X-ray data modelled in the triclinic space group *P*-1. The Yb-O1/O2 bond lengths of 2.234(2) and 2.229(2) Å respectively, indicating that the unencumbered/rigid phen˙-O_2 ligand adopts a symmetric coordination, which has also been observed in transition metal phen˙-O_2 *ketyl* complexes.[23] Examination of the tbbq˙-O_2 and the phen˙-O_2 chelating sites, featuring the binding of the O(1),C(51)/C(52),O(2) atoms shows the following trends: they are near aromatic in nature with each

bond length lying between a double and single bond, as they have shorter C–C bond lengths and longer C–O bond lengths than observed in the respective di-ketones (tbbq: C(51)–C(52): 1.551(2) Å, average: C=O: 1.217 Å,[24] and phen: C(51)–C(52): ~1.532 Å, average: C=O: 1.221 Å).[25] Therefore, it can be inferred that, for both **5** and **6**, the free electron and anionic charge is stabilised by resonance across the OCCO moiety (Scheme 3).

Treatment of 1a with acenaphthalene-1,2-dione (acen): Upon addition of acen to **1a** in either C_6D_6, PhMe, or THF, a colour change to light yellow/brown was observed. However, complete oxidation (as evidenced by ^{1}H NMR spectroscopy) was only observed after 24 hours, due to the poor solubility of the acen ligand. EPR analysis of the solution gave a value of g = 2.0073, supporting radical/*ketyl* formation. Unlike **5** and **6**, the acen˙-O_2 derivative crystallised as a mono-solvated species with an additional lattice solvent molecule, [Yb(DippForm)$_2$(acen˙-O_2)(thf)]·THF (**7**·THF), where the presence of the coordinating thf had a significant impact on the radical/anion distribution of the acen˙-O_2 *ketyl* in the solid state. Elemental analysis for vacuum-dried crystals indicated loss of THF of crystallisation, but not ligated thf.

Complex **7**·THF crystallises as green/brown dichroic plates, with X-ray data modelled and refined in the triclinic space group *P*-1. The ytterbium centre is seven-coordinate, with two κ(*N*,*N*′) DippForm ligands, one thf ligand, and an asymmetrically chelating acen˙-O_2 *ketyl* (Figure 5), with Yb-O1/2 bond lengths of 2.266(2) and 2.354(2) Å respectively. Such asymmetric coordination is probably due to an electrostatic and steric repulsion caused by the close proximity of O2 to the THF co-ligand (O2···O3: 2.724(3) Å), making the radical/anion favour the less congested O1 atom (O1···O3: 3.628(3) Å), and hence a shorter Yb-O1 bond length. This unequal distribution of charge and free electron within the *ketyl* is further supported by the intra-ligand bonding. The O2–C52 bond (1.227(2) Å) is much shorter than O1–C51 (1.274(4) Å), and has a value closer to that observed in neutral acen (average: C=O: 1.193 Å).[26] The C–C bond also shows a slight degree of shortening at 1.493(4) Å (acen ~ 1.53 Å),[26] suggesting there is a some degree of resonance stabilisation across the donor site.

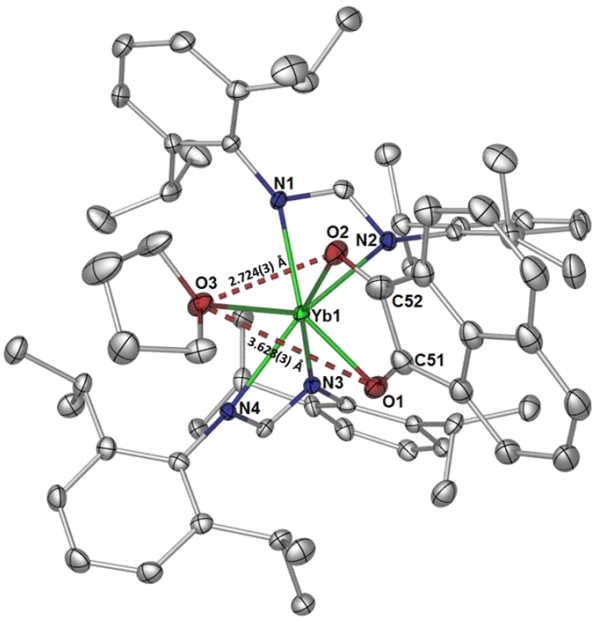


Figure 5. Molecular structure of [Yb(DippForm)$_2$(acen˙-O_2)(thf)]·THF (**7**·THF). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvent removed for clarity. Selected bond lengths (Å) for **7**·THF**:** Yb1-O1: 2.266(2), Yb1-

O2: 2.354(2), Yb1-N1: 2.342(2), Yb1-N2: 2.436(2), Yb1-N3: 2.390(2), Yb1-N4: 2.372(2), O1-C51: 1.274(4), C51-C52: 1.493(4), C52-O2: 1.227(4).

Currently there are no crystallographically characterised complexes reported for the acen˙-O_2 *ketyl*,[21] perhaps because of its limited solubility in common solvents. However, there is an example of a complex containing a coordinated neutral acen ligand, [$TiCl_4$(acen)],[27] and some di-anionic-binolate $acen^{2-}$ Ge^{IV} complexes.[28]

To determine if the presence of coordinated thf does influence the ketyl symmetry, an unsolvated analogue of **7**·THF was sought. Treatment of **1b** with acen in PhMe gave a light yellow/purple solution. Slow crystallisation from PhMe, gave dichroic green/golden crystals of [Yb(DippForm)$_2$(acen˙-O_2)] (**8**). The X-ray data were solved and refined in the triclinic space group *P*-1. There are two molecules within the asymmetric unit (Figure 6). As expected, without the presence of the competing thf co-ligand, the acen˙-O_2 *ketyl* adopts more symmetrical coordination to ytterbium, with a coordination environment similar to that observed in **6**. A scheme of the charge/radical distribution in **7** and **8** are shown in Scheme 3.

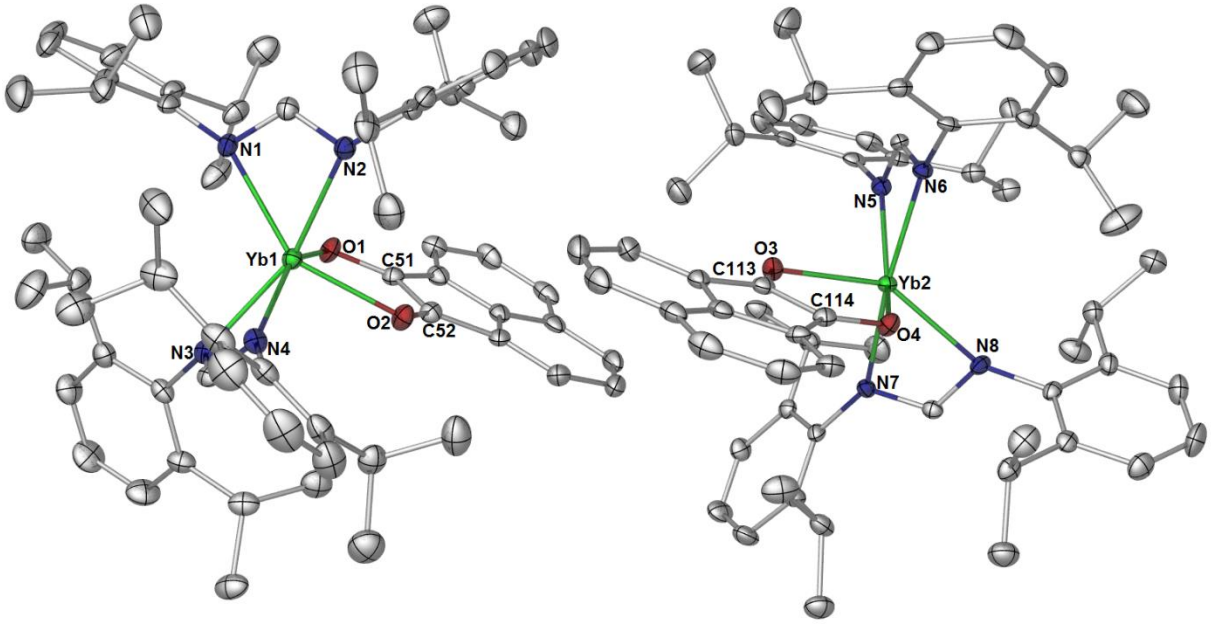
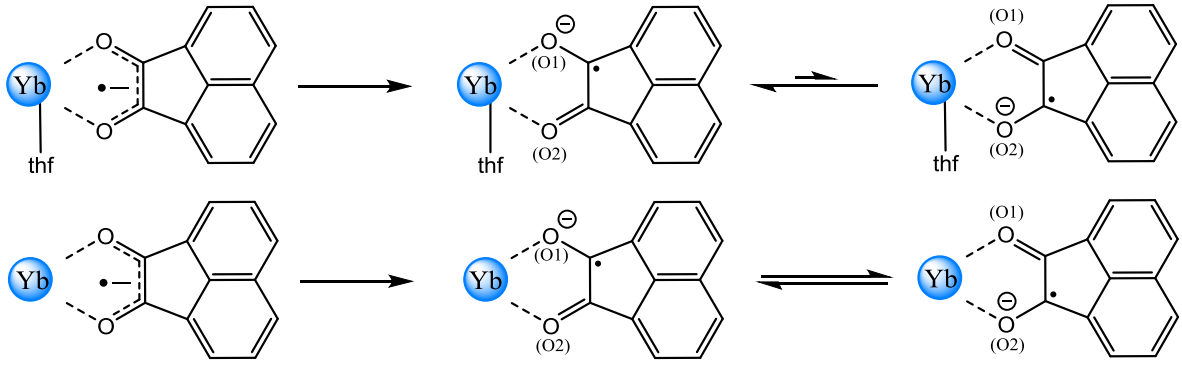


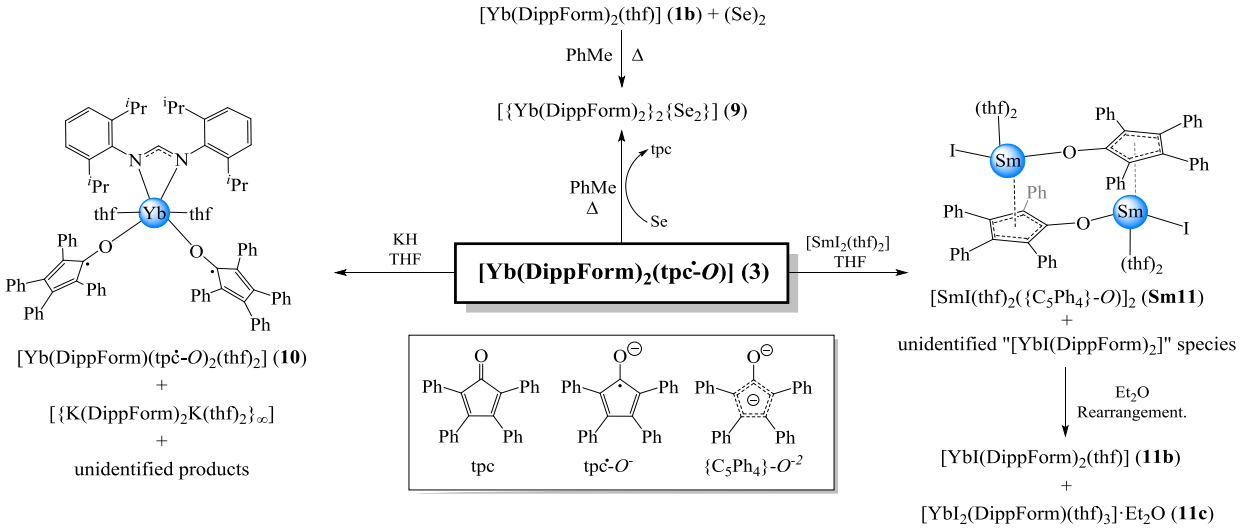
Figure 6. Asymmetric unit of [Yb(DippForm)$_2$(acen˙-O_2)] (**8**) showing both molecules. Ellipsoids shown at 50% probability, hydrogen atoms removed for clarity. Selected bond lengths (Å) for **8**: Yb(1)-O(1): 2.2391(19), Yb(1)-O(2): 2.2552(20), Yb(1)-N(1): 2.356(2), Yb(1)-N(2): 2.318(2), Yb(1)-N(3): 2.326(2), Yb(1)-N(4): 2.316(2), C(51)-O(1): 1.287 (3), C(52)-O(2): 1.278(3), C(51)-C(52): 1.444(4); Yb(2)-O(3): 2.2470(18), Yb(2)-O(4): 2.2424(19), Yb(2)-N(5): 2.352(2), Yb(2)-N(6): 2.302(2), Yb(2)-N(7): 2.302(2), 2.350(2), C(113)-O(3): 1.284(3), C(114)-O(4): 1.281(3), C(113)-C(114): 1.450(4)



Scheme 3. Simplified diagram of charge/radical distribution in complexes **7** (*top*) and **8** (bottom, the latter also analogous to compounds **5** and **6**), highlighting the effect of coordinated thf on the *ketyl* ligand.

The reactivity of [Yb(DippForm)$_2$(tpc˙-O)] (3), and formation of the tetracyclone dianion ({C$_5$Ph$_4$}-O)$^{2-}$:

As [Yb(DippForm)$_2$(tpc˙-*O*)] (**3**) is the first rare-earth complex containing the tpc˙-*O* ketyl, its general reactivity towards oxidising (CS_2, Se) and reducing agents: (KH, Mg^0, Yb^0, or [$SmI_2(thf)_2$]) was examined. The products obtained are outlined in Scheme 4.

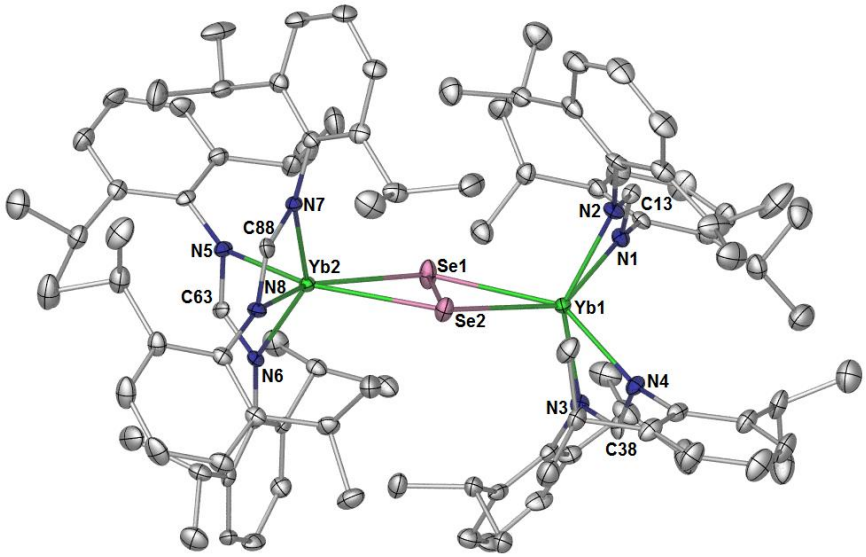


Scheme 4. Reactions of [Yb(DippForm)$_2$(tpc˙-*O*)] (**3**) with: Se, KH, amd [$SmI_2(thf)_2$]. No reaction was observed between **3** and CS_2, Mg, or Yb^0.

Treatment of 3 with oxidants: When **3** was heated with elemental Se for one hour in PhMe at 60°C, the solution slowly changed colour to purple, indicating the tpc˙-*O ketyl* was oxidised to neutral tpc. The delayed reaction is likely a result of the poor solubility of Se in PhMe. The ^{1}H NMR spectrum of the reaction mixture after separation of tpc, was very broad (over the range: -21.43 – 38.44 ppm), with no clearly identifiable species, but the paramagnetism is consistent with a Yb^{III} species such as a selenide or diselenide species. A putative product, [{Yb(DippForm)$_2$}$_2${Se}$_2$] (**9**) was obtained as pink crystals by treatment of **1b** with Se in PhMe at 50°C. X-ray crystallography established the structure of **9** (Figure 7). The ^{1}H NMR spectrum of **9** was also complicated, and although it was different from that of the above reaction mixture, overlapping peaks could be identified. This is likely that the above reaction mixture had additional products (e.g. [{Yb(DippForm)$_2$}$_2$(Se)]) which gave additional resonances. By contrast, no oxidation of tpc˙-*O* was observed when **3** was treated with CS_2, even with heating.

The X-ray data for [{Yb(DippForm)$_2$}$_2${Se$_2$}]·PhMe (**9**·PhMe) were solved and refined in the monoclinic space group $P2_1/n$ with the whole dimer within the asymmetric unit. Each ytterbium atom is coordinated by two κ(*N*,*N*′) DippForm ligands and by both selenium atoms, giving both ytterbium atoms a coordination number of six. This is the first ytterbium diselenide dimer crystallographically characterised. The dimer is constructed in a staggered conformation, where the DippForm ligands (N1/2,N3/4) connected to Yb(1) are rotated 79.4° from the DippForm

ligands (N5/6, N7/8) bound to Yb(2). This array deviates from the two analogous Cp* derivatives [{Ln(Cp*)$_2$}$_2${Se$_2$}] (Ln = Nd and Sm), which adopt an



eclipsed Cp* array.[29] Interestingly, both ytterbium atoms coordinate marginally closer to Se(1) than Se(2), indicating that the di-selenide ligand does not lie at the centre of the metals. This is also reflected in the bond angles, with the Yb(1)-Se(1)-Yb(2) bond angle (132.20(2)°) slightly larger than the Yb(1)-Se(2)-Yb(2) bond angle (129.22(2)°).

Figure 7. Molecular structure of [{Yb(DippForm)$_2$}$_2${Se$_2$}]·PhMe (**9**·PhMe). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvent removed for clarity. Selected bond lengths and angles for **9**: Yb1-Se1: 2.8296(6), Yb1-Se2: 2.8617(6), Yb1-N1: 2.317(4), Yb1-N2: 2.262(4), Yb1-N3: 2.269(4), Yb1-N4: 2.325(4), Yb2-Se1: 2.8402(6), Yb2-Se2: 2.8761(6), Yb2-N5: 2.330(4), Yb2-N6: 2.309(3), Yb2-N7: 2.306(4), Yb2-N8: 2.289 (4), Se1-Se2: 2.3747(4).

Treatment of 3 with reducing agents (KH, Mg^0, Yb^0, 1a): Addition of KH to **3** in THF and heating at 60°C, caused a significant colour change from orange to dark green. Crystallisation from a concentrated solution in THF/Et$_2$O gave dark yellow crystals. X-ray crystallography indicated the formation of an unusual di-*ketyl* complex: [Yb(DippForm)(tpc$^{\cdot}$-*O*)$_2$(thf)$_2$]·Et$_2$O (**10**·Et$_2$O, Figure 8). The crystal data were solved and refined in the orthorhombic space group $P4_32_12$ with the whole complex and two half Et$_2$O molecules within the asymmetric unit.

The six-coordinate ytterbium atom in **10**·Et_2O has one chelating DippForm ligand, two thf ligands and also two *cisoid*-tpc˙-*O*$^-$ radical ligands, which coordinate to Yb in a near linear fashion, similar to the fn˙-*O*$^-$ coordination in **2**·THF, and unlike the bent tpc˙-*O*$^-$ coordination in **3**·PhMe.

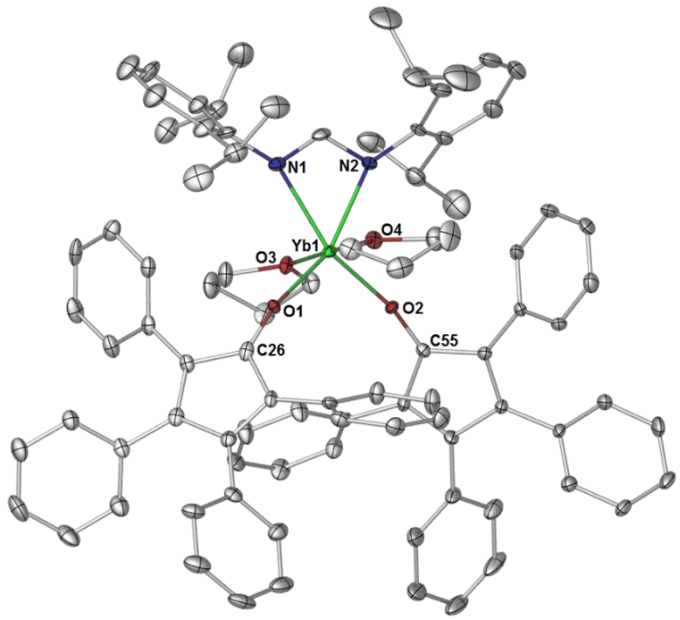


Figure 8. Molecular structure of [Yb(DippForm)(tpc˙-*O*)$_2$(thf)$_2$]·Et_2O (**10**·Et_2O). Ellipsoids shown at 50% probability, lattice solvates and hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (º) for **10**·Et_2O: Yb1-O1: 2.126(5), Yb1-O2: 2.115(5), Yb1-N1: 2.391(6), Yb1-N2: 2.367(7), Yb1-O3: 2.300(5), Yb1-O4: 2.310(5), O1-C26: 1.299(10), O2-C55: 1.308(9), C26-C55 (non-bonding): 4.919(19), O1-Yb1-O2: 103.40(19), C26-O1-Yb1: 163.3(5), C55-O2-Yb1: 167.6(5), O3-Yb-O4: 178.36 (18).

Despite the presence of two *cisoid* tpc˙-*O* radicals, *they do not undergo radical C–C coupling* (C26-C55: 4.919(19) Å, non-bonding), and EPR analysis on a solution of **10**·Et_2O in PhMe gave a strong *g* signal at *g* = 2.0034, indicating the *ketyl* is also present in solution. Currently there is only one other *diketyl* species which displays such a

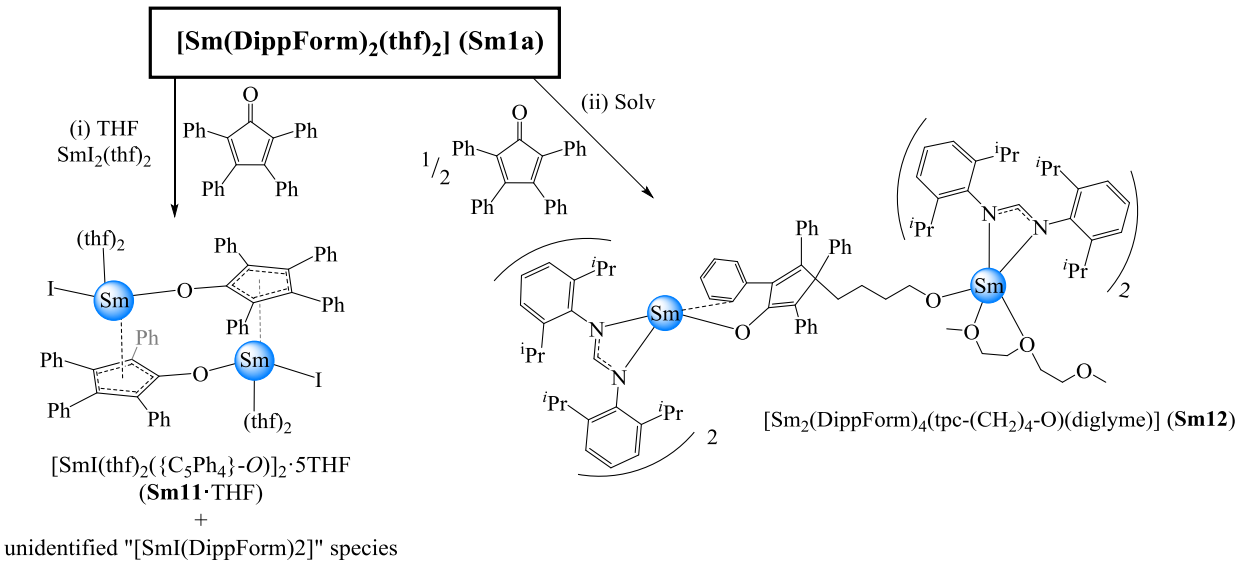
cisoid-diketyl arrangement,[21] namely [Ca(fn˙-*O*)$_2$(hmpa)$_3$] (hmpa = hexamethylphosphoramide),[7a] with an O-Ca-O angle of: 114.20º, more than 10º wider than that observed in **10**·Et$_2$O. In addition, this calcium complex is only stable in the presence of hmpa, whereas **10**·Et$_2$O is stable in Et$_2$O, PhMe, or THF. It is likely that due to the large steric bulk and rigid nature of the tpc˙-*O*$^-$ radical, C–C coupling is hindered. The close tpc˙-*O* – tpc˙-*O* proximity in **10**·Et$_2$O may result from crowding by neighbouring ligands. Redissolving the dried reaction mixture (that gave **10**·Et$_2$O) in THF gave crystals of a THF/Et$_2$O solvate (**10**·$^1/_4$THF/$^1/_4$Et$_2$O), and also small white crystals of [{K(thf)$_2$}{K(DippForm)$_2$}]$_\infty$ a compound which was previously synthesised by a protolysis reaction between K{N(SiMe$_3$)$_2$} and DippFormH.[30] A dried sample of **10**·Et$_2$O gave a satisfactory microanalysis for the lattice-Et$_2$O-free complex.

Treatment of 3 with divalent samarium compounds: It has been previously reported that tpc can undergo two single electron reductions to produce a di-anionic, 1-oxido-2,3,4,5-tetraphenylcyclopentadienide(2-) species, {C$_5$Ph$_4$}-*O*)$^{2-}$.[31] In the few crystallised complexes of the ({C$_5$Ph$_4$}-*O*)$^{2-}$ ligand, it typically bridges two metal centres in a μ-η^5(C$_5$Ph$_4$):κ(O) manner.[31-32] Of these examples, none involve rare-earth metals, and currently there is only one example of a di-anionic 1-oxido-cyclopentadienide (2-) rare-earth complex known, namely [{TmI$_2$(thf)$_2$}(μ-{2,5-^{t}Bu$_2$C$_5$H$_2$}-*O*){TmI$_2$(thf)$_3$}], formed by treatment of 2,5-di-*tert*-butyl-cyclopentadienone with two equivalents of TmI$_2$(thf)$_2$,[33] where one Tm atom is bound by oxygen and the other is η^5 ligated by the 2,5-^{t}Bu$_2$C$_5$H$_2$ moiety. To generate a 1-oxido-2,3,4,5-tetraphenyl-cyclopentadienide(2$^-$) ligand ({C$_5$Ph$_4$}-*O*)$^{2-}$ from the tpc˙-*O ketyl* in **3**, complex **3** (dissolved in THF or PhMe) was heated over Mg^0 or activated Yb metal, but no reaction occurred in either case. Further, addition of another equivalent of **1b** to **3** also did not give any indication of reactivity. Therefore, s stronger reducing agent is needed to further reduce the *ketyl*, namely either [SmI$_2$(thf)$_2$], or the previously reported Sm analogue of **1a**, [Sm(DippForm)$_2$(thf)$_2$] (**Sm1a**).[10c]

Upon treatment of **3** with [SmI$_2$(thf)$_2$], and heating, a red/orange solution was obtained. Crystallisation from hexane/THF produced both colourless and small light red crystals. X-ray crystallography showed the colourless crystals were a trivalent samarium half-sandwich dimer containing two ({C$_5$Ph$_4$}-*O*)$^{2-}$ ligands, namely: [{SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$]·2THF (**Sm11**·2THF, Figure 9). As **Sm11**·2THF is the product of a ligand redistribution process, it is likely that [YbI(DippForm)$_2$(thf)$_n$] is the other initial product. After separation of **Sm11**·2THF, concentration and addition of Et$_2$O gave a turbid solution, from which two sets of crystals were isolated, namely light orange blocks of anticipated [YbI(DippForm)$_2$(thf)] (**11b**, Figure 10, *left*) and colourless blocks of [YbI$_2$(DippForm)(thf)$_3$]·Et$_2$O (**11c**·Et$_2$O, Figure 10, *right*). The latter is possibly generated from the rearrangement of **11b**, which should also give [Yb(DippForm)$_3$], but this species was not detected. Unfortunately, due to the nature of the mixture, and the similar solubility of the two compounds, the two were not readily separated, and additional characterisation was not possible.

To avoid difficulties in metal identification, a "ytterbium free" synthetic approach was adopted for **11**. Thus, **Sm1a** was treated with tpc in a ratio of either 2:1 or 1:1. When free tpc was treated with two equivalents of [Sm(DippForm)$_2$(thf)$_2$] (**Sm1a**), a colour change occurred, but the reaction mixture appeared heterogeneous, and crystallisation was problematic. After several different crystallisation methods were attempted, crystals were obtained from a diglyme/hexane mixture. X-ray crystallography revealed the formation of a ring-opened THF species,

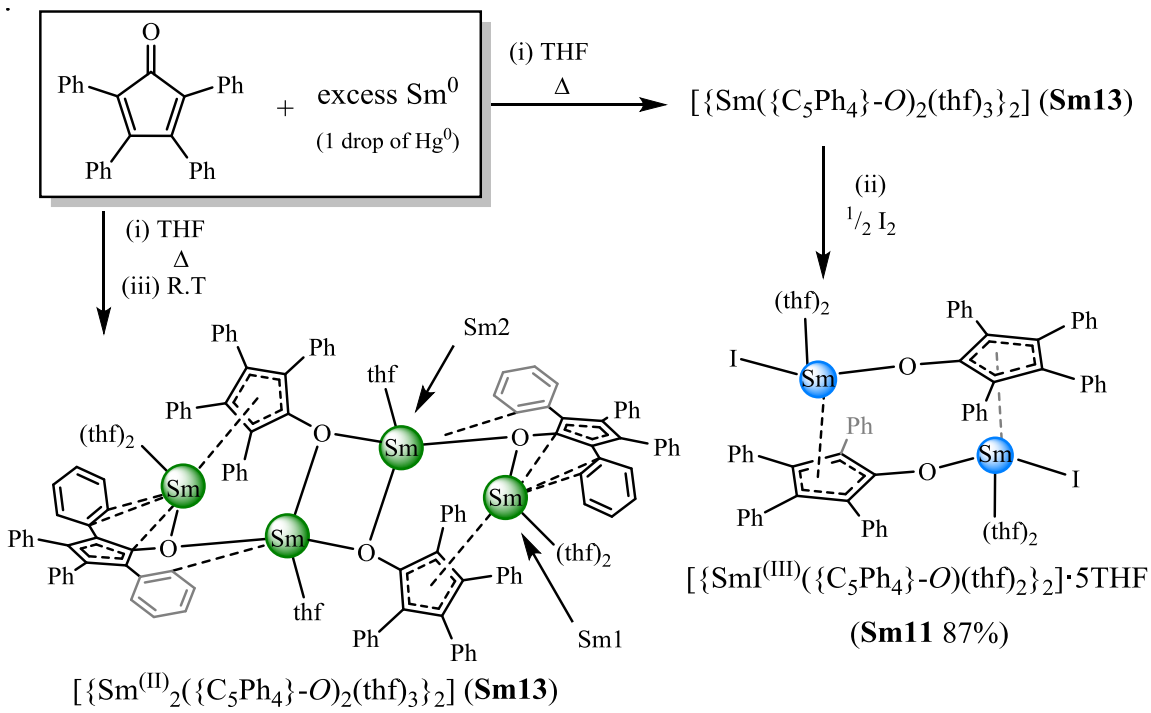
[{Sm(DippForm)$_2$}$_2$(μ-O-C$_5$Ph$_4$-(CH$_2$)$_4$-O)(diglyme)]·Solv (Solv = Hexane, ½ diglyme, **Sm12**·Solv) (Scheme 5, Figure S2). Similar activation of THF by C$_5$Me$_5$-Ln complexes has been observed both in the reaction between [Sm(C$_5$Me$_5$)$_2$(thf)$_2$][BPh$_4$] and KC$_5$Me$_5$,[34] and in the reaction between LnCl$_3$ and NaC$_5$Me$_5$ (Ln = La, Nd, Tm, Lu).[35] Treatment of **Sm1a** with one equivalent of tpc, followed by addition of one equivalent of SmI$_2$(thf)$_2$ gave red crystals, which X-ray crystallography identified as [{SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$]·5THF (**Sm11**·5THF), a different solvate from the forgoing **Sm11**·2THF, in low crystal yield (22%). No other products could be identified from the reaction mixture.



Scheme 5. Reactions between one equivalent of [Sm(DippForm)$_2$(thf)$_2$] (**Sm1a**) and either (i) 1 equivalent of tpc, and one equivalent of SmI$_2$(thf)$_2$; or (ii) half an equivalent of tpc. (i) All reagents were combined (first **Sm1a** and tpc, then SmI$_2$(thf)$_2$ was added) and shaken in THF, giving red crystals of [SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$]·5THF (**Sm11**·5THF); (ii) reagents combined in PhMe, crystals were obtained from a diglyme/hexane mixture (see Experimental for all solvents used).

Obtaining a high yield of **Sm11** when starting with either **3** or [Sm(DippForm)$_2$(thf)$_2$] (**Sm1a**) was not possible, as its formation involves a ligand redistribution process, and consequential difficult separation from the other metal-organic species. Therefore, an alternative synthesis was sought. It was envisioned that if a "[Sm^{II}({C$_5$Ph$_4$}-*O*)]" complex could be generated, subsequent oxidation with iodine should allow facile access to **Sm11**. By heating tpc over activated samarium metal in THF, a dark green/brown solution formed. Crystallisation from this reaction mixture, after separation from the metal, gave small green/brown crystals. Unfortunately the crystals diffracted poorly and were very air and temperature sensitive, but the use of the Australian Synchrotron, enabled suitable, rapid data collection, and indicated the formation of a tetranuclear Sm^{III} complex, [{Sm$_2$({C$_5$Ph$_4$}-*O*)$_2$(thf)$_3$}$_2$], containing four ({C$_5$Ph$_4$}-*O*)$^{2-}$ ligands (**Sm13**, Scheme 6). The complex was not stable in solution or when exposed to vacuum, making additional characterisation impossible. However when **Sm13** was synthesised in THF, and treated *in situ* with iodine, dimeric [{SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$]·5THF (**Sm11**·5THF) was obtained in a high crystal yield (87%, Scheme 6). Despite sending single crystals for elemental analysis, the % carbon value for **Sm11** was always much lower than expected. However, after briefly drying the crystals, a satisfactory metal analysis was obtained, for the composition [{SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$]·2THF (loss of three THF of crystallisation). This is a likely facile loss, given the

successful isolation of **Sm11**·2THF (Figure 9, Scheme 4). This route makes **Sm11** conveniently available as a metathesis reagent to form functionalised [$Sm^{III}(C_5Ph_4$-O)R] compounds.



Scheme 6. Deliberate synthesis of [{SmI({C_5Ph_4}-*O*)$(thf)_2$}$_2$] as **Sm11**·5THF, and crystallisation of [{Sm_2({C_5Ph_4}-*O*)$_2$$(thf)_3$}$_2$] (**Sm13**). (i) Stirred at 50°C for 12 h, separated from excess Sm^0 by filtration; (ii) Addition of I_2 without stirring, giving crystals of **Sm11**·5THF; (iii) Concentration of the THF solution *in vacuo* and storage at room temperature.

Crystallographic discussion for complexes: Sm11, 11b, 11c, and Sm13

Data for **Sm11**·2THF were modelled and refined in the monoclinic space group $P2_1/n$, with half the dimer, and one THF of crystallisation in the asymmetric unit. The structure contains the first ({C_5Ph_4}-*O*)$^{2-}$ ligand bound to a rare-earth metal, and is a semi-metallocene with a core comprising the two centroids of the {C_5Ph_4} rings, the two coordinating oxygen atoms of the ({C_5Ph_4}-*O*)$^{2-}$ ligands and the two samarium metal centres. The (C1-O1-Sm1) geometry around the anionic oxygen of {C_5Ph_4}-*O* (154.2(3)°) is in-between a linear (180°) and a tetrahedral (109.28°) molecular geometry. When the smaller Ru^{2+} metal is used with a similar ligand to ({C_5Ph_4}-*O*)$^{2-}$, namely 1-oxido-3,4-di(4-tolyl)-2,5-diphenylcyclopentadienide, ({C_5(tol)$_2Ph_2$}-*O*)$^{2-}$, the resulting complex, [{Ru({C_5(tol)$_2Ph_2$}-*O*)$(CO)_2$}$_2$],[36] has a Ru-Cent(Cp) distance of 1.88 Å (*cf.* Sm1-Cent, Figure 9), with a corresponding C1-O1-Ru1 angle of 140.13.[21]

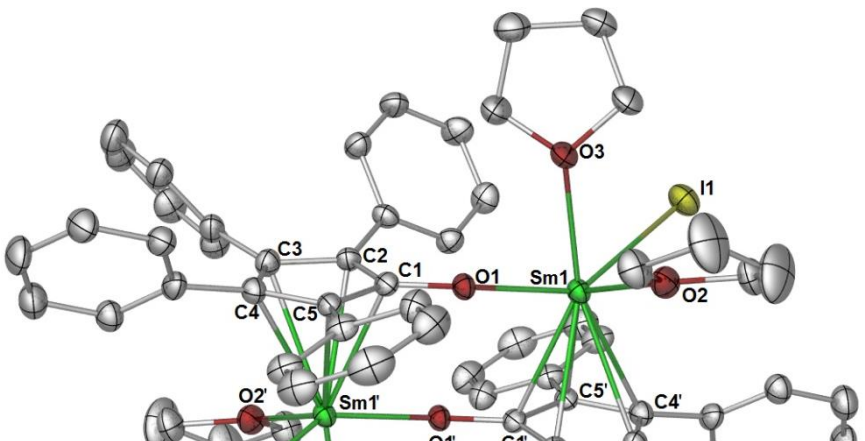


Figure 9. Molecular structure of [{SmI({C_5Ph_4}-*O*)$(thf)_2$}$_2$]·2THF (**Sm11**·2THF), ellipsoids shown at 50% probability, hydrogen atoms and lattice solvent removed for clarity. Selected bond lengths (Å) and angles (°) for **Sm11**·2THF: Sm1-C1′: 2.736(5), Sm1-C2′: 2.770(5), Sm1-C3′: 2.851(5), Sm1-C4′: 2.850(5), Sm1-C5: 2.790(5), Sm-O1: 2.163(3), O1-C1: 1.340(6), Sm1-I1: 3.0922(8), Sm1-O2: 2.407(4), Sm1-O3: 2.528(4), Sm1-Cent(C1′-C5′): 2.520(4), C1-C2: 1.431(7), C2-C3: 1.441(7), C3-C4: 1.403 (7), C4-C5: 1.461(7), C5-C1: 1.430(7), Sm1-O1-Cent(C1-C5): 153.45, Sm1-Cent(C1′-C5′)-Sm1′: 83.111(17), O1-Sm1-Cent(C1′-C5′): 101.39(9).

Crystallographic data for **11b** were solved and refined in the triclinic space group *P*-1, with the whole molecule within the asymmetric unit (Figure 10, *left*). Complex **11b** is isostructural and isomorphous with the reported samarium derivative [SmI(DippForm)$_2$(thf)], which was obtained from the reaction of iodine with [Sm(DippForm)$_2$(thf)$_2$].[10c] Crystal data for **11c**·Et_2O were modelled and refined in the orthorhombic space group *Pbca*, with the whole molecule and one lattice Et_2O within the asymmetric unit (Figure 10, *right*). Currently, **11c**·Et_2O is the first crystallographically characterised example of a terminal di-iodido rare-earth amidinate complex,[21] although a di-bromido analogue, [Sm(DippForm)$(Br)_2(thf)_3$],[10c] and a similar cerium di-chlorido analogue, [Ce(EtForm)$Cl_2(thf)_3$] (EtForm = *N*,*N*′-bis(2,6-diethylphenyl)formamidinate),[37] are known. The iodide ligands coordinate to ytterbium in a *transoid* manner (I1-Yb1-I2: 168.181(15)º), and deviations from 180º are likely due to the repulsion by the neighbouring isopropyl groups of the DippForm ligand.

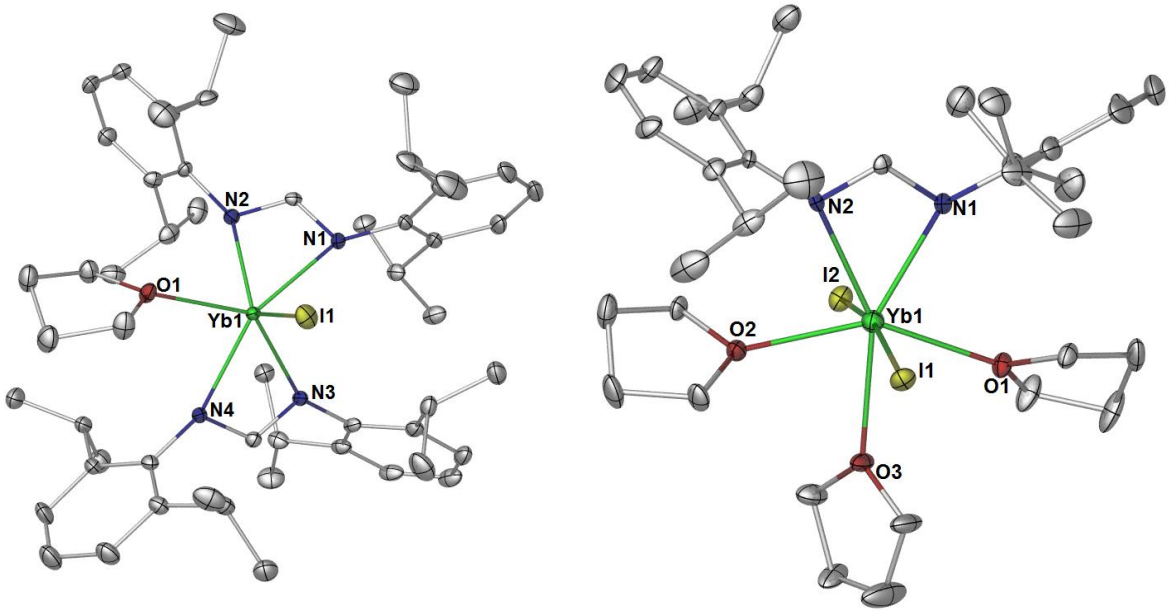


Figure 10. Molecular structures of [YbI(DippForm)$_2$(thf)] (**11b**, *left*) and [YbI_2(DippForm)$(thf)_3$]·Et_2O (**11c**·Et_2O, *right*). Ellipsoids shown at 50% probability, hydrogen atoms, and lattice solvents removed for clarity. Selected bond

lengths (Å) for **11b**: Yb1-N1: 2.393(3), Yb1-N: 2.300(3), Yb1-N3: 2.336(3), Yb1-N4: 2.358(3), Yb1-I1: 2.8975(7), Yb-O1: 2.352(2). Selected bond lengths (Å): for **11c**·Et_2O: Yb1-N1: 2.418(5), Yb1-N2: 2.439(5), Yb1-I1: 3.0842(6), Yb1-I2: 3.0834(6), Yb1-O1: 2.437(4), Yb1-O2: 2.440(4), Yb1-O3: 2.525(4).

The X-ray data for **Sm13** were solved and refined in the monoclinic space group $P2_1/n$, with half the molecule within the asymmetric unit (Figure 11). There are two different $(\{C_5Ph_4\}\text{-}O)^{2-}$ and Sm environments in the dimer. One $(\{C_5Ph_4\}\text{-}O)^{2-}$ ligand bridges three Sm atoms through C1-C5 and O1. The C_5Ph_4 component binds η^5 to Sm1 as in **Sm11** (Figure 10). The oxygen atom (O1) points to the middle of the molecule, and bridges to Sm2 and Sm2′. The second $(\{C_5Ph_4\}\text{-}O)^{2-}$ ligand (C6-C10, O2), bridges two metals by the oxygen atom (O2), but does not display η^5 coordination to either metal centre. Instead this C_5Ph_4 ring has a "slipped" arrangement, binding η^2(C71,C72; Ph) and η^2(C6,O2) to Sm1. Furthermore, there is additional coordination to Sm2 by an *ortho*-carbon of the phenyl ring C106-C110 (Sm2-C106: 2.833(17) Å). Such a bond length is significantly shorter than the analogous interaction observed in **3**·PhMe (Yb-C57D, *c.f.* Figure 2), despite the larger Sm^{2+} ionic radius. In total, with two additional thf ligands, Sm1 has a coordination number of eight, and, with only one thf ligand, Sm2 has the low coordination number of five. It should be noted that this "slipped" mode of coordination observed for the second $(\{C_5Ph_4\}\text{-}O)^{2-}$ ligand is highly unusual, and differs from the few previous examples of "slipped" Cp coordination, such as the η^6-coordination of a phenyl ring of C_5Ph_5,[38] as observed in $[Fe(C_5Ph_5)(\{C_5Ph_4\}\text{-}\eta^6(Ph))]$.[38b]

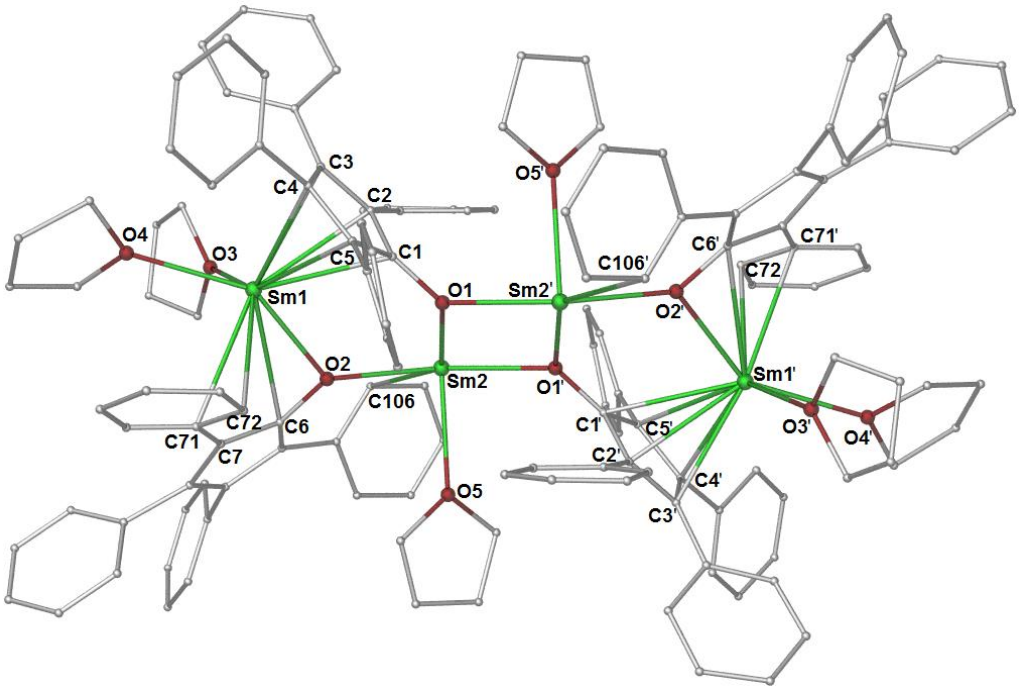


Figure 11. Molecular structure of $[\{Sm_2(\{C_5Ph_4\}\text{-}O)_2(thf)_3\}_2]$ (**Sm13**). Atoms shown as spheres for simplicity. Hydrogen atoms removed for clarity. Selected bond lengths (Å) of **Sm13**: Sm1-(cp range = 2.791(17)-2.954(17)),

Sm1-O2: 2.415(13), Sm1-C6: 2.969(19), Sm1-C71: 3.029(18), Sm1-C72: 2.96(2), Sm1-O3: 2.620(14), Sm1-O4: 2.621(16), Sm2-O1: 2.416 (17), Sm2-O2: 2.399(12), Sm2-O1′: 2.402(13), Sm2-C106: 2.833(17), Sm2-O5: 2.574(15).

Theoretical investigations (DFT) – Ketyl complex formation and formation of [Ln(DippForm)$_2$(thf){μ-OC(Ph)=(C$_6$H$_5$)-C(Ph)$_2$O}Ln(DippForm)$_2$] (Ln = Sm (Smht), Yb (Ybht):

The successful isolation of the stable ketyl complexes **1, 2, 5-8, 10,** as well as the complexes of the further reduced 1-oxido-2,3,4,5-tetraphenylcyclopentadienide(2-) ion in **Sm11 and Sm13** makes the formation of the head-to-tail coupling product, [Ln(DippForm)$_2$(thf){μ-OC(Ph)=(C$_6$H$_5$)-C(Ph)$_2$O}Ln(DippForm)$_2$] (Ln = Sm , Yb) from **1a** or **1c** and benzophenone (see Introduction) even more surprising., Thus, the nature of the [Ln(DippForm)$_2$(bp$^{\cdot}$-*O*] (Ln = Sm, Yb) *ketyl* intermediate formed in this reaction was investigated through theoretical approaches (DFT). A possible reaction pathway that yielded the head-to-tail product, [Ln(DippForm)$_2$(thf){μ-OC(Ph)=(C$_6$H$_5$)-C(Ph)$_2$O}Sm(DippForm)$_2$] (Ln = Sm (**Smht**), Yb (**Ybht**), Scheme 1i) was also investigated. Due to the importance of ketyl radical formation in SmI$_2$ chemistry, the calculations were performed on the samarium species, but these values are a representative for both metals (an average difference of 1.0 kcal.mol^{-1} was found in between Sm and Yb, with reaction with Yb being slightly less favourable). Formation of the benzophenone ketone adduct, [Sm(DippForm)$_2$(thf)(Ph$_2$C$^{\cdot}$-*O*)], is computed to be slightly endothermic by 1.0 kcal.mol^{-1}, that is more or less athermic as it is below the precision of the method used. From this adduct, the formation of the *ketyl* radical by a single electron transfer (SET) is predicted to be endothermic by only 9.0 kcal.mol^{-1} when only scalar relativistic effects are included, and exothermic by 7.7 kcal.mol^{-1} when spin-orbit has been taken into account (Figure 12).

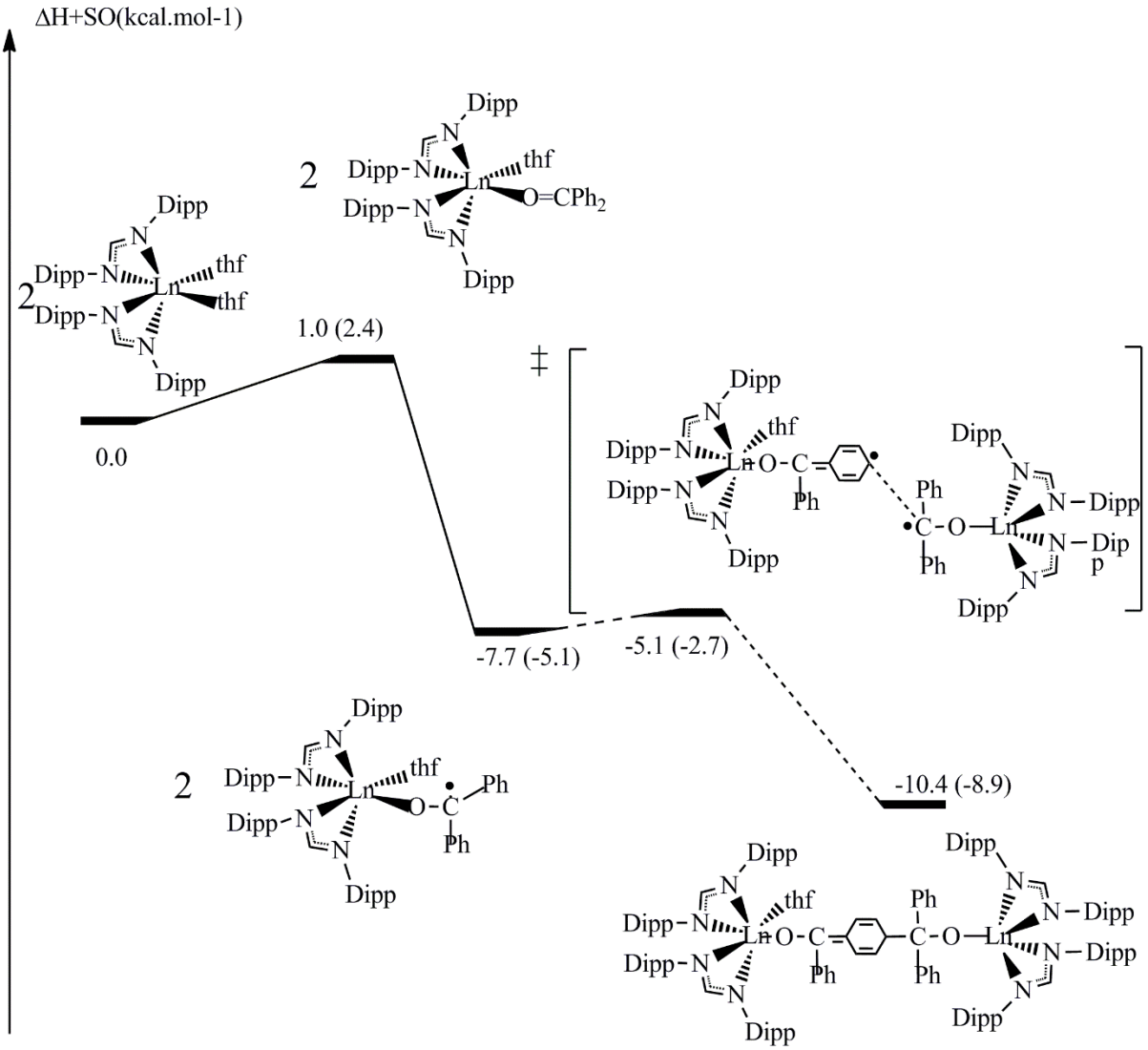


Figure 12: Computed enthalpy including spin-orbit correction profile in kcal.mol^{-1} at 298K for the reaction of [Sm(DippForm)$_2$(thf)$_2$] with bp. This energy profile is analogous for [Yb(DippForm)$_2$(thf)$_2$] and the value between bracket relates to Yb.

The nature of the *ketyl* radical was analysed by scrutinising the SOMOs of the complex (Figure 13). As shown, the SOMO is mainly located on the benzophenone, in line with the radical character of the *ketyl* ligand. Moreover, the major contributions to the SOMO are located at the *ipso* carbon of the benzophenone but also at the *para* carbon of the associated phenyl ring. The spin density was also computed, and was found that 0.63 spin is located at the *ipso* carbon and only 0.37 spin for the *para* position. Therefore, a radical coupling between two *ketyl* radical positions can be envisioned. However, due to steric repulsion, the coupling between the two *ipso* carbons was found not to be possible computationally, where every attempt led to dissociation of the resulting pinacol complex back to the *ketyl*.

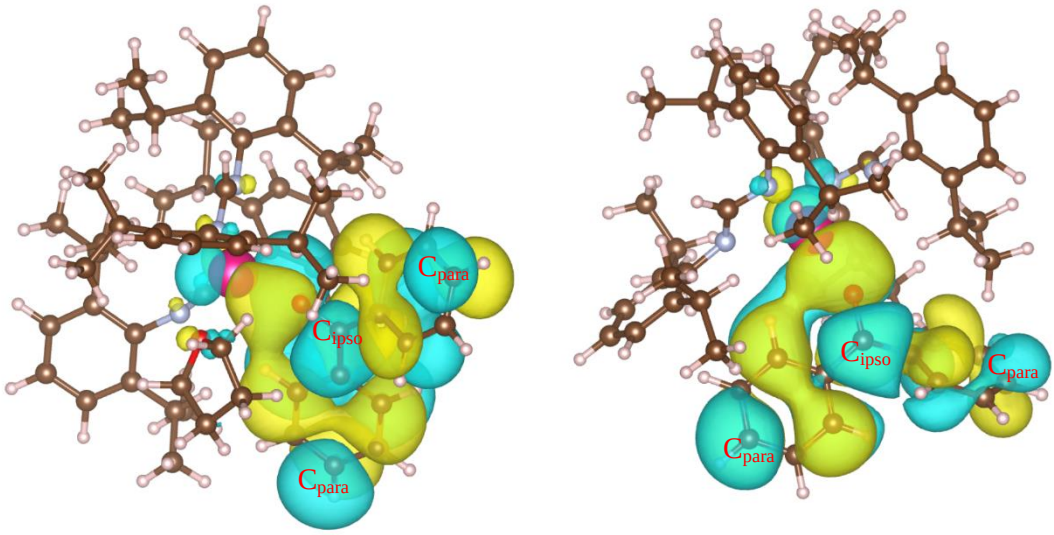


Figure 13: 3D plot of the SOMO orbital of the ketyl radical in two different orientations

A radical C–C coupling was found by using a scan procedure where the *ipso* carbon of one *ketyl* radical couples with the *para* carbon of the second *ketyl*, ultimately giving **Smht**. The activation barrier is very low when compared to the *ketyl* radical 2.6 kcal.mol^{-1}. The C-C distance is long 3.58 Å but the two carbon atoms appears to be strongly pyramidalised in line with an easy coupling reaction (Figure 14).

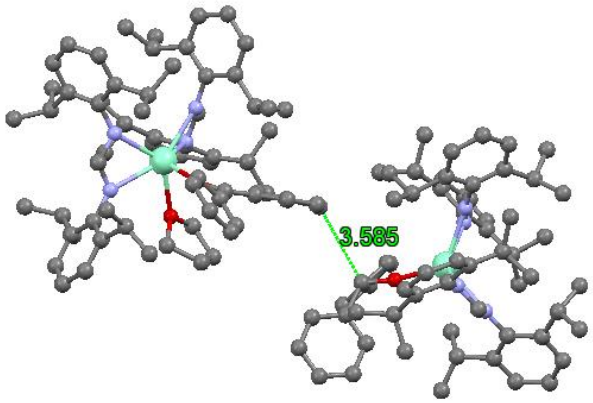


Figure 14: 3D representation of the radical coupling transition state

Following the intrinsic reaction coordinates from the transition state, it leads to the formation of the final coupling product. However, all the scalar relativistic enthalpies are positive and one can wonder why these complexes could be formed experimentally and especially because the oxidation potentials are -1.55 V (Sm) and -1.05 V (Yb). Our calculations indicate that the formation of the radical is not stabilized by electronic effects when only scalar relativistic effects are taken into account. This result seems not to match with the experimental oxidation potential of the two divalent lanthanides but it should be kept in mind that these potentials also include spin-orbit effects. This was in particular demonstrated by Vallet et al.[39] when computing the redox potential of early actinide is aqueous solution. Although it is known that a molecular complex the spin-orbit effect is quenched by the molecular

environment, it is not fully quenched as shown by Kefalidis et al. on SmI_2.[40] In order to qualitatively account for the spin-orbit correction, one can define from the J-states the putative position of the scalar relativistic state E_{SR}^{M} using Landé rules, that is an average-position of the different possible J-states as follow :

$$E_{SR}^{M} = \frac{\sum_J (2J+1)E_J}{\sum_J (2J+1)}$$

This scalar relativistic state corresponds to the one computed using our DFT approach. Therefore, the effect of the spin-orbit for a given oxidation state on the scalar relativistic state is given by :

$$E_{SO}^{M} = E_J - E_{SR}^{M}$$

Where E_J is the energy of the lowest J state as the calculation is carried out at 0K. Defining this for the two oxidation state, it is therefore possible to define the differential spin-orbit effect of the single electron transfer step according to the formula:

$$\Delta E_{SO} = E_{SO}^{Sm^{3+}} - E_{SO}^{Sm^{2+}}$$

Based on the experimental spectra,[41] it is found that ΔE_{SO} is -15.7 kcal.mol^{-1} favouring the oxidation state +III of Sm and -12.6 kcal.mol^{-1} for Yb. A spin-orbit calculation was carried out with the EPCISO code[42] developed by one of us and available in the Molcas code[43] and the obtained value for the ΔE_{SO} are -17.4 kcal.mol^{-1} for Sm and -14.2 kcal.mol^{-1} for Yb, in line with the reported value here.

This head-to-tail coupling product is 3.7 kcal.mol^{-1} more stable than the *ketyl* radical, and therefore it is unlikely that [Ln(DippForm)$_2$(bp$^{\cdot}$-*O*)(thf)] can be readily isolated, and thus different ketones needed to be considered, to give stable [Ln(DippForm)$_2$(*ketyl*)(thf)] as described in the present study.

Conclusion

Treating divalent ytterbium formamidinate complexes [Yb(DippForm)$_2$(thf)$_n$] (n = 2 (**1a**), n = 1 (**1b**)) with the aromatic ketones 9-fluorenone (fn) or 2,3,4,5-tetraphenylcyclopentadienone (tpc) gave the first two rare-earth amidinate *ketyl* complexes [Yb(DippForm)$_2$(fn$^{\cdot}$-*O*)(thf)]·THF (**2**·THF) and [Yb(DippForm)$_2$(tpc$^{\cdot}$-*O*)] (**3**). Both compounds showed remarkable stability in non-coordinating solvents (Et_2O, C_6D_6, PhMe), a rare trait for rare-earth *ketyl* complexes. When perfluorobenzoquinone (pfb) was treated with either **1a** or **1b**, C–F activation was observed giving the terminal fluoride complex [YbF(DippForm)$_2$(thf)] (**4a**) in moderate yield, and in one case, formation of an unusual fluoride/oxide cluster [$Yb_5F_6O_2$(DippForm)$_5$] (**4b**). Reduction of 1,2-diketones: 3,5-di-*tert*-butyl-benzo-1,2-quinone (tbbq), phenanthrene-9,10-dione (phen), or acenaphthalene-1,2-dione (acen) gave *ketyl* complexes: [Yb(DippForm)$_2$(tbbq$^{\cdot}$-O_2)], [Yb(DippForm)$_2$(phen$^{\cdot}$-O_2)], and [Yb(DippForm)$_2$(acen$^{\cdot}$-O_2)(thf)] (**7**). An unsolvated analogue of **7**, namely [Yb(DippForm)$_2$(acen$^{\cdot}$-O_2)] (**8**) was obtained from PhMe. As *ketyl* **3** contained the first example of a tpc$^{\cdot}$-*O* rare-earth *ketyl*, its general reactivity towards oxidants (CS_2, Se) and reducing agents (KH, Mg^0, Yb^0, and [SmI_2(thf)$_2$]) was investigated. The tpc$^{\cdot}$-*O*$^-$ *ketyl* ligand could be oxidised to tpc, or further reduced to form a di-anionic ({C_5Ph_4}-*O*)$^{2-}$ ligand. Two products obtained from these reactivity studies were of special interest: namely a

di-ketyl species [Yb(DippForm)(tpc˙-*O*)$_2$(thf)$_2$]·Et$_2$O (**10**·Et$_2$O) and the samarium semi-metallocene [{SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$] (**Sm11**) obtained from treatment of **3** with either KH or [SmI$_2$(thf)$_2$], respectively. Reduction of tpc by activated Sm^0 metal, gave a [{Sm$_2$({C$_5$Ph$_4$}-*O*)$_2$(thf)$_3$}$_2$] complex, which reacted with iodine to give **Sm11** in good yields.

Experimental section:

General considerations: All reactions were undertaken using Schlenk line and glove box techniques. Solvents (THF, PhMe, hexane, dme, diglyme, C$_6$D$_6$) were purified by distillation over sodium or sodium benzophenone, and were degassed prior to use. Metals were purchased from Santuko America, and were freshly filed before use. NMR experiments were recorded on a Bruker Avance 300 spectrometer or a Bruker Avance 400 spectrometer (where specified), ^{1}H NMR resonances were referenced to TMS by way of the residual ^{1}H resonances of C$_6$D$_6$. EPR spectra were recorded using a Bruker Elexsys E500 x-band spectrometer, which was fitted with an ER036 Teslameter. ^{19}F-NMR data were {^{1}H} decoupled and referenced to external CFCl$_3$. Microanalyses were performed by the elemental analysis service of London Metropolitan University. Metal analyses were performed from a modified literature procedure.[44] Prior to HCl treatment and buffering with hexamine, the samples were boiled with a H$_2$SO$_4$/HNO$_3$ mixture until dry. IR spectra were recorded on a Perkin–Elmer 1600 Fourier transform infrared spectrometer ($\tilde{\nu}$ = 4000–500 cm^{-1}), as either mulls in sodium-dried Nujol, or as crystalline species immersed in crystallography oil (*n*-Paratone) run on a Agilent Cary 630 FTIR instrument. [Yb(DippForm)$_2$(thf)$_2$] and [Yb(DippForm)$_2$(thf)],[10d, 11b] [SmI$_2$(thf)$_2$],[45] and [Sm(DippForm)$_2$(thf)$_2$],[10a] were synthesised by published procedures. ^{1}H NMR spectra for all *ketyl* complexes were complex and uninterpretable, thus the peaks are presented without integration or assignment. The spectra have been reproduced in the supplementary information. Furthermore, the ^{1}H NMR spectrum of crystals of **Sm11**·5THF gave no observable resonances within the range (50 to -50 ppm).

General methods for the oxidation of [Yb(DippForm)$_2$(thf)$_2$] (1a) or [Yb(DippForm)$_2$(thf)] (1b) by ketones and 1,2-diketones: **1a**, or **1b**, and an equimolar amount of one of the following ketones: 9-fluorenone (fn), perfluorobenzophenone (pfb), or 2,3,4,5-tetraphenylcyclopentadienone (tpc), or one of the following 1,2-diketones: 3,5-di-*tert*-butyl-benzo-1,2-quinone (tbbq), phenanthrene-9,10-dione (phen), or acenaphthalene-1,2-dione (acen), were combined in C$_6$D$_6$ and added to an NMR tube. All reaction mixtures displayed an immediate colour change, and quantitative oxidation, as determined by ^{1}H NMR spectroscopy which showed the complete consumption of starting materials **1a** or **1b**. After analysis, a small aliquot was extracted, diluted with THF and analysed by UV/Vis spectroscopy (where specified). The remaining solutions were transferred from the NMR tube to a Schlenk flask, dried *in vacuo* and the residue crystallised from THF/hexane mixtures (**2**·THF, **4a, 5, 7**) or PhMe (**3, 6, 8**).

[Yb(DippForm)$_2$(fn˙-*O*)(thf)]·THF (2·THF): 1a (0.045 g, 0.043 mmol) and fn (0.007 g, 0.04 mmol); gave a deep maroon/brown solution. ^{1}H NMR (C$_6$D$_6$, 303.2K): δ = -1.22 (br s), 0.29 (s), 1.17 (m), 1.37 (m, β-THF), 2.01 (br s), 3.55 (m, α-THF), 3.77 (br s), 8.21 (s), 16.00 (br s), 51.76 (s), 54.09 ppm (s); Vis (C$_6$D$_6$, THF): λ_{max} = 415, 440, 548-600 (br) nm. Crystallised from THF/Hexane as pink/yellow dichroic blocks of [Yb(DippForm)$_2$(fn˙-O)(thf)]·THF (**2**·THF). Crystal yield = ~0.03 g, (50%); m.p. 140-144°C dec; IR (Nujol): $\tilde{\nu}$ = 1663 (w), 1589 (m), 1273 (s), 1190 (m),

1134 (w), 1104 (m), 1077 (m), 1049 (m), 1019 (m), 940 (w), 861 (w), 799 (s), 759 (m), 722 cm^{-1}(m); 1723 cm^{-1} (m, observed upon exposure of mull to air). Elemental analysis calcd. (%) for $C_{69}H_{90}N_4O_{2.5}Yb$ (1188.51, half a lattice THF lost upon drying): C 69.72; H 7.63; N 4.71; found: C 69.35; H 7.63; N 4.68. EPR (PhMe, 25°C): g = 2.0076.

[Yb(DippForm)$_2$(tpc$^{\cdot}$-*O*)] (3): *Method a):* tpc (0.006 g, 0.016 mmol) and **1b** (0.015 g, 0.016 mmol) gave a deep orange solution; ^{1}H NMR (C_6D_6, 303.2K, 400 MHz): δ = -62.81 (s), -48.10 (s), -38.68 (s), -13.02 (br s), 0.30 (s), 1.18 (m), 1.37 (m, β-THF), 3.41 (s, α-THF), 9.56 (br s), 26.64 (s), 27.72 (s), 30.6 (br s), 53.92 ppm (br s); adding an additional 0.035 g of tpc to the reaction mixture caused no changes in the above resonances. Vis (C_6D_6, PhMe): 765, 484 nm. For characterisations, see *Method b*. CS_2 (two drops) was added to the reaction mixture and the solution was heated. Upon concentration (*in vacuo*) and addition of PhMe, bright orange crystals of **3**·PhMe formed and were identified by unit cell comparison with the authentic sample (a = 12.49, b = 13.02, c = 44.29, β = 95.74). *Method c):* tpc (0.068 g, 0.18 mmol) and **1b** (0.172 g, 0.176 mmol) were dissolved in PhMe (5 mL), resulting in an immediate colour change to golden red. The solution was heated at 60ºC for one hour, and then concentrated *in vacuo* to ~1 mL. The sample was stored under vacuum producing [Yb(DippForm)$_2$(tpc$^{\cdot}$-*O*)]·PhMe **(3**·PhMe) as deep orange crystals. Crystal yield: 0.17 g (85%); IR (oil): $\tilde{\nu}$ = 1662 (w), 1593 (vw), 1507 (vs), 1312 (m), 1262 (vs), 1233 (m), 1187 (m), 1098 (m), 1019 (m), 942 (m), 846 (w), 799 (vs), 752 cm^{-1} (s); elemental analysis calcd. (%) for $C_{79}H_{90}N_4OYb$ (1284.66, loss of lattice PhMe): C 73.86, H 7.06, N 4.36; Found: C 73.90, H 7.16, N 4.41. Heating crystals of **3** over either activated Yb^0 (activated by 1 drop of Hg^0) or Mg^0 in THF or PhMe gave no indication of a colour change or reaction. Compound **3** gave no observable EPR signal in PhMe.

[YbF(DippForm)$_2$(thf)] (4a) and [Yb$_5$F$_6$O$_2$(DippForm)$_5$] (4b): *Method a)* **1a** (0.058 g, 0.055 mmol) and pfb (0.021 g, 0.058 mmol); gave a deep purple on solvent addition, and the colour immediately changed to deep blue. ^{1}H NMR (C_6D_6, 303.2 K): δ = -4.99 (br s), 1.07 (br s), 1.16 (m), 1.40 (m, *β*-THF), 1.76 (br s), 3.16 (s), 3.43 (br s, *α*-THF), 4.14 (br s), 9.50 (br s), 19.99 (br s), 41.9 ppm (br s). ^{19}F {^{1}H} NMR (C_6D_6, 303.2 K): δ = -159.1 (m, 4 F, *m*-F), -145.4 (m, 2 F, *p*-F), -141.6 ppm (m, 4 F, *o*-F), additional small peaks at < 5% integration not included. Vis (C_6D_6, THF): λ_{max} = 614 nm. The solution was filtered, and crystallisation gave [YbF(DippForm)$_2$(thf)] (**4a**) as colourless blocks. Yield = 0.02 g, (30%); m.p. 180-190°C dec; IR (crystal oil): $\tilde{\nu}$ = 1663 (w), 1590 (s), 1269 (s), 1193 (s), 1107 (m), 1042 (m), 1009 (s), 934 (w), 870 (m), 800 (w), 766 cm^{-1} (m). Elemental analysis calcd. (%) for $C_{54}H_{78}FN_4OYb$ (991.30): C 65.43; H 7.93; N 5.65; found: C 62.78, H 7,19, N 6.39. Satisfactory C,H,N analyses could not be obtained even for single crystals. *Method b)* **1b** (0.13 g, 0.13 mmol) and pfb (0.048 g, 0.13 mmol) were dissolved in PhMe (3 mL) producing a bright blue colour and stirred for 15 minutes before evaporation to dryness *in vacuo*. Hexane was added and the sample was heated producing a mixed slurry of yellow and green powder within a light red solution. The mixture was heated at 50°C for three days producing light yellow crystals of **4a** along the wall of the Schlenk flask. Yield = 0.040 g, (31%); Elemental analysis calcd. (%) for $C_{54}H_{78}FN_4OYb$ (991.30): C 65.43; H 7.93; N 5.65, Yb 17.46; Found: C 60.83, H 8.01, N 5.59, Yb 17.41. The sample was examined under a microscope before elemental/metal analysis and appeared as uniform colourless block crystals, which were identified by unit cell comparison with the sample from method a. Cooling the solution produced a white microcrystalline powder, a small amount of which was extracted and immersed in crystallography oil, revealing several small yellow/pink crystals of [Yb$_5$F$_6$O$_2$(DippForm)$_5$] (**4b**) identified by X-ray crystallography.

[Yb(DippForm)$_2$(tbbq$^{\cdot}$-*O*$_2$)] (5): 1a (0.070 g, 0.067 mmol) and tbbq (0.015 g, 0.068 mmol), gave an olive green/brown solution. ^{1}H NMR (C_6D_6, 303.2 K, only major peaks): δ = -19.74 (br s), -15.92 (s) , -15.26 (s), -14.72 (s), 0.12 (br s), 1.14 (m): 1.36 (m, α-THF), 3.38 (s), 3.42 (m, β-THF), 6.45 (br s), 7.07 (br s), 11.13 (br s), 12.77 (s), 16.99 (s), 22.09 ppm (s). The product, [Yb(DippForm)$_2$(tbbq$^{\cdot}$-*O*$_2$)] (**5**), crystallised from a THF/hexane mixture as blue/yellow dichroic plates and was identified by X-ray crystallography. Crystal yield: ~0.030 g (40%); IR(Nujol): $\tilde{\nu}$ = 1667 (w), 1638 (vw), 1577 (m), 1296 (w), 1273 (s), 1253 (m), 1199 (s), 1181 (m), 1113 (w), 1097 (w), 1057 (w), 1044 (w), 1028 (w), 1014 (w), 983 (w), 950 (m), 863 (m), 825 (w), 801 (s), 758 cm^{-1}(s); Elemental analysis Calcd. (%) for: $C_{64}H_{90}N_4O_2Yb$ (1120.43): C 68.60; H 8.10; N 5.00; found: C 68.48; H 8.26; N 5.10. EPR (PhMe, 25^{o}C): g = 2.008.

[Yb(DippForm)$_2$(phen$^{\cdot}$-*O*$_2$)] (6): 1a (0.025 g, 0.024 mmol) and phen (0.005 g, 0.02 mmol); golden yellow/green solution. ^{1}H NMR (C_6D_6, 303.2K): δ = -20.98 (s), 0.26 (s), 1.14 (m), 1.57 (br s, α-THF), 3.38 (m, β-THF), 3.87 (m), 6.26 (br s), 12.74 (br s), 14.69 (br s), 32.75 (s), 41.88 ppm (s). Vis (C_6D_6, THF): λ_{max} = 412, 644 nm. The product, [Yb(DippForm)$_2$(phen$^{\cdot}$-*O*$_2$)] (**6**), was crystallised from PhMe as deep green/yellow dichroic plates and identified by X-ray crystallography. Crystal yield: 0.016 g, (60%); m.p. 250-252^{o}C; IR (Nujol): $\tilde{\nu}$ = 1667 (w), 1656 (w), 1562 (m), 1291 (w), 1270 (s), 1236 (s), 1197 (m), 1180 (w), 1161 (m), 1109 (w), 1079 (vw), 1041 (vw), 950 (vw), 934 (vw), 801 (w), 755 (s), 727 (m), 719 (w), 685 (m), 679 (m), 669 cm^{-1} (s). Elemental analysis calcd. (%) for $C_{64}H_{78}N_4O_2Yb$ (1108.37): C 69.35; H 7.09; N5.05; found: C 69.23; H 7.17; N 5.18. EPR (PhMe, 25^{o}C): g = 2.0036.

[Yb(DippForm)$_2$(acen$^{\cdot}$-*O*$_2$)(thf)]·THF (7·THF) and [Yb(DippForm)$_2$(acen$^{\cdot}$-*O*$_2$)] (8): 1a (0.11 g, 0.11 mmol) and acen (0.021 g, 0.15 mmol); gave a yellow/brown solution upon mixing, but required ~24 h before all acen had dissolved. ^{1}H NMR: (C_6D_6, 303.2K, smaller peaks not included): δ = -93.20 (s), -69.16 (s), -36.21 (s), -9.64 (s), -8.92 (s), 0.14 (br s), 1.16 (s), 1.33 (br s, THF), 1.88 (s), 3.41 (thf), 4.75 (s), 5.32 (s), 8.20 (br s), 13.08 (br s), 17.07 (br s), 23.80 (s), 29.45 (s), 32.21 ppm (s). Vis (C_6D_6, THF): λ_{max} = 407 and 745 nm. The product was crystallised from a THF/hexane mixture as green/brown dichroic plates, X-ray crystallographic analysis gave the composition: [Yb(DippForm)$_2$(acen$^{\cdot}$-*O*$_2$)(thf)]·THF (**7**·THF). Crystal yield: 0.067 g, (50%); m.p. 170-175°C dec; IR (Nujol): $\tilde{\nu}$ = 1667 (w), 1598 (s), 1577 (m), 1322 (s), 1271 (s), 1195 (m), 1148 (w), 1016 (w), 1004 (w), 940 (m), 797 (m), 762 (s), 726 cm^{-1} (s). Elemental analysis calcd. (%) for: $C_{66}H_{84}N_4O_3Yb$ (1154.44, loss of THF of crystallisation upon vacuum drying): C 68.67; H 7.33; N 4.85. Found C 68.50; H 7.46; N 4.93; EPR (PhMe, 25^{o}C): g = 2.0073. **1b** (0.114 g, 0.120 mmol) and acen (0.021 g, 0.12 mmol) were dissolved in PhMe. After two days, the mixture was concentrated affording green/golden crystals of 2[Yb(DippForm)$_2$(acen$^{\cdot}$-*O*$_2$)] (**9**), identified by X-ray crystallography. Crystal yield: 0.064 g, (50%).

Reactivity of [Yb(DippForm)$_2$(tpc$^{\cdot}$-O)] (3):

[Yb(DippForm)$_2$(tpc$^{\cdot}$-O)] with Se: **1b** (0.11 g, 0.11 mmol), and tpc (0.04 g, 0.10 mmol) were mixed in PhMe forming **3** in situ. An excess of Se (0.0055g, 0.69 mmol) was added after one hour, and the reaction mixture was heated to 60ºC. The solution slowly changed colour from orange to deep purple. Filtration and concentration of the reaction mixture produced dichroic purple/yellow crystals of tpc (a = 26.25, b = 8.24, c = 21.63, β = 119.79, consistent with literature[17]). The solution was concentrated, and then filtered repeatedly until crystals of tpc no longer formed. The solution was evaporated to dryness (*in vacuo*), and C_6D_6 was added. The spectrum was complicated, with multiple resonances and no clear product was identified (Refer to supporting information, Figure S5).

Deliberate synthesis of [{Yb(DippForm)$_2$}$_2$(Se$_2$)]·PhMe (9·PhMe): Se (0.009 g, 0.113 mmol) and **1b** (0.108 g, 0.111 mmol) were combined in PhMe giving a pink solution. The reaction mixture was heated at 50°C for one hour before the solution was filtered and concentrated giving light pink crystals of [{Yb(DippForm)$_2$}$_2$(Se$_2$)]·PhMe (**9**·PhMe). Yield: ~ 0.08 g (74%), IR (oil): $\tilde{\nu}$ = 1663 (vw), 1591 (vw), 1505 (vs), 1461 (vs), 1386 (s), 1364 (vs), 1317 (s), 1269 (vs), 1231 (s), 1193 (s), 1178 (m), 1115 (m), 1105 (m), 1054 (m), 1042 (m), 1010 (m), 947 (s), 936 (m), 899 (w), 798 (s), 753 (vs), 711 (s), 697 cm^{-1} (s); 1H NMR (C_6D_6, 300): δ = -84.57 (s), -43.77 (s), -25.02 (s), -21.98 (s), -17.83 (s), -13.30 (s), -6.11 (s), 0.41 (s), 1.22 (s), 2.11 (s, PhMe), 2.74 (s), 4.15 (s), 7.10 (m, PhMe), 9.96 (s), 15.45 (s), 17.74 (s), 18.16 (s), 23.16 (s), 25.86 (s), 34.08 (br s), 41.45 (s), 45.53 ppm (s); Elemental analysis calcd. (%) for $C_{107}H_{148}N_8Se_2Yb_2$ (2050.45): C 62.68, H 7.28, N 5.46; Found: C 62.49, H 7.04, N 5.61.

[Yb(DippForm)$_2$(tpc˙-O)] with KH: **1a** (0.11 g, 0.11 mmol) and tpc (0.04 g, 0.10 mmol) were stirred in THF, giving **3** *in situ*, and after one hour KH (0.004 g, 0.09 mmol) was added. The sample was heated at 60ºC and the solution changed colour to deep green after one hour. The solution was filtered, concentrated, and Et_2O was added. Large yellow block crystals formed and were identified as [Yb(DippForm)(tpc˙-*O*)$_2$(thf)$_2$]·Et_2O (**10**·Et_2O). The crystals were dried *in vacuo* after X-ray analysis. Yield of **10**: ~0.05 g, (31%); Elemental analysis calcd. (%) for $C_{91}H_{91}N_2O_4Yb$ (1449.74, loss of lattice Et_2O): C 75.39, H 6.33, N 1.93; Found: C 75.26, H 6.37, N 2.04; EPR (PhMe, 25ºC): g = 2.0034. The reaction mixture was dried and fresh THF was added, the solution was concentrated and hexane was added, producing small yellow block crystals of a solvate different from **10**·Et_2O, namely [Yb(DippForm)(tpc˙-*O*)$_2$(thf)$_2$]·$^1/_4Et_2O$·$^1/_4$THF: IR(oil): $\tilde{\nu}$ = 1592 (m), 1526 (s), 1314 (s), 1281 (s), 1234 (m), 1186 (m), 1102 (m), 1062 (s), 1015 (s), 910 (m), 849 (m), 801 (m), 751 (vs), 697 cm^{-1} (vs). Vis (PhMe): 468 nm; Small white crystals of [K(thf)$_2$K(DippForm)$_2$]·THF were also identified (a = 10.79, b = 26.14, c = 11.81, β = 115.42, unit cell consistent with literature).[30]

[Yb(DippForm)$_2$(tpc˙-O)] with SmI$_2$(thf)$_2$: **3** (0.10 g, 0.09 mmol) was dissolved in THF (5-10 mL) and $SmI_2(thf)_2$ (0.049 g, 0.09 mmol) was added. The reaction mixture was heated and filtered from an insoluble precipitate. Concentration of the red/orange solution, and addition hexane produced colourless block crystals of [{SmI({C_5Ph_4}-*O*)(thf)$_2$}$_2$]·2THF (**Sm11**·2THF**,** crystal yield = ~ 0.02 g, ~25%, identified by X-ray crystallography), and unidentified light red crystals (possibly **Sm11**·5THF, for characterisation see below). The solution was extracted from the crystals of **Sm11**·2THF, evaporated to dryness (*in vacuo*) and Et_2O was added. The solution was separated from insoluble residue, and heating the solution (after concentration), produced two sets of crystals: light orange crystals of [YbI(DippForm)$_2$(thf)] (**11b**) and colourless block crystals of [YbI$_2$(DippForm)(thf)$_3$]·Et_2O (**11c**), which were both analysed and identified by X-ray crystallography.

Treatment of [Sm(DippForm)$_2$(thf)$_2$] with one, or half an equivalent of tpc: *Method a) with one equivalent of tpc*: [Sm(DippForm)$_2$(thf)$_2$] (0.17 g, 0.16 mmol) and tpc (0.06 g, 0.16 mmol) were dissolved in THF (~5-7 mL). After one hour $SmI_2(thf)_2$ (0.09g, 0.16 mmol) was added, and the reagents were shaken. Upon standing for two hours, white/red crystals formed. The supernatant was filtered from the crystals, and the red crystals were analysed by X-ray crystallography, revealing the formation of [{SmI({C_5Ph_4}-*O*)(thf)$_2$}$_2$]·5THF (**Sm11**·5THF). Yield: 0.08 g (22%). Elemental analysis calcd. (%) for $C_{94}H_{112}I_2O_{11}Sm_2$ (1972.33): C 57.23, H 5.72; Found: C 49.82, H 5.11. *Method b) with half an equivalent of tpc*: [Sm(DippForm)$_2$(thf)$_2$] (0.19 g, 0.18 mmol), was treated with tpc (0.034 g, 0.09 mmol)

in PhMe producing a deep red/orange solution. The solution was concentrated (~1-2 mL) and stored under vacuum. Crystallisation was attempted by the following means: dissolution in hexane (at R.T, or at -20ºC, or *in vacou*); evaporation to dryness and dissolution in Et_2O (~3 mL), addition of THF (1 mL) and storage at -20ºC. After several days the solution was evaporated to dryness, and diglyme and hexane (1 : 2 mL) were added. Upon storage at -78ºC, small light green crystals of [{Sm(DippForm)$_2$}$_2$(*O*-C_5Ph_4-$(CH_2)_4$O)(diglyme)}]·C_6H_{14}·$^1/_2$DIGLYME (**Sm12·Solv**) formed, and were identified by X-ray crystallography.

Synthesis of [{Sm_2(*{C_5Ph_4}-O)$_2$*(thf)$_3$}$_2$] (Sm13): Sm metal (0.52 g, 3.54 mmol, one drop of Hg^0) and tpc (0.25g, 0.65 mmol) were stirred in THF at 50ºC for 12 hours. The solution was filtered, and the solution concentrated *in vacuo*. Upon standing at R.T small brown/yellow crystals of [{Sm_2(*{C_5Ph_4}-O)$_2$*(thf)$_3$}$_2$] (**Sm13**) formed. The crystals readily decomposed upon exposure to vacuum, yielding a brown powder insoluble in THF.

Deliberate synthesis of [{SmI({C_5Ph_4}-*O*)(thf)$_2$}$_2$] (Sm11) from Sm13: The synthesis of **Sm13** was repeated, however after filtration from the metal residues, iodine was immediately added (0.073 g, 0.57 mmol). Upon standing deep red crystals of **Sm1**·5THF formed. Yield: ~0.60 g (87%); IR (oil): 1595 (s), 1499 (vs), 1315 (w), 1279 (w), 1219 (m), 1177 (w), 1117 (w), 1064 (vs), 1024 (s), 908 (s), 836 (vs), 799 (s), 746 (s), 701 (vs), 670 cm^{-1} (vs); Elemental analysis Calcd. (%) for ($C_{82}H_{88}I_2O_8Sm_2$ – loss of three lattice THF upon standing): C 56.08, H 5.05, Sm 17.12; found: C 40.37, H 3.06, Sm 17.81.

X-Ray crystallography: Complexes were measured on either Oxford Gemini ultra diffractometer (**2**·THF**, 4a**, **8**) at 100.15 K where absorption corrections and integrations were performed using SORTAV[46], or on a 'Bruker APEX-II CCD' diffractometer at 100.15 K, mounted on a fibre loop in paratone crystallography oil. Absorption corrections were completed using Apex II program suite using SADABS.[47] (**9·PhMe**) or at the Australian synchrotron on either the MX1 (**4b, 3, Sm11·2THF, 11b, 11c, 10·Et_2O, Sm12·Solv**, **Sm11·5THF, Sm13, 5, 7**) or MX2 (**10·$^1/_4$THF·$^1/_4$$Et_2O$**, **6**) macromolecular beamlines, data integration was completed using Blu-ice[48] and XDS[49] software programs. Structural solutions were obtained by either Direct methods[50] (**2**·THF, **4b, Sm11·2THF**), Patterson[50] (**4a**) or charge flipping[51] (**3, 9·PhMe, 11b, 11c·Et_2O, 10·Et_2O, 10·$^1/_4$THF·$^1/_4$$Et_2O$, Sm12·Solv**, **Sm11·5THF**, **5**. **6**, **7**, 8) methods and refined using full matrix least squares methods against F^2 using SHELX2013, within the OLEX 2[51] graphical interface. CCDC: **2** (1502590), **3** (1502595), **4a** (1502594), **4b** (1502598), **5** (1502601), **6** (1502591), **7** (1502592), **8** (1502600), **9** (1502588), **10·Et_2O** (1502596), **10·$^1/_4$THF/·$^1/_4$$Et_2O$** (1502593), **11b** (1502599), **11c** (1502597), **Sm11·2THF** (1502585), **Sm12·5THF** (1502587), **Sm12·Solv** (1502589), **Sm13** (1502586) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Yb(DippForm)$_2$(fn˙-O)(thf)]·THF (2·THF): $C_{71}H_{94}N_4O_3Yb$ (M =1224.54 g/mol): triclinic, space group P-1 (no. 2), a = 14.5107(9) Å, b = 15.1906(16) Å, c = 16.7608(16) Å, α = 96.578(8)°, β = 95.072(6)°, γ = 118.045(9)°, V = 3196.3(5) $Å^3$, Z = 2, T = 123.01(18) K, μ(MoKα) = 1.511 mm^{-1}, *Dcalc* = 1.272 g/cm^3, 35113 reflections measured ($3.74° \leq 2\Theta \leq 50°$), 11258 unique ($R_{int}$ = 0.1089, R_{sigma} = 0.2288) which were used in all calculations. The final R_1 was 0.0518 ($I > 2\sigma(I)$) and wR_2 was 0.0810 (all data). Notes: SQUEEZE[49] was used to remove highly disordered low

occupancy THF molecule in lattice. Residual Q peak ~ 1.75 remaining in the structural solution due to slight crystal twinning.

[Yb(DippForm)$_2$(tpc$^{\bullet}$-O)]·PhMe (3·PhMe): $C_{86}H_{98}N_4OYb$ (M =1376.72 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 12.473(3) Å, b = 13.182(3) Å, c = 44.172(9) Å, β = 95.86(3)°, V = 7225(3) Å^3, Z = 4, T = 100.15 K, μ(synchrotron) = 1.343 mm^{-1}, *Dcalc* = 1.266 g/cm^3, 57787 reflections measured (1.854° ≤ 2Θ ≤ 54.996°), 16399 unique (R_{int} = 0.0469, R_{sigma} = 0.0424) which were used in all calculations. The final R_1 was 0.0567 (I > 2σ(I)) and wR_2 was 0.1432 (all data). Notes: One isopropyl group carbon atom disordered over two positions and was modelled using the PART command, and was further restrained with ISOR commands. One lattice PhMe solvate disordered within lattice and was left isotropic.

[YbF(DippForm)$_2$(thf)] (4a): $C_{54}H_{78}FN_4OYb$ (M =991.30): monoclinic, space group $P2_1/n$ (no. 14), a = 20.554(4) Å, b = 12.1596(16) Å, c = 21.568(3) Å, β = 110.316(17)°, V = 5055.1(13) Å^3, Z = 4, T = 123.00(14) K, μ(MoKα) = 1.894 mm^{-1}, *Dcalc* = 1.302 g/mm^3, 26067 reflections measured (3.9 ≤ 2Θ ≤ 50), 8922 unique (R_{int} = 0.0924, R_{sigma} = 0.1297) which were used in all calculations. The final R_1 was 0.0468 (I >2σ(I)) and wR_2 was 0.0789 (all data). Note: Solution contained disordered isopropyl groups, modelled with PART refinement with free occupancy. Two residual peaks (~1.8) remain due to an absorption anomaly from the synchrotron collection.

[Yb$_5$F$_6$O$_2$(DippForm)$_5$] (4b): $C_{125}H_{175}F_6N_{10}O_2Yb_5$ (M =2828.94 g/mol): orthorhombic, space group *Pccn* (no. 56), a = 21.771(4) Å, b = 21.771(4) Å, c = 31.009(6) Å, V = 14698(5) Å^3, Z = 4, T = 123.15 K, μ(Synchrotron) = 3.201 mm^{-1}, *Dcalc* = 1.278 g/cm^3, 112040 reflections measured (2.954° ≤ 2Θ ≤ 50°), 12279 unique (R_{int} = 0.0590, R_{sigma} = 0.0303) which were used in all calculations. The final R_1 was 0.0691 (I > 2σ(I)) and wR_2 was 0.2342 (all data). Note: Complex contained one completely disordered DippForm ligand over two positions, PART refinement and EXYZ commands used to assist in modelling, ISOR command used on disordered phenyl rings, EXYZ and 3 Carbon atoms remained isotropic, isopropyl CH_3 groups which could not be modelled by split/PART refinement were restrained with ISOR commands. A residual peak (Q =2.5) within the middle of the structure was observed, however it is due to absorption artefact from the synchrotron collection, attempts to model as an oxygen, carbon, or hydrogen atom were unsuccessful resulting in an unstable solution. Data was initially integrated in the hexagonal space group *P*4/*ncc*, and the model contained only two ytterbium atoms within the asymmetric unit. However, an attempt at a structural solution in this space group was difficult due to the aforementioned disorder, and therefore the data was solved in an orthorhombic cell: *Pccn*, leading to lowered completeness.

[Yb(DippForm)$_2$(tbbq$^{\bullet}$-*O$_2$*)](5): $C_{64}H_{90}N_4O_2Yb$ (M =1120.46): triclinic, space group *P*-1 (no. 2), a = 12.835(3) Å, b = 14.778(3) Å, c = 17.206(3) Å, α = 93.65(3)°, β = 94.00(3)°, γ = 114.57(3)°, V = 2945.3(12) Å^3, Z = 2, T = 100.15 K, μ(synchrotron) = 1.632 mm^{-1}, *Dcalc* = 1.263 g/mm^3, 47038 reflections measured (2.386 ≤ 2Θ ≤ 50), 10387 unique (R_{int} = 0.0485, R_{sigma} = 0.0337) which were used in all calculations. The final R_1 was 0.0427 (I > 2σ(I)) and wR_2 was 0.1180 (all data).

[Yb(DippForm)$_2$(phen$^{\bullet}$-*O$_2$*)](6): $C_{64}H_{78}N_4O_2Yb$ (M =1108.34): triclinic, space group *P*-1 (no. 2), a = 13.177(3) Å, b = 13.338(3) Å, c = 17.293(4) Å, α = 94.18(3)°, β = 93.44(3)°, γ = 109.39(3)°, V = 2847.8(11) Å^3, Z = 2, T = 100.15 K, μ(synchrotron) = 1.687 mm^{-1}, *Dcalc* = 1.293 g/mm^3, 42037 reflections measured (2.372 ≤ 2Θ ≤ 50),

9929 unique (R_{int} = 0.0579, R_{sigma} = 0.0437) which were used in all calculations. The final R_1 was 0.0271 (I > 2σ(I)) and wR_2 was 0.0667 (all data).

[Yb(DippForm)$_2$(acen˙-*O*$_2$)(thf)]·THF (7·THF): $C_{70}H_{92}N_4O_4Yb$ (*M* =1226.51): triclinic, space group *P*-1 (no. 2), *a* = 12.077(2) Å, *b* = 12.403(3) Å, *c* = 23.208(5) Å, *α* = 88.29(3)°, *β* = 75.89(3)°, *γ* = 65.73(3)°, *V* = 3063.8(13) Å^3, *Z* = 2, *T* = 100.15 K, μ(synchrotron) = 1.578 mm^{-1}, *Dcalc* = 1.330 g/mm^3, 48246 reflections measured (1.816 ≤ 2Θ ≤ 50), 10467 unique (R_{int} = 0.0643, R_{sigma} = 0.0403) which were used in all calculations. The final R_1 was 0.0301 (I > 2σ(I)) and wR_2 was 0.0773 (all data).

2[Yb(DippForm)$_2$(acen˙-*O*$_2$)] (2 x 8): $C_{124}H_{152}N_8O_4Yb_2$ (*M* =2164.61 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 12.5479(5) Å, *b* = 20.9512(7) Å, *c* = 22.4925(7) Å, *α* = 109.576(3)°, *β* = 99.456(3)°, *γ* = 91.990(3)°, *V* = 5470.0(3) Å^3, *Z* = 2, *T* = 123.01(10) K, μ(MoKα) = 1.755 mm^{-1}, *Dcalc* = 1.314 g/cm^3, 47229 reflections measured (3.742° ≤ 2Θ ≤ 49.996°), 19253 unique (R_{int} = 0.0331, R_{sigma} = 0.0443) which were used in all calculations. The final R_1 was 0.0269 (I > 2σ(I)) and wR_2 was 0.0609 (all data).

[{Yb(DippForm)$_2$}$_2$(Se)$_2$]·PhMe (9·PhMe): $C_{107}H_{148}N_8Se_2Yb_2$ (*M* =2050.33 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 18.334(3) Å, *b* = 24.603(4) Å, *c* = 21.647(3) Å, *β* = 93.874(5)°, *V* = 9742(3) Å^3, *Z* = 4, *T* = 100.0 K, μ(MoKα) = 2.706 mm^{-1}, *Dcalc* = 1.398 g/cm^3, 57139 reflections measured (4.454° ≤ 2Θ ≤ 50°), 17146 unique (R_{int} = 0.0564, R_{sigma} = 0.0592) which were used in all calculations. The final R_1 was 0.0341 (I > 2σ(I)) and wR_2 was 0.0752 (all data). Note: Disordered lattice PhMe modelled with PART refinement, atoms of PhMe were left isotropic.

[Yb(DippForm)(tpc˙-O)$_2$(thf)$_2$]·Et$_2$O (10·Et$_2$O): $C_{95}H_{101}N_2O_5Yb$ (*M* =1523.92 g/mol): tetragonal, space group $P4_32_12$ (no. 96), *a* = 17.214(2) Å, *c* = 58.133(12) Å, *V* = 17226(6) Å^3, *Z* = 8, *T* = 100.15 K, μ(Synchrotron) = 1.136 mm^{-1}, *Dcalc* = 1.180 g/cm^3, 173464 reflections measured (2.468° ≤ 2Θ ≤ 54.998°), 19763 unique (R_{int} = 0.0811, R_{sigma} = 0.0386) which were used in all calculations. The final R_1 was 0.0511 (I > 2σ(I)) and wR_2 was 0.1245 (all data). Note: Disordered Et_2O solvent of crystallisation in lattice, left as anisotropic. SQUEEZE command [52] used to remove highly disordered Et_2O molecule from lattice.

[Yb(DippForm)(tpc˙-O)$_2$(thf)$_2$]·$^1/_4$THF·$^1/_4$Et$_2$O (10·$^1/_4$THF/·$^1/_4$Et$_2$O): $C_{93}H_{95.5}N_2O_{4.5}Yb$ (*M* =1486.35 g/mol): tetragonal, space group $P4_32_12$ (no. 96), *a* = 17.222(3) Å,*c* = 58.227(12) Å, *V* = 17270(7) Å^3, *Z* = 8, *T* = 100.15 K, μ(Synchrotron) = 1.131 mm^{-1}, *Dcalc* = 1.143 g/cm^3, 159198 reflections measured (2.466° ≤ 2Θ ≤ 54.996°), 19645 unique (R_{int} = 0.1225, R_{sigma} = 0.0555) which were used in all calculations. The final R_1 was 0.0535 (I > 2σ(I)) and wR_2 was 0.1385 (all data).Note: Disordered THF ligands modelled with PART refinement. Highly disordered solvent within lattice, THF molecule left as isotropic, potentially additional low occupancy solvent within lattice however attempts to model residual peaks as either Et_2O or THF was unsuccessful and were left un-modelled.

[{SmI({C$_5$Ph$_4$}-*O*)(thf)$_2$}$_2$]·2THF (Sm11·2THF): $C_{82}H_{88}I_2O_8Sm_2$ (*M* =1756.02 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 13.279(3) Å, *b* = 21.998(4) Å, *c* = 13.552(3) Å, *β* = 116.57(3)°,*V* = 3540.5(15) Å^3, *Z* = 2, *T* = 100 K, μ(Synchrotron) = 2.571 mm^{-1}, *Dcalc* = 1.647 g/cm^3, 35623 reflections measured (3.57° ≤ 2Θ ≤ 54.998°), 8133 unique (R_{int} = 0.0694, R_{sigma}= 0.0482) which were used in all calculations. The final R_1 was 0.0432 (I > 2σ(I)) and wR_2 was 0.1038 (all data).

[{SmI({C_5Ph_4}-*O*)$(thf)_2$}$_2$]·5THF (Sm11·5THF): $C_{94}H_{112}I_2O_{11}Sm_2$ (*M* =1972.33 g/mol): trigonal, space group *R*-3 (no. 148), *a* = 38.514(5) Å, *c* = 16.994(3) Å, *V* = 21831(8) Å^3, *Z* = 9, *T* = 173 K, μ(synchrotron) = 1.887 mm^{-1}, *Dcalc* = 1.350 g/cm^3, 51906 reflections measured (2.69° ≤ 2Θ ≤ 49.998°), 8533 unique (R_{int} = 0.0427, R_{sigma} = 0.0219) which were used in all calculations. The final R_1 was 0.0409 (I > 2σ(I)) and wR_2 was 0.1165 (all data).

[YbI(DippForm)$_2$(thf)] (11b): $C_{54}H_{78}IN_4OYb$ (*M* =1099.14 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 11.660(2) Å, *b* = 14.413(3) Å, *c* = 16.208(3) Å, *α* = 83.61(3)°, *β* = 77.55(3)°, *γ* = 79.81(3)°, *V* = 2610.3(10) Å^3, *Z* = 2, *T* = 100.15 K, μ(synchrotron) = 2.422 mm^{-1}, *Dcalc* = 1.398 g/cm^3, 52444 reflections measured (2.582° ≤ 2Θ ≤ 56.212°), 12474 unique (R_{int} = 0.0840, R_{sigma} = 0.0554) which were used in all calculations. The final R_1 was 0.0380 (I > 2σ(I)) and wR_2 was 0.0994 (all data).

[YbI_2(DippForm)(thf)$_3$]·Et_2O (11c·Et_2O): $C_{41}H_{68}I_2N_2O_4Yb$ (*M* =1079.81 g/mol): orthorhombic, space group *Pbca* (no. 61), *a* = 19.369(4) Å, *b* = 19.142(4) Å, *c* = 24.572(5) Å, *V* = 9110(3) Å^3, *Z* = 8, *T* = 100.15 K, μ(synchrotron) = 3.446 mm^{-1}, *Dcalc* = 1.575 g/cm^3, 89233 reflections measured (3.316° ≤ 2Θ ≤ 54.998°), 10454 unique (R_{int} = 0.0702, R_{sigma} = 0.0311) which were used in all calculations. The final R_1 was 0.0488 (I > 2σ(I)) and wR_2 was 0.1523 (all data). Notes: One carbon atom on coordinated THF disordered over two positions, refined with part refinement and constrained with ISOR command.

[{Sm(DippForm)$_2$}$_2$(*O*-C_5Ph_4-$(CH_2)_4$O)(diglyme)}]·C_6H_{14}/·$^1/_2$DIGLYME (Sm12·Solv): $C_{145.5}H_{197}N_8O_6Sm_2$ (*M* =2454.80 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 15.901(3) Å, *b* = 21.705(4) Å, *c* = 23.788(5) Å, *α* = 100.60(3)°, *β* = 106.37(3)°, *γ* = 100.24(3)°, *V* = 7510(3) Å^3, *Z* = 2, *T* = 100.15 K, μ(Synchrotron) = 0.824 mm^{-1}, *Dcalc* = 1.086 g/cm^3, 144674 reflections measured (1.842° ≤ 2Θ ≤ 56.038°), 35730 unique (R_{int} = 0.0729, R_{sigma} = 0.0562) which were used in all calculations. The final R_1 was 0.0553 (I > 2σ(I)) and wR_2 was 0.1754 (all data). Notes: ISOR command used to restrain disordered atoms, non-coordinating atoms (C114, C116, O5) on diglyme bound to Sm2 were highly disordered, attempted solution with multiple part refinements was unstable, modelled as only 50% occupancy. Lattice solvent highly disordered and modelled as isotropic.

[{Sm_2({C_5Ph_4}-*O*)$_2$(thf)$_3$}$_2$] (Sm13): $C_{140}H_{128}O_{10}Sm_4$ (*M* =2571.95 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 13.150(3) Å, *b* = 18.692(4) Å, *c* = 23.466(5) Å, *β* = 102.81(3)°, *V* = 5624(2) Å^3, *Z* = 4, *T* = 100(2) K, μ(Synchrotron) = 2.120 mm^{-1}, *Dcalc* = 1.519 g/cm^3, 30180 reflections measured (2.814° ≤ 2Θ ≤ 48.244°), 8642 unique (R_{int} = 0.2224, R_{sigma} = 0.1629) which were used in all calculations. The final R_1 was 0.0992 (I > 2σ(I)) and wR_2 was 0.2784 (all data). Notes: Very poor diffraction, despite suitable crystal size. It required extended exposure to X-ray source, causing decomposition the X-ray beam.

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checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p21n_a

Bond precision: C-C = 0.0093 A Wavelength=0.71070

Cell: a=13.279(3) b=21.998(4) c=13.552(3)
alpha=90 beta=116.57(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	3540.6(16)	3540.5(15)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C74 H72 I2 O6 Sm2, 2(C4 H8 O)	C74 H72 I2 O6 Sm2, 2(C4 H8 O)
Sum formula	C82 H88 I2 O8 Sm2	C82 H88 I2 O8 Sm2
Mr	1756.04	1756.02
Dx,g cm-3	1.647	1.647
Z	2	2
Mu (mm-1)	2.571	2.571
F000	1748.0	1748.0
F000'	1746.04	
h,k,lmax	17,28,17	17,28,17
Nref	8138	8133
Tmin,Tmax	0.912,0.975	0.000,0.000
Tmin'	0.879	

Correction method= # Reported T Limits: Tmin=0.000 Tmax=0.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 27.499

R(reflections)= 0.0432(5925) wR2(reflections)= 0.1037(8133)

S = 1.048 Npar= 424

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.3 Ratio
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C8 Check
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C3S Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C4S Check

```
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0093 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C3     -   C4     ...       1.40 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C7     -   C8     ...       1.42 Ang.
```

Alert level G

```
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.       8.43 Why ?
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Sm1    --  I1      ..       30.0 su
PLAT343_ALERT_2_G Unusual          Angle Range in Main Residue for     C1     Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C2     Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C3     Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C4     Check
PLAT343_ALERT_2_G Unusual          Angle Range in Main Residue for     C5     Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          8 Note
PLAT793_ALERT_4_G The Model has Chirality at C2      (Centro SPGR)         S Verify
PLAT793_ALERT_4_G The Model has Chirality at C3      (Centro SPGR)         R Verify
PLAT793_ALERT_4_G The Model has Chirality at C4      (Centro SPGR)         S Verify
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   7 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  11 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  11 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

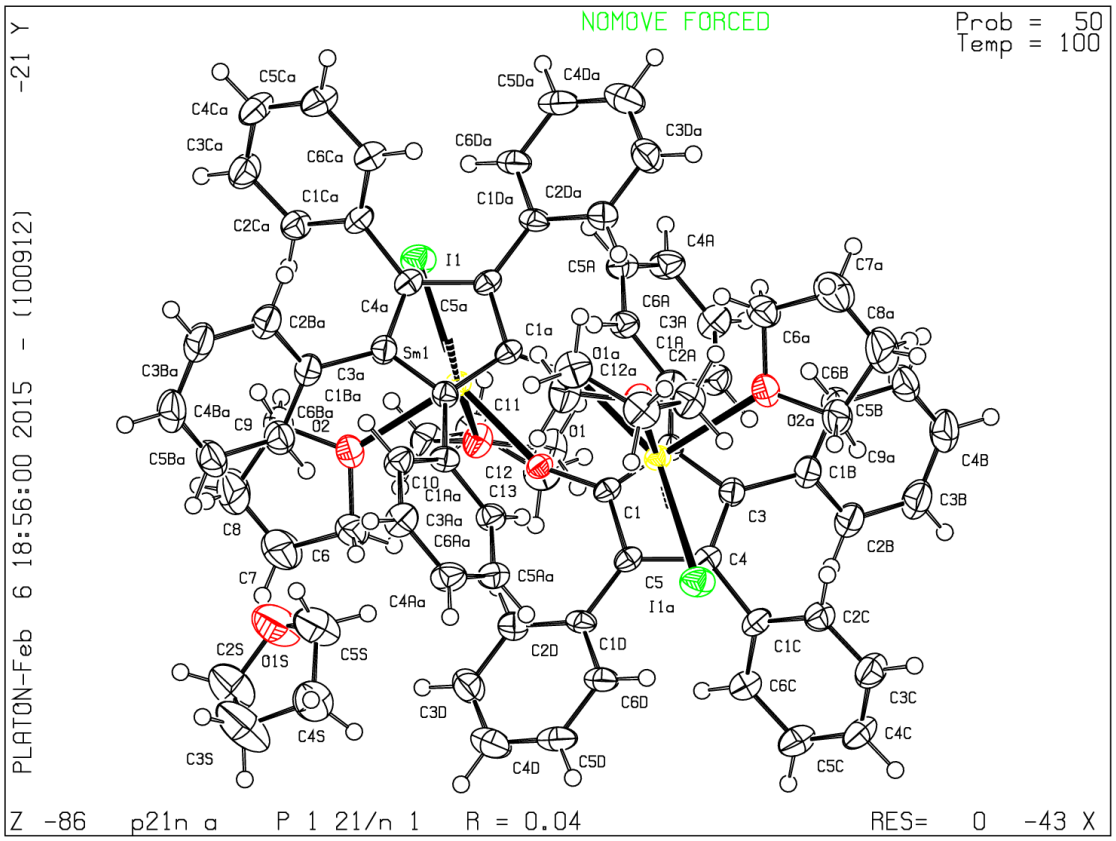
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 29/01/2015; check.def file version of 29/01/2015

[SmI(TPO)(thf)2]2(THF)2 (Sm1)

Datablock p21n_a - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p21n

Bond precision: C-C = 0.0086 A Wavelength=0.71080

Cell: **a=12.473(3)** **b=13.182(3)** **c=44.172(9)**
alpha=90 **beta=95.86(3)** **gamma=90**
Temperature: **100 K**

	Calculated	Reported
Volume	7225(3)	7225(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C79 H90 N4 O Yb, C7 H8	C79 H90 N4 O Yb, C7 H8
Sum formula	C86 H98 N4 O Yb	C86 H98 N4 O Yb
Mr	1376.73	1376.72
Dx,g cm-3	1.266	1.266
Z	4	4
Mu (mm-1)	1.343	1.343
F000	2880.0	2880.0
F000'	2879.30	
h,k,lmax	16,17,57	16,17,57
Nref	16583	16399
Tmin,Tmax	0.938,0.961	0.356,0.431
Tmin'	0.935	

Correction method= MULTI-SCAN

Data completeness= 0.989 **Theta(max)= 27.498**

R(reflections)= 0.0567(13983) **wR2(reflections)= 0.1432(16399)**

S = 1.368 **Npar= 915**

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

RADNW01_ALERT_1_C The radiation wavelength lies outside the expected range
for the supplied radiation type. Expected range 0.71065-0.71075
Wavelength given = 0.71080
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 5.6 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 6.1 Ratio
PLAT332_ALERT_2_C Large Phenyl C-C Range C1A -C1D 0.16 Ang.

```
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0086 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          2 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      51.30 Why ?
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =             1 Note
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =           100 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....           6 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #       2 Note
             C7 H8
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #       3 Note
             C7 H8
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............      12 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   8 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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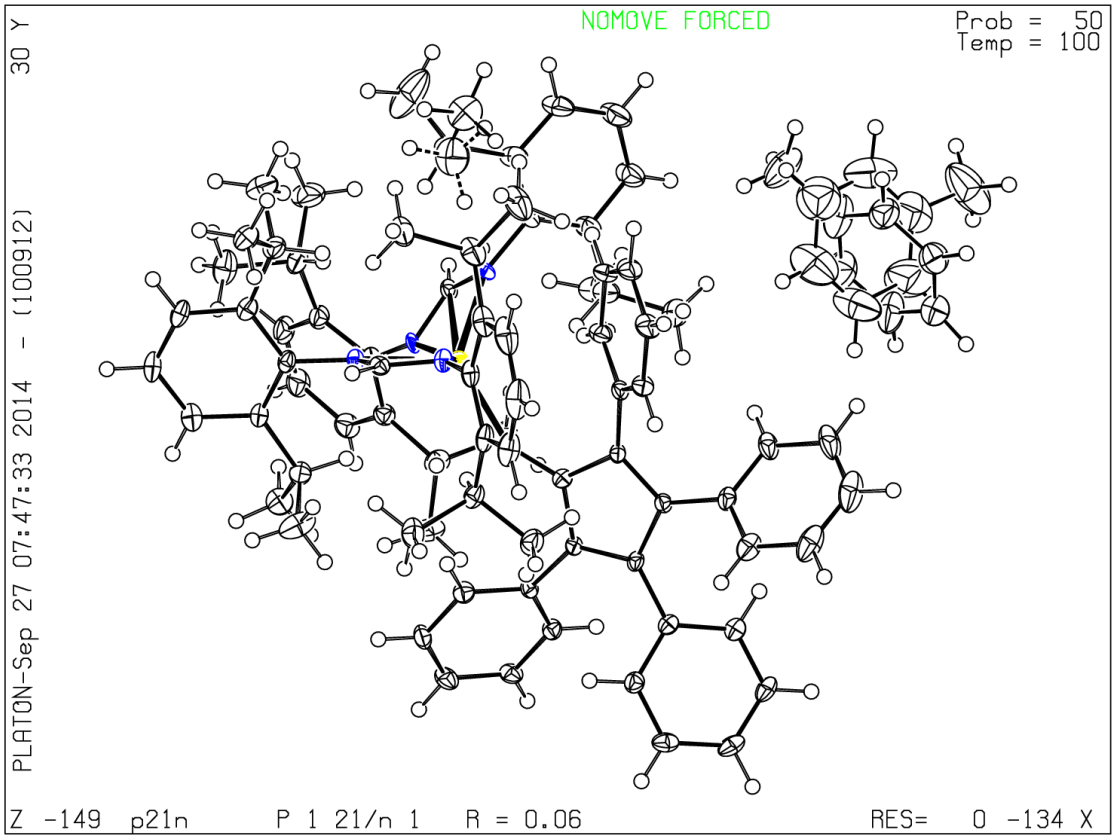
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 20/08/2014; check.def file version of 18/08/2014

Datablock p21n - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p21n

Bond precision: C-C = 0.0172 A **Wavelength=0.71080**

Cell: **a=21.771(4)** **b=21.771(4)** **c=31.009(6)**
alpha=90 **beta=90** **gamma=90**
Temperature: **123 K**

	Calculated	Reported
Volume	14698(6)	14698(5)
Space group	P c c n	P c c n
Hall group	-P 2ab 2ac	-P 2ab 2ac
Moiety formula	C125 H175 F6 N10 O2 Yb5	C125 H175 F6 N10 O2 Yb5
Sum formula	C125 H175 F6 N10 O2 Yb5	C125 H175 F6 N10 O2 Yb5
Mr	2828.96	2828.94
Dx,g cm-3	1.278	1.278
Z	4	4
Mu (mm-1)	3.201	3.201
F000	5660.0	5660.0
F000'	5654.40	
h,k,lmax	25,25,36	25,25,34
Nref	12940	12279
Tmin,Tmax	0.858,0.968	0.338,0.430
Tmin'	0.852	

Correction method= MULTI-SCAN

Data completeness= 0.949 **Theta(max)= 25.000**

R(reflections)= 0.0691(9028) **wR2(reflections)= 0.2342(12279)**

S = 1.059 **Npar= Npar = 699**

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 1591 Ang3

Alert level B
Crystal system given = orthorhombic
SYMMS02_ALERT_1_B The unit-cell lengths a and b should not be equal for an

```
           orthorhombic cell
  Cell      21.7710   21.7710   31.0090
  Angles    90.0000   90.0000   90.0000
PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low .......      0.949 Note
PLAT241_ALERT_2_B High      Ueq as Compared to Neighbors for .....       C60A Check
PLAT241_ALERT_2_B High      Ueq as Compared to Neighbors for .....       C62B Check
```

Alert level C

```
RADNW01_ALERT_1_C  The radiation wavelength lies outside the expected range
           for the supplied radiation type. Expected range 0.71065-0.71075
           Wavelength given =    0.71080
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        3.2 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C38    --  C40     ..        5.7 su
PLAT234_ALERT_4_C Large Hirshfeld Difference C1     --  C17     ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C17    --  C18     ..       0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C20    --  C21     ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C21    --  C22     ..       0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C26    --  C27     ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C27    --  C28     ..       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C41    --  C42     ..       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C45    --  C46B    ..       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C45    --  C47     ..       0.19 Ang.
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....         F3 Check
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....         F4 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....         C2 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....         C9 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C17 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C23 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C27 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C38 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C45 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C49 Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.0172 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C1F    -   C2     ...       1.40 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C27    -   C28    ...       1.40 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         11 Why ?
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT Unusually Large.       0.14 Why ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      53.63 Why ?
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =          16 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          9 Note
PLAT774_ALERT_1_G Suspect X-Y Bond in CIF:   YB2    --  YB1     ..       3.75 Ang.
PLAT774_ALERT_1_G Suspect X-Y Bond in CIF:   YB1    --  YB2     ..       3.75 Ang.
PLAT774_ALERT_1_G Suspect X-Y Bond in CIF:   YB3    --  YB2     ..       3.84 Ang.
PLAT774_ALERT_1_G Suspect X-Y Bond in CIF:   YB3    --  YB1     ..       3.84 Ang.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         54 Note
PLAT952_ALERT_5_G Reported and Calculated Lmax Values Differ by ..          2 Check
```

```
   1 ALERT level A = Most likely a serious problem - resolve or explain
   4 ALERT level B = A potentially serious problem, consider carefully
  25 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  12 ALERT level G = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
```

```
 20 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
 10 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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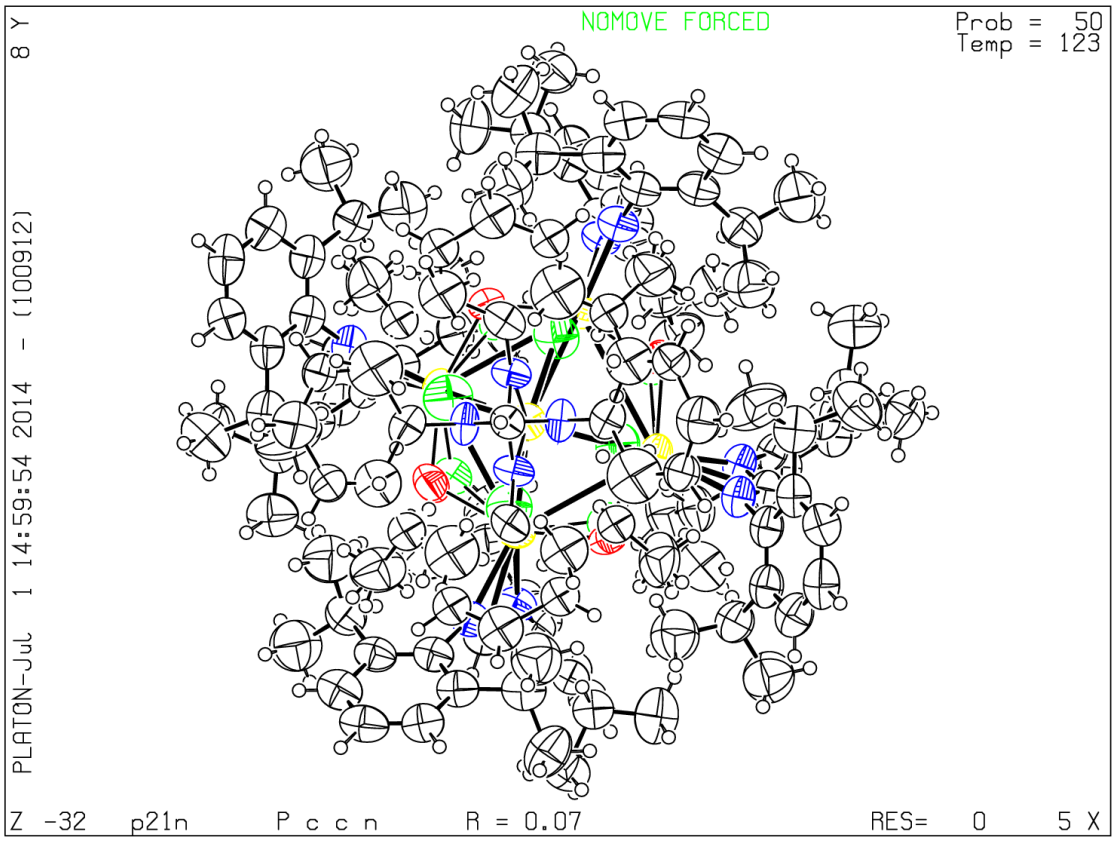
PLATON version of 05/02/2014; check.def file version of 05/02/2014

[Yb5F6O2(DippForm)5] (3b)

Datablock p21n - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: c222

Bond precision: C-C = 0.0109 A **Wavelength=0.71073**

Cell: **a=17.222(3)** **b=17.222(3)** **c=58.227(12)**
alpha=90 **beta=90** **gamma=90**
Temperature: **100 K**

	Calculated	Reported
Volume	17270(7)	17270(7)
Space group	P 43 21 2	P 43 21 2
Hall group	P 4nw 2abw	P 4nw 2abw
Moiety formula	4(C91 H90.50 N2 O4 Yb), C8 H18 O2	C91 H90.5 N2 O4 Yb, 0.25(C4 H8 O), 0.25(C4 H10 O)
Sum formula	C372 H380 N8 O18 Yb4	C93 H95 N2 O4.50 Yb
Mr	5943.02	1485.74
Dx,g cm-3	1.143	1.143
Z	2	8
Mu (mm-1)	1.131	1.131
F000	6184.0	6184.0
F000'	6182.99	
h,k,lmax	22,22,75	22,22,73
Nref	19860[11129]	19645
Tmin,Tmax	0.973,0.989	0.365,0.433
Tmin'	0.945	

Correction method= # Reported T Limits: Tmin=0.365 Tmax=0.433
AbsCorr = MULTI-SCAN

Data completeness= 1.77/0.99 **Theta(max)= 27.498**

R(reflections)= 0.0535(18965) **wR2(reflections)= 0.1385(19645)**

S = 1.094 **Npar= 966**

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT411_ALERT_2_A Short Inter H...H Contact H6 .. H51B .. 1.74 Ang.
PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 223 Ang3

Alert level B

```
PLAT230_ALERT_2_B Hirshfeld Test Diff for    O3     --  C36     ..        8.0 su
PLAT987_ALERT_1_B The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level C

```
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.123
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        4.1 Ratio
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        3.4 Ratio
PLAT222_ALERT_3_C Large Non-Solvent  H     Uiso(max)/Uiso(min) ...        4.6 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    O3     --  C39     ..        6.0 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    O4     --  C40     ..        7.0 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C9     --  C10     ..        6.5 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C16    --  C17     ..        6.5 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C16    --  C18     ..        5.2 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C23    --  C24     ..        6.5 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C24    --  C25     ..        6.3 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C70    --  C75     ..        5.5 su
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....        C37 Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0109 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H6     ..  H51A    ..       2.11 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H60    ..  H37A    ..       2.11 Ang.
PLAT413_ALERT_2_C Short Inter XH3 .. XHn     H25B   ..  H49B    ..       2.14 Ang.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         5 Note
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....     0.067 Note
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ............      0.25 Ratio
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.     23.89 Why ?
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         4 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C37    --  C1A     ..        6.3 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  O3      ..        7.9 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  O4      ..        6.4 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  N1      ..        5.2 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  N2      ..        5.9 su
PLAT300_ALERT_4_G Atom Site Occupancy of >C38    is Constrained at      0.750 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1A    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O6     is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O7     is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1B    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C8     is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C44    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C45    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C48    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C49    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C50    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C51    is Constrained at      0.250 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =            3 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms ( 188.50) in Resd. #         1 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........        10 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #         2 Note
             C8 H18 O2
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       628 Note
PLAT952_ALERT_5_G Calculated (ThMax) and CIF-Reported Lmax Differ          2 Units
```

2 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully

```
 17 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 29 ALERT level G = General information/check it is not something unexpected

  3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 24 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
 17 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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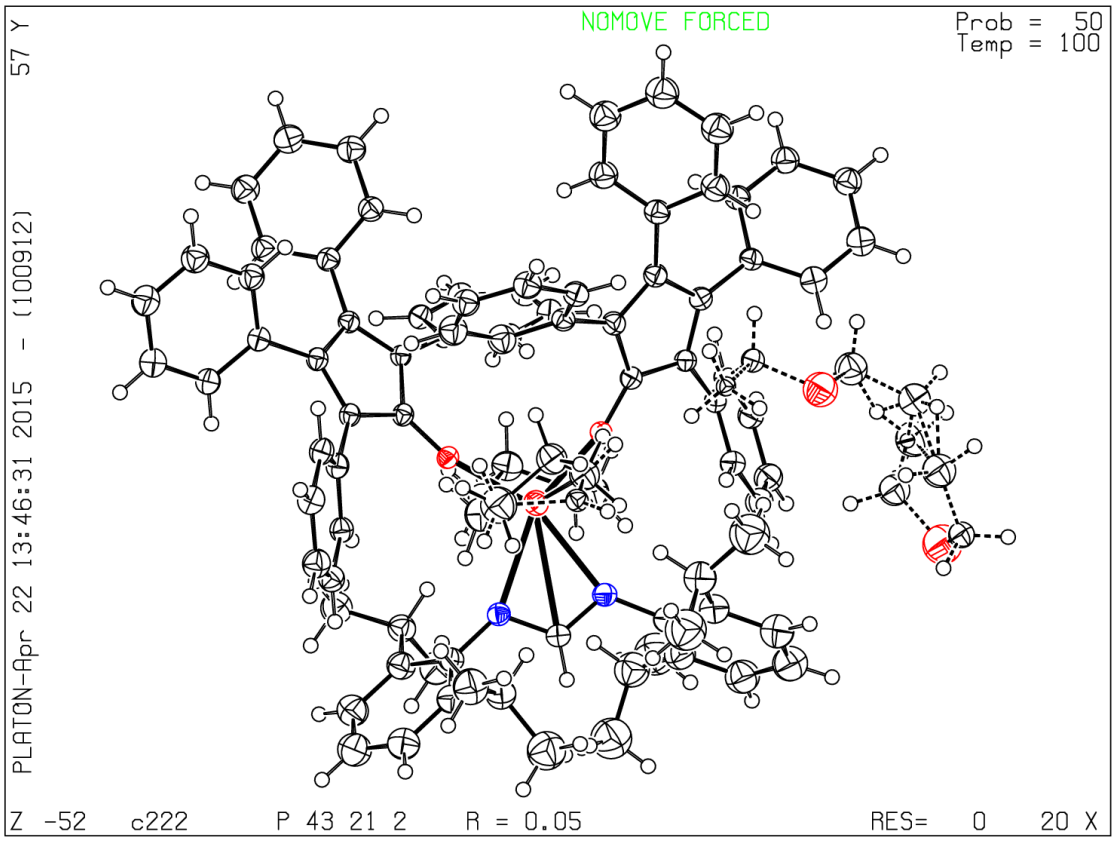
PLATON version of 29/01/2015; check.def file version of 29/01/2015

[Yb(DippForm)(TPC-O)2(thf)2]thfEt2O (6c2)

Datablock c222 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mer12

```
Bond precision:  C-C = 0.0102 A          Wavelength=0.71090

Cell:          a=12.835(3)       b=14.778(3)      c=17.206(3)
               alpha=93.65(3)    beta=94.00(3)    gamma=114.57(3)
Temperature:   100 K
```

	Calculated	Reported
Volume	2945.3(13)	2945.3(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C64 H90 N4 O2 Yb	C64 H90 N4 O2 Yb
Sum formula	C64 H90 N4 O2 Yb	C64 H90 N4 O2 Yb
Mr	1120.45	1120.43
Dx,g cm-3	1.263	1.263
Z	2	2
Mu (mm-1)	1.632	1.632
F000	1176.0	1176.0
F000’	1175.57	
h,k,lmax	15,17,20	15,17,20
Nref	10388	10387
Tmin,Tmax	0.984,0.984	0.000,0.000
Tmin’	0.984	

```
Correction method= # Reported T Limits: Tmin=0.000 Tmax=0.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 25.000

R(reflections)= 0.0427( 9393)     wR2(reflections)= 0.1179( 10387)

S = 1.158                 Npar= 662
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

```
PLAT184_ALERT_1_A Missing _cell_measurement_theta_min value ......     Please Do !
PLAT185_ALERT_1_A Missing _cell_measurement_theta_max value ......     Please Do !
```

Alert level C

```
RADNW01_ALERT_1_C  The radiation wavelength lies outside the expected range
           for the supplied radiation type. Expected range 0.71065-0.71075
           Wavelength given =    0.71090
PLAT220_ALERT_2_C Non-Solvent Resd 1   C   Ueq(max)/Ueq(min) Range        4.3 Ratio
PLAT222_ALERT_3_C Non-Solvent Resd 1   H Uiso(max)/Uiso(min) Range        5.4 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C20    --  C21     ..        5.5 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C9 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C48 Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.01023 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          5 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      14.57 Why ?
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.03 Degree
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          3 Report
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         30 Note
```

```
   2 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   7 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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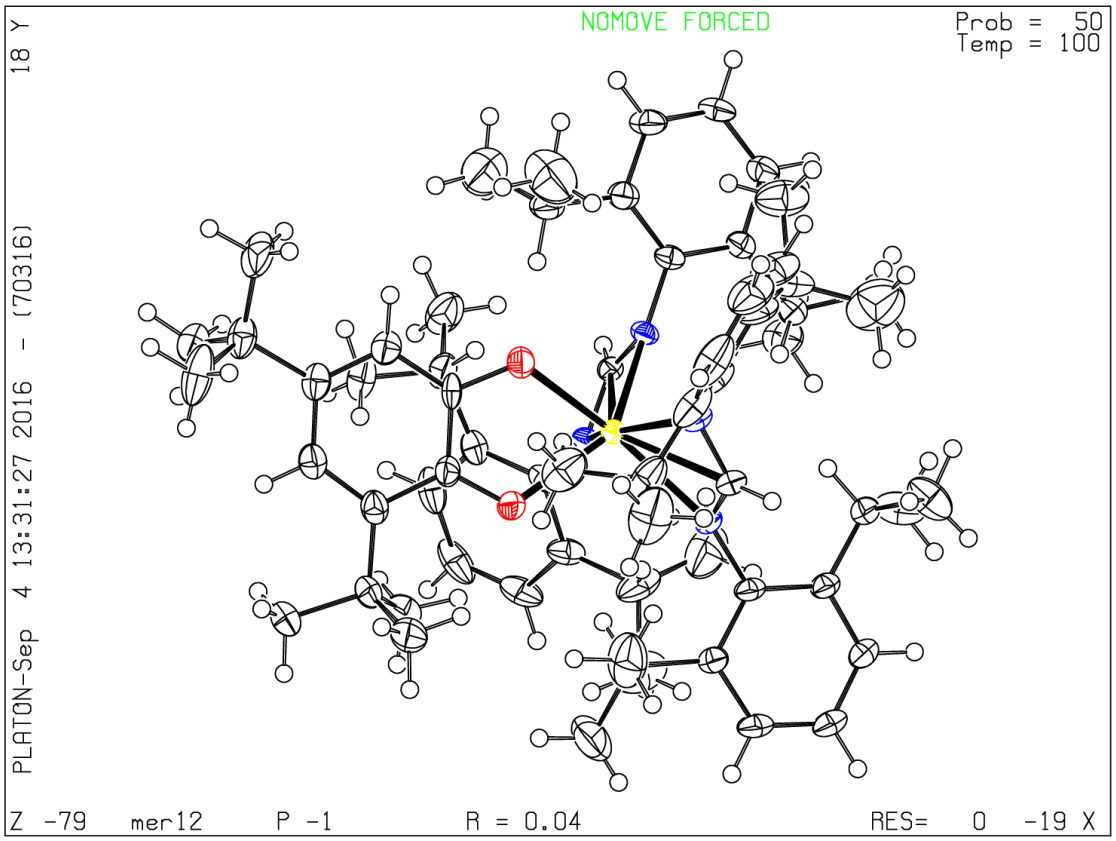
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 11/08/2016; check.def file version of 04/08/2016

[Yb(DippForm)2(TBBQ)](7)

Datablock mer12 - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: dw02

Bond precision: C-C = 0.0046 A Wavelength=0.71073

Cell: **a=12.5479(5)** **b=20.9512(7)** **c=22.4925(7)**
alpha=109.576(3) **beta=99.456(3)** **gamma=91.990(3)**
Temperature: **123 K**

	Calculated	Reported
Volume	5469.9(4)	5470.0(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C62 H76 N4 O2 Yb	2(C62 H76 N4 O2 Yb)
Sum formula	C62 H76 N4 O2 Yb	C124 H152 N8 O4 Yb2
Mr	1082.31	2164.61
Dx,g cm-3	1.314	1.314
Z	4	2
Mu (mm-1)	1.755	1.755
F000	2248.0	2248.0
F000'	2247.13	
h,k,lmax	14,24,26	14,24,26
Nref	19262	19253
Tmin,Tmax	0.663,0.966	0.791,1.000
Tmin'	0.585	

Correction method= MULTI-SCAN

Data completeness= 1.000 **Theta(max)= 24.998**

R(reflections)= 0.0269(15875) **wR2(reflections)= 0.0609(19253)**

S = 1.028 **Npar= Npar =1275**

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C85 Check
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 76 Ang3

Alert level G

PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check

```
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ............       2.00 Ratio
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..........    0.00300 Degree
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #         89 Check
              O1   -C51  -YB1     1.555   1.555   1.555             44.21 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        150 Check
              O2   -C52  -YB1     1.555   1.555   1.555             44.72 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        181 Check
              O4   -C114 -YB2     1.555   1.555   1.555             44.72 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        196 Check
              O3   -C113 -YB2     1.555   1.555   1.555             44.81 Deg.
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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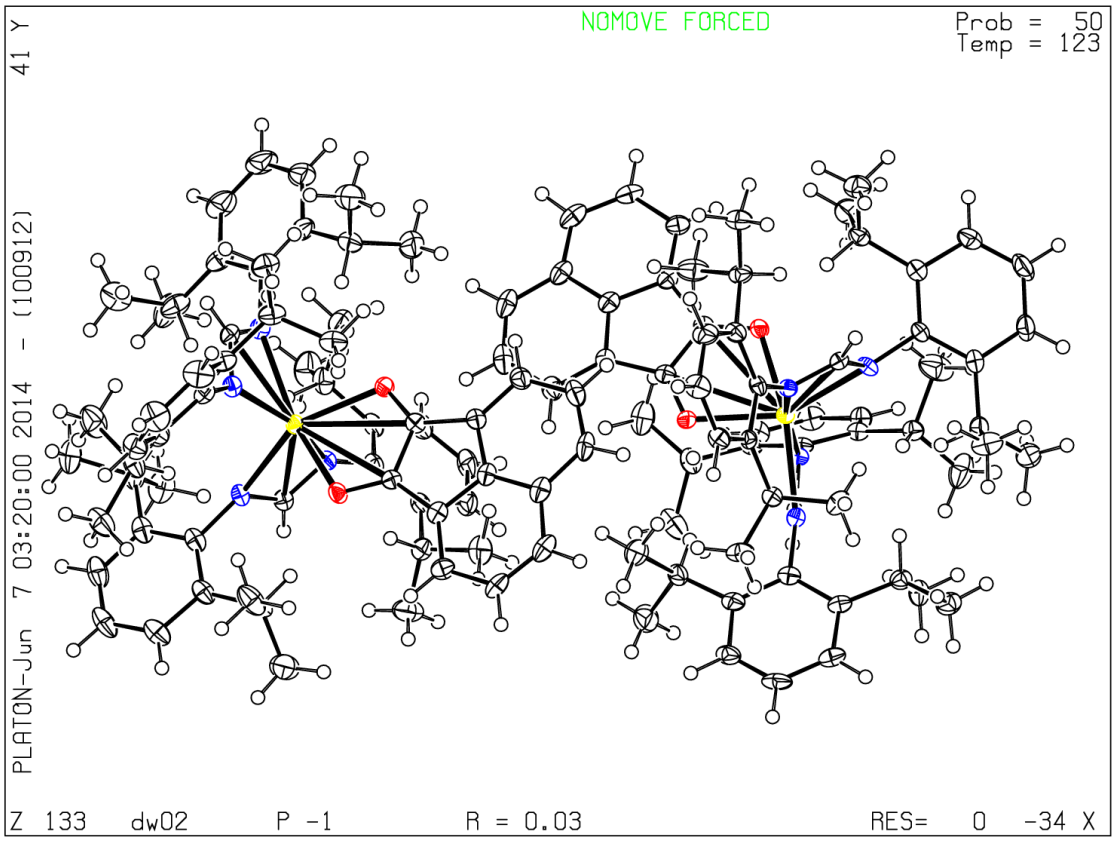
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/02/2014; check.def file version of 05/02/2014

[Yb(DippForm)2(ace)] (10)

Datablock dw02 - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p1_a

Bond precision: C-C = 0.0057 A Wavelength=0.71090

Cell: a=11.660(2) b=14.413(3) c=16.208(3)
alpha=83.61(3) beta=77.55(3) gamma=79.81(3)
Temperature: 100 K

	Calculated	Reported
Volume	2610.2(9)	2610.3(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C54 H78 I N4 O Yb	C54 H78 I N4 O Yb
Sum formula	C54 H78 I N4 O Yb	C54 H78 I N4 O Yb
Mr	1099.15	1099.14
Dx,g cm-3	1.398	1.398
Z	2	2
Mu (mm-1)	2.422	2.422
F000	1122.0	1122.0
F000'	1120.60	
h,k,lmax	15,19,21	15,19,21
Nref	12747	12474
Tmin,Tmax	0.917,0.930	0.000,0.000
Tmin'	0.908	

Correction method= MULTI-SCAN

Data completeness= 0.979 Theta(max)= 28.106

R(reflections)= 0.0380(11148) wR2(reflections)= 0.0994(12474)

S = 1.083 Npar= 566

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

RADNW01_ALERT_1_C The radiation wavelength lies outside the expected range
for the supplied radiation type. Expected range 0.71065-0.71075
Wavelength given = 0.71090
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.1 Ratio
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 48 Ang3

Alert level G

```
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal .........    0.03000 Degree
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  I1      ..        6.7 su
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
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   2 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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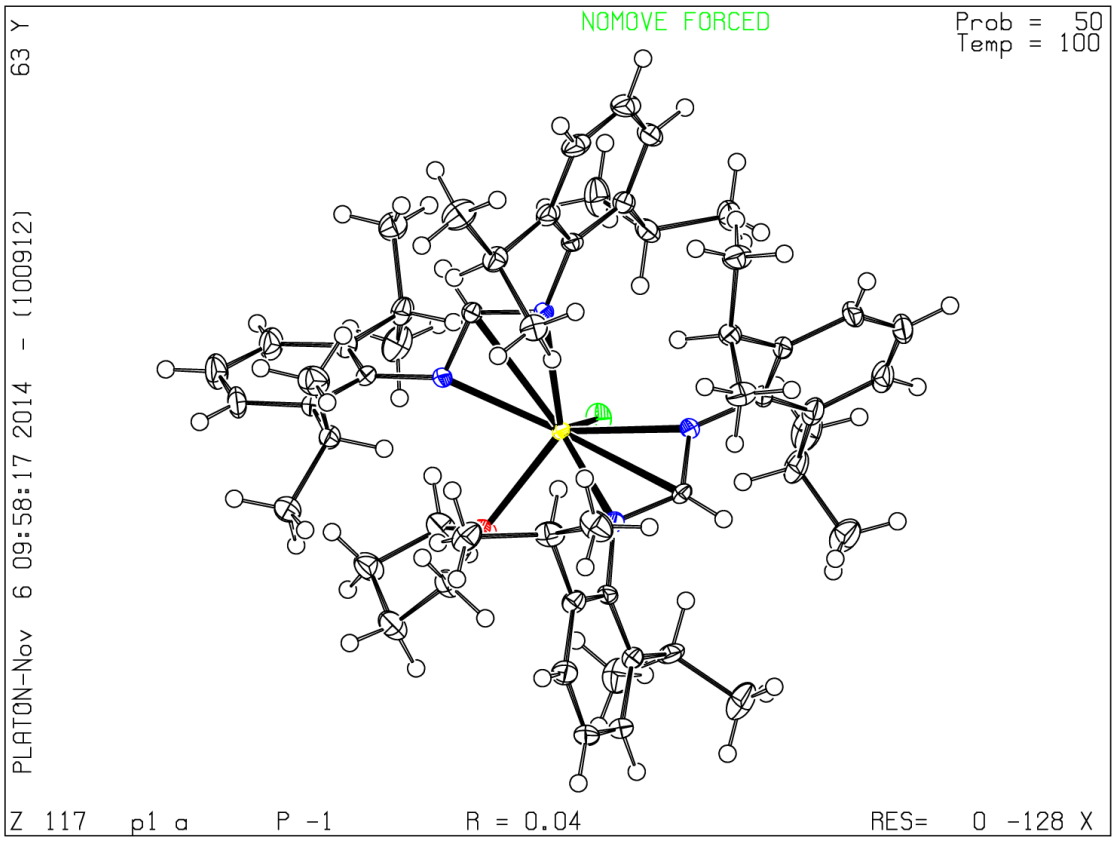
PLATON version of 20/08/2014; check.def file version of 18/08/2014

[Yb(DippForm)2(thf)I] (6a)

Datablock p1_a - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: r3_a

Bond precision: C-C = 0.0094 A Wavelength=0.71073

Cell: **a=38.514(5) b=38.514(5) c=16.994(3)**
alpha=90 beta=90 gamma=120
Temperature: 173 K

	Calculated	Reported
Volume	21831(8)	21831(8)
Space group	R -3	R -3
Hall group	-R 3	-R 3
Moiety formula	C74 H72 I2 O6 Sm2, 5(C4 H8 O)	C74 H72 I2 O6 Sm2, 5(C4 H8 O)
Sum formula	C94 H112 I2 O11 Sm2	C94 H112 I2 O11 Sm2
Mr	1972.36	1972.33
Dx,g cm-3	1.350	1.350
Z	9	9
Mu (mm-1)	1.887	1.887
F000	8946.0	8946.0
F000'	8937.66	
h,k,lmax	45,45,20	45,45,20
Nref	8539	8533
Tmin,Tmax	0.913,0.945	0.000,0.000
Tmin'	0.910	

Correction method= # Reported T Limits: Tmin=0.000 Tmax=0.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 24.999

R(reflections)= 0.0409(7956) wR2(reflections)= 0.1165(8533)

S = 1.069 Npar= 489

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT214_ALERT_2_B Atom C16S (Anion/Solvent) ADP max/min Ratio 5.4 prolat
PLAT411_ALERT_2_B Short Inter H...H Contact H11A .. H16A .. 1.89 Ang.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
           a literature citation. This should be contained in the
           _exptl_absorpt_process_details field.
           Absorption correction given as Multi-scan
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent .........          4
PLAT223_ALERT_4_C Large Solvent/Anion H    Ueq(max)/Ueq(min) .....        3.9 Ratio
PLAT243_ALERT_4_C High  'Solvent' Ueq as Compared to Neighbors of        C11S Check
PLAT243_ALERT_4_C High  'Solvent' Ueq as Compared to Neighbors of        O14S Check
PLAT244_ALERT_4_C Low   'Solvent' Ueq as Compared to Neighbors of        C13S Check
PLAT244_ALERT_4_C Low   'Solvent' Ueq as Compared to Neighbors of        C18S Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0094 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C3     -   C4     ...       1.42 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C10S   -   C11S   ...       1.39 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C11S   -   C12S   ...       1.39 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C16S   -   C17S   ...       1.38 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H7CA   ..  H16B    ..       2.10 Ang.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         5 Note
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.     466.13 Why ?
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         7 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Sm1    --  I1      ..       5.5 su
PLAT300_ALERT_4_G Atom Site Occupancy of <O0AA   is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C5S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C6S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C7S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C8S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O1S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C2S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C3S    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C4S    is Constrained at      0.250 Check
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =          20 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   3.25) in Resd. #          4 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   3.25) in Resd. #          5 Check
PLAT343_ALERT_2_G Unusual          Angle Range in Main Residue for     C1      Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C2      Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C3      Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C4      Check
PLAT343_ALERT_2_G Unusual sp3      Angle Range in Main Residue for     C5      Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          22 Note
PLAT793_ALERT_4_G The Model has Chirality at C2      (Centro SPGR)          R Verify
PLAT793_ALERT_4_G The Model has Chirality at C3      (Centro SPGR)          S Verify
PLAT793_ALERT_4_G The Model has Chirality at C4      (Centro SPGR)          R Verify
PLAT793_ALERT_4_G The Model has Chirality at C5      (Centro SPGR)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............          7 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   2 ALERT level B = A potentially serious problem, consider carefully
  13 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  28 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  15 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
  24 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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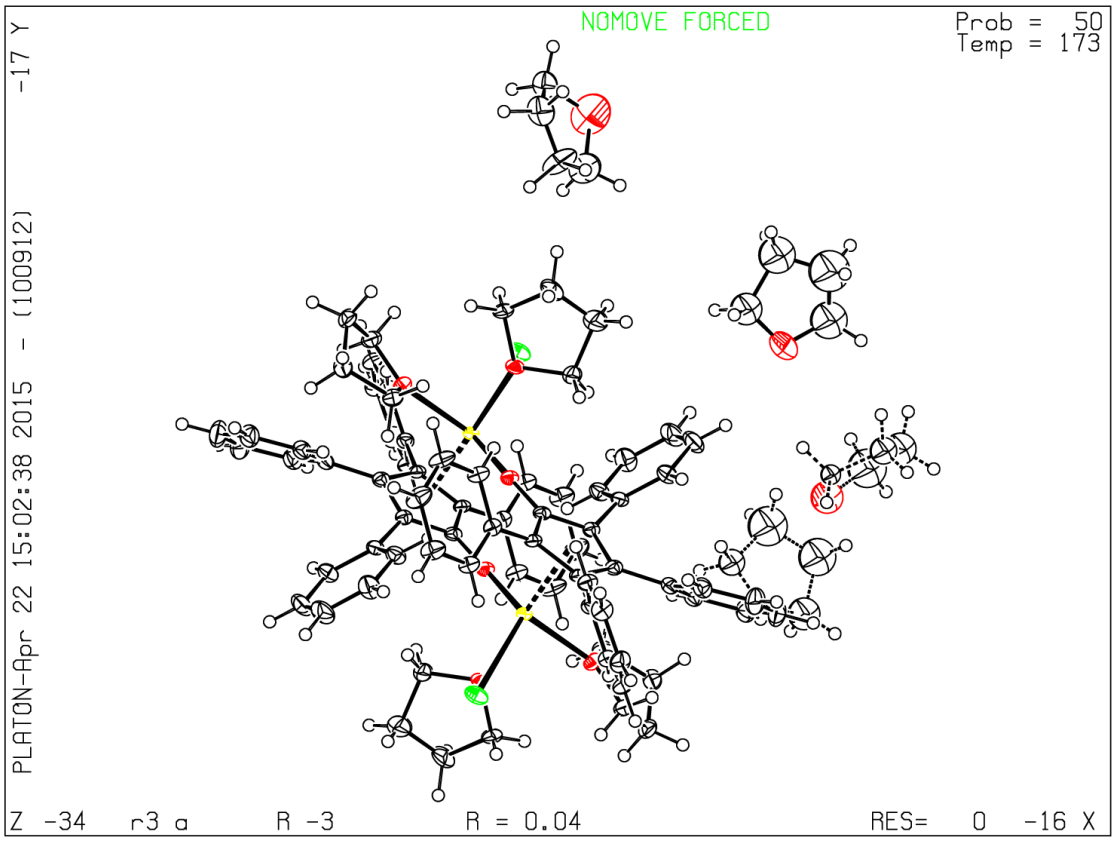
PLATON version of 29/01/2015; check.def file version of 29/01/2015

[{SmI(TPC)(thf)2}2]5THF (Sm15THF)

Datablock r3_a - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p2

Bond precision: C-C = 0.0308 A Wavelength=0.71090

Cell: a=13.150(3) b=18.692(4) c=23.466(5)
alpha=90 beta=102.81(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	5624(2)	5624(2)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C140 H124 O10 Sm4	C70 H62 O5 Sm2
Sum formula	C140 H124 O10 Sm4	C70 H62 O5 Sm2
Mr	2567.84	1283.89
Dx,g cm-3	1.516	1.516
Z	2	4
Mu (mm-1)	2.120	2.120
F000	2584.0	2584.0
F000'	2583.53	
h,k,lmax	15,21,26	14,21,26
Nref	8948	8642
Tmin,Tmax	0.979,0.989	0.000,0.000
Tmin'	0.979	

Correction method= MULTI-SCAN

Data completeness= 0.966 Theta(max)= 24.122

R(reflections)= 0.0991(4731) wR2(reflections)= 0.2792(8642)

S = 1.031 Npar= 694

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
PLAT234_ALERT_4_A Large Hirshfeld Difference C68 -- C69 .. 0.32 Ang.

Alert level B
RINTA01_ALERT_3_B The value of Rint is greater than 0.18
Rint given 0.222

```
           Crystal system given = monoclinic
THETM01_ALERT_3_B  The value of sine(theta_max)/wavelength is less than 0.575
           Calculated sin(theta_max)/wavelength =    0.5749
PLAT019_ALERT_1_B  _diffrn_measured_fraction_theta_full/_max < 1.0      0.879 Report
PLAT020_ALERT_3_B The value of Rint is greater than 0.12 .........      0.222 Report
PLAT234_ALERT_4_B Large Hirshfeld Difference C6     --  C7      ..       0.26 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference C60    --  C61     ..       0.26 Ang.
PLAT342_ALERT_3_B Low Bond Precision on  C-C Bonds ...............     0.0308 Ang.
```

Alert level C

```
RADNW01_ALERT_1_C  The radiation wavelength lies outside the expected range
           for the supplied radiation type. Expected range 0.71065-0.71075
           Wavelength given =    0.71090
RFACR01_ALERT_3_C  The value of the weighted R factor is > 0.25
           Weighted R factor given   0.279
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ...................       0.28 Report
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.78 Report
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        4.1 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C3     --  C4      ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C31    --  C38     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C34    --  C36     ..       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C55    --  C56     ..       0.22 Ang.
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....        C56 Check
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....        C60 Check
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....        C65 Check
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....        C68 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C61 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C69 Check
PLAT369_ALERT_2_C Long   C(sp2)-C(sp2) Bond  C16    -   C17    ...       1.54 Ang.
PLAT369_ALERT_2_C Long   C(sp2)-C(sp2) Bond  C38    -   C39    ...       1.53 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          1 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ............       0.50 Ratio
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT Unusually Large.       0.13 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      37.36 Why ?
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          6 Note
```

```
   1 ALERT level A = Most likely a serious problem - resolve or explain
   7 ALERT level B = A potentially serious problem, consider carefully
  17 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  13 ALERT type 2 Indicator that the structure model may be wrong or deficient
   7 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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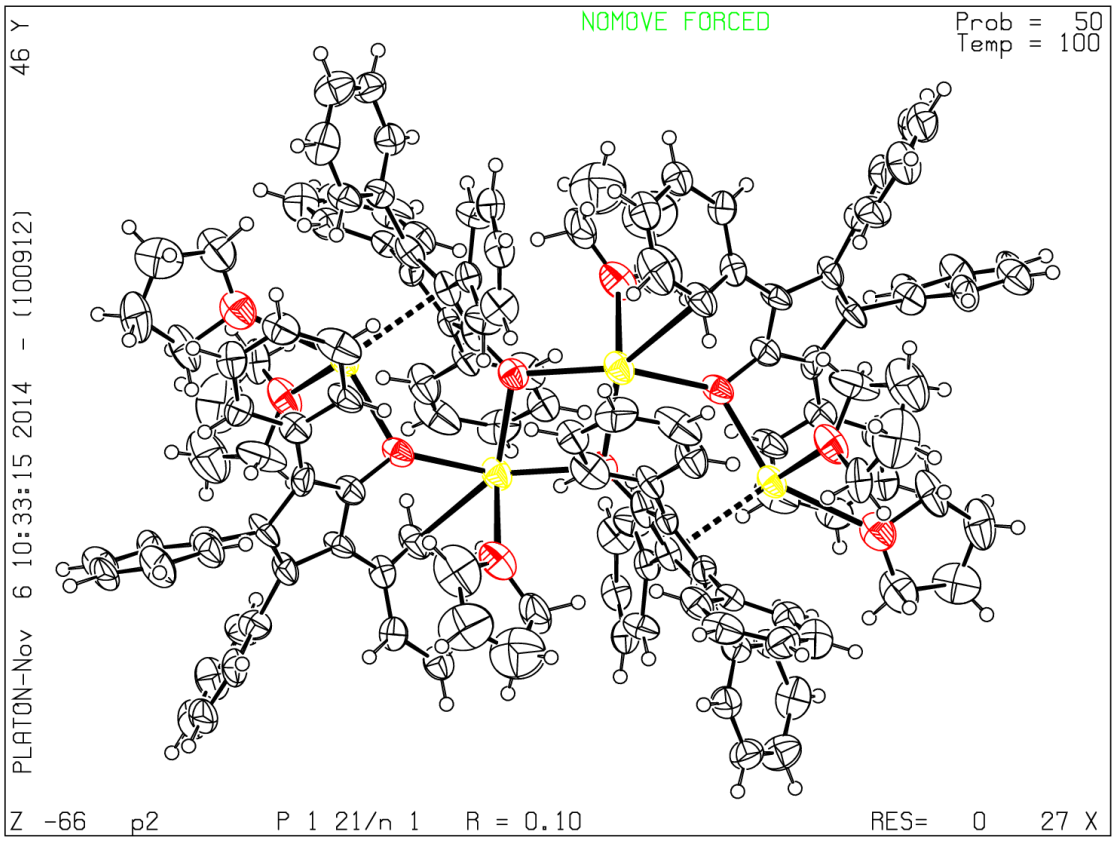
PLATON version of 20/08/2014; check.def file version of 18/08/2014

[{Sm2(TPC)2(thf)3}2] (Sm3)

Datablock p2 - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p4

Bond precision: C-C = 0.0118 A Wavelength=0.71080

Cell: a=17.214(2) b=17.214(2) c=58.133(12)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	17226(5)	17226(6)
Space group	P 43 21 2	P 43 21 2
Hall group	P 4nw 2abw	P 4nw 2abw
Moiety formula	C91 H91 N2 O4 Yb, C4 H10 O	C91 H91 N2 O4 Yb, C4 H10 O
Sum formula	C95 H101 N2 O5 Yb	C95 H101 N2 O5 Yb
Mr	1523.82	1523.81
Dx,g cm-3	1.175	1.175
Z	8	8
Mu (mm-1)	1.136	1.136
F000	6360.0	6360.0
F000'	6359.07	
h,k,lmax	22,22,75	20,22,75
Nref	19805[11099]	19763
Tmin,Tmax	0.960,0.966	0.000,0.000
Tmin'	0.956	

Correction method= # Reported T Limits: Tmin=0.000 Tmax=0.000
AbsCorr = MULTI-SCAN

Data completeness= 1.78/1.00 Theta(max)= 27.499

R(reflections)= 0.0511(18869) wR2(reflections)= 0.1247(19763)

S = 1.150 Npar= 933

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 232 Ang3

Alert level B
PLAT987_ALERT_1_B The Flack x is >> 0 - Do a BASF/TWIN Refinement Please Check

Alert level C

```
RADNW01_ALERT_1_C  The radiation wavelength lies outside the expected range
           for the supplied radiation type. Expected range 0.71065-0.71075
           Wavelength given =    0.71080
PLAT213_ALERT_2_C Atom C90            has ADP max/min Ratio .....        3.6 oblate
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range       4.5 Ratio
PLAT221_ALERT_2_C Large Solv./Anion  C     Ueq(max)/Ueq(min) Range       4.1 Ratio
PLAT222_ALERT_3_C Large Non-Solvent  H     Uiso(max)/Uiso(min) ...       4.7 Ratio
PLAT223_ALERT_4_C Large Solvent/Anion H    Ueq(max)/Ueq(min) .....       4.0 Ratio
PLAT223_ALERT_4_C Large Solvent/Anion H    Ueq(max)/Ueq(min) .....       4.0 Ratio
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.0118 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact  H3EA   ..  H1JA    ..      2.09 Ang.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         7 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         2 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 2*sigma from Zero .....     0.008 Note
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.     86.52 Why ?
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         7 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  O1      ..       5.4 su
PLAT300_ALERT_4_G Atom Site Occupancy of *O5     is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1E    is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1F    is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1H    is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1I    is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *O7     is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C0AA   is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1B    is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1D    is Constrained at     0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1J    is Constrained at     0.500 Check
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =          100 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   7.50) in Resd. #         2 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   7.50) in Resd. #         3 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....             98 Note
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         30 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .....                19 Note
PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ          2 Units
```

```
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```

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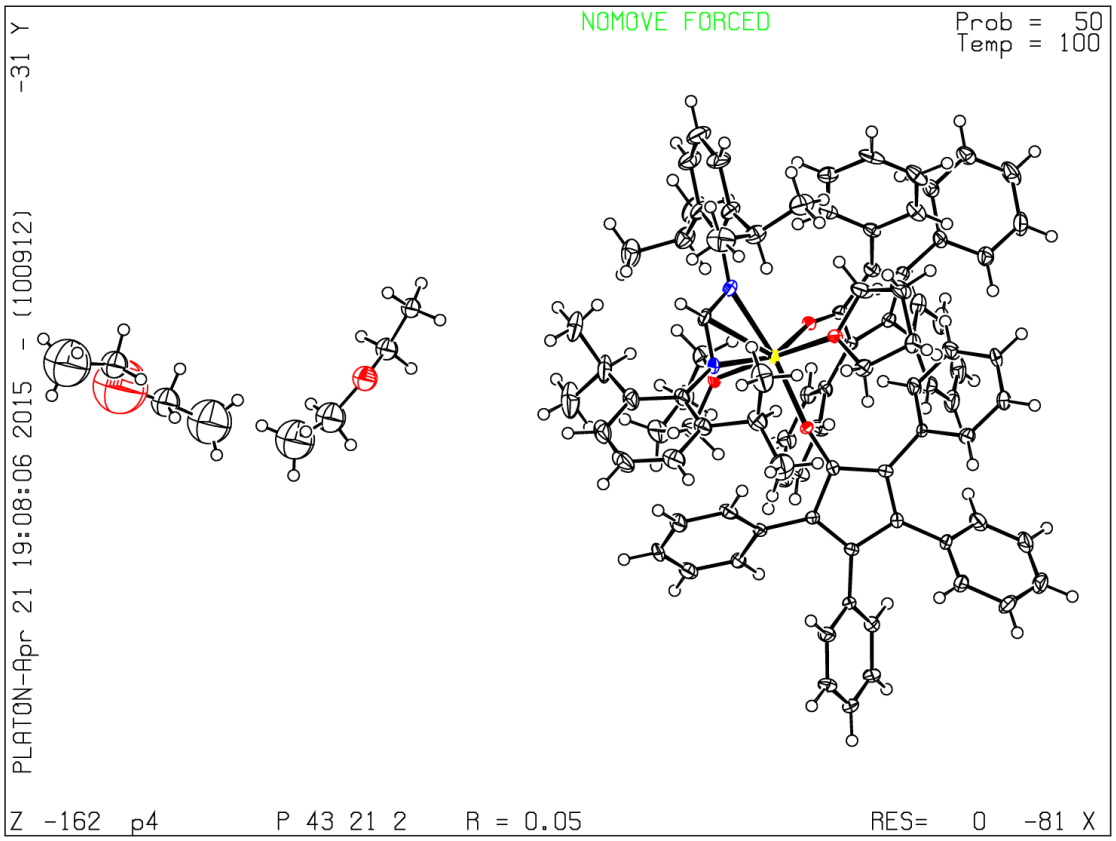
PLATON version of 29/01/2015; check.def file version of 29/01/2015

[Yb(Dipp)(TPC)2(thf)2]2Et2O (6c)

Datablock p4 - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: dw208

Bond precision: C-C = 0.0089 A Wavelength=0.71073

Cell: a=14.5107(9) b=15.1906(16) c=16.7608(16)
alpha=96.578(8) beta=95.072(6) gamma=118.045(9)
Temperature: 123 K

	Calculated	Reported
Volume	3196.3(6)	3196.3(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C67 H86 N4 O2 Yb, C4 H8 O	C67 H86 N4 O2 Yb, C4 H8 O
Sum formula	C71 H94 N4 O3 Yb	C71 H94 N4 O3 Yb
Mr	1224.55	1224.54
Dx,g cm-3	1.272	1.272
Z	2	2
Mu (mm-1)	1.511	1.511
F000	1284.0	1284.0
F000'	1283.62	
h,k,lmax	17,18,19	20,21,24
Nref	11263	11258
Tmin,Tmax	0.834,0.970	0.917,1.000
Tmin'	0.636	

Correction method= # Reported T Limits: Tmin=0.917 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 25.000

R(reflections)= 0.0518(8451) wR2(reflections)= 0.0810(11258)

S = 0.960 Npar= 765

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for C1A -- C64 .. 11.0 su
PLAT601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of . 149 Ang3

Alert level C

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.12 Report
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        4.9 Ratio
PLAT222_ALERT_3_C Large Non-Solvent  H     Uiso(max)/Uiso(min) ...        4.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C1H    --  C1L     ..       0.25 Ang.
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....        C1A Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....        C64 Check
PLAT243_ALERT_4_C High  'Solvent' Ueq as Compared to Neighbors of         C1H Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.0089 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C1F    -   C1H    ...       1.38 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          5 Report
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C1A    --  C1C     ..       12.8 su
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C1B    --  C67     ..        5.5 su
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C9     --  C11     ..        8.2 su
PLAT300_ALERT_4_G Atom Site Occupancy of >C1B    is Constrained at      0.670 Check
PLAT300_ALERT_4_G Atom Site Occupancy of >C11    is Constrained at      0.550 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1C    is Constrained at      0.330 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1D    is Constrained at      0.450 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *O1J    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *O1K    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1L    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1M    is Constrained at      0.500 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =              3 Note
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =             40 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....           25 Note
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      111 Check
             H67A -C67  -H67C    1.555   1.555   1.555            23.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      114 Check
             H67B -C67  -H67D    1.555   1.555   1.555            23.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      124 Check
             C1C  -C67  -C1B     1.555   1.555   1.555            24.50 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      233 Check
             H9B  -C9   -H9A     1.555   1.555   1.555            19.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      244 Check
             C1D  -C9   -C11     1.555   1.555   1.555            31.20 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      330 Check
             H1AA -C1A  -H1AD    1.555   1.555   1.555            24.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      331 Check
             H1AB -C1A  -H1AC    1.555   1.555   1.555            26.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #      339 Check
             C1B  -C1A  -C1C     1.555   1.555   1.555            25.70 Deg.
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #        2 Note
             C4 H8 O
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       30 Note
PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ        -3 Units
PLAT951_ALERT_5_G Calculated (ThMax) and CIF-Reported Kmax Differ        -3 Units
PLAT952_ALERT_5_G Calculated (ThMax) and CIF-Reported Lmax Differ        -5 Units
```

```
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  2 ALERT level B = A potentially serious problem, consider carefully
  9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 29 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 11 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
 21 ALERT type 4 Improvement, methodology, query or suggestion
  4 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

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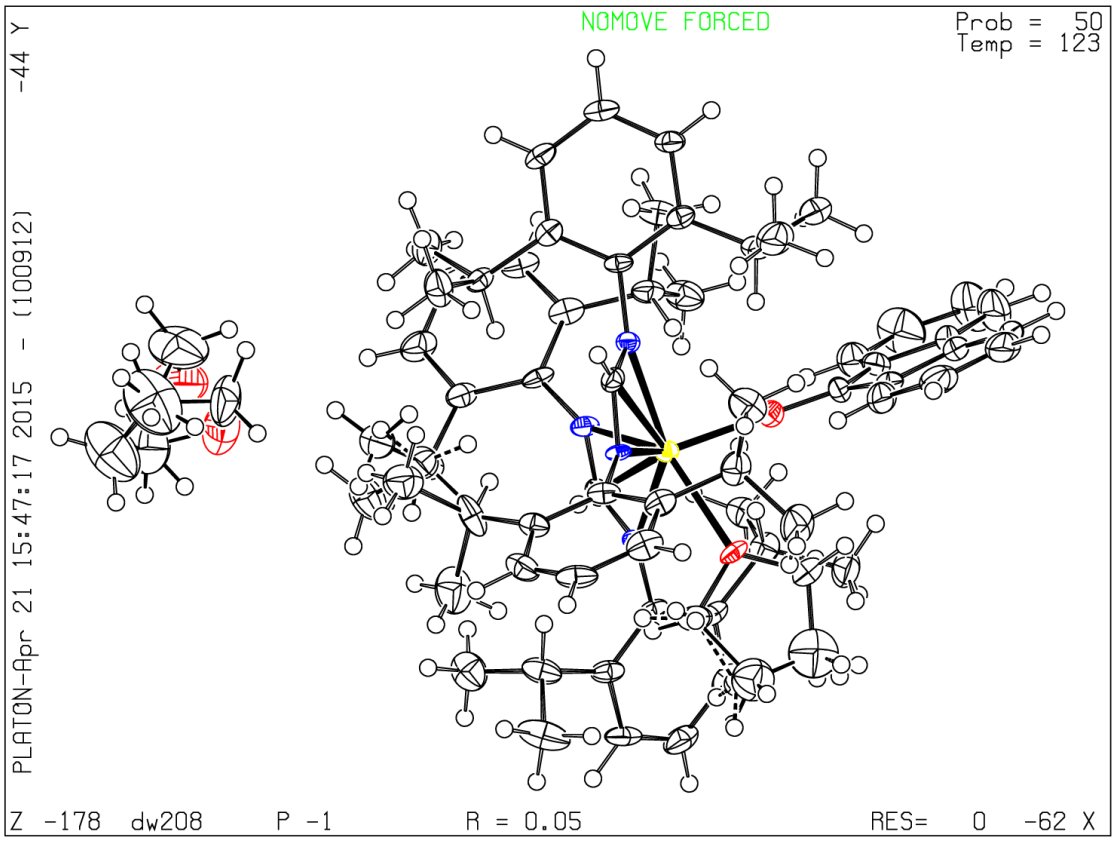
PLATON version of 29/01/2015; check.def file version of 29/01/2015

[Yb(Dipp)2(FNO)(thf)]thf (2)

Datablock dw208 - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: pb

Bond precision: C-C = 0.0103 A **Wavelength=0.71090**

Cell: **a=19.369(4)** **b=19.142(4)** **c=24.572(5)**
alpha=90 **beta=90** **gamma=90**
Temperature: **100 K**

	Calculated	Reported
Volume	9110(3)	9110(3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C37 H59 I2 N2 O3 Yb, C4 H9 O	C37 H59 I2 N2 O3 Yb, C4 H9 O
Sum formula	C41 H68 I2 N2 O4 Yb	C41 H68 I2 N2 O4 Yb
Mr	1079.81	1079.81
Dx,g cm-3	1.575	1.575
Z	8	8
Mu (mm-1)	3.446	3.446
F000	4288.0	4288.0
F000'	4278.82	
h,k,lmax	25,24,31	25,24,31
Nref	10455	10454
Tmin,Tmax	0.883,0.902	0.000,0.000
Tmin'	0.842	

Correction method= MULTI-SCAN

Data completeness= 1.000 **Theta(max)= 27.499**

R(reflections)= 0.0488(8299) **wR2(reflections)= 0.1523(10454)**

S = 1.057 **Npar= 470**

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

RADNW01_ALERT_1_C The radiation wavelength lies outside the expected range
for the supplied radiation type. Expected range 0.71065-0.71075
Wavelength given = 0.71090
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 4.5 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.7 Ratio

```
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....       C36 Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.0103 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         1 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.     71.54 Why ?
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  I1      ..      38.0 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Yb1    --  I2      ..      36.0 su
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =          2 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....        8 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints .....           6 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
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   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

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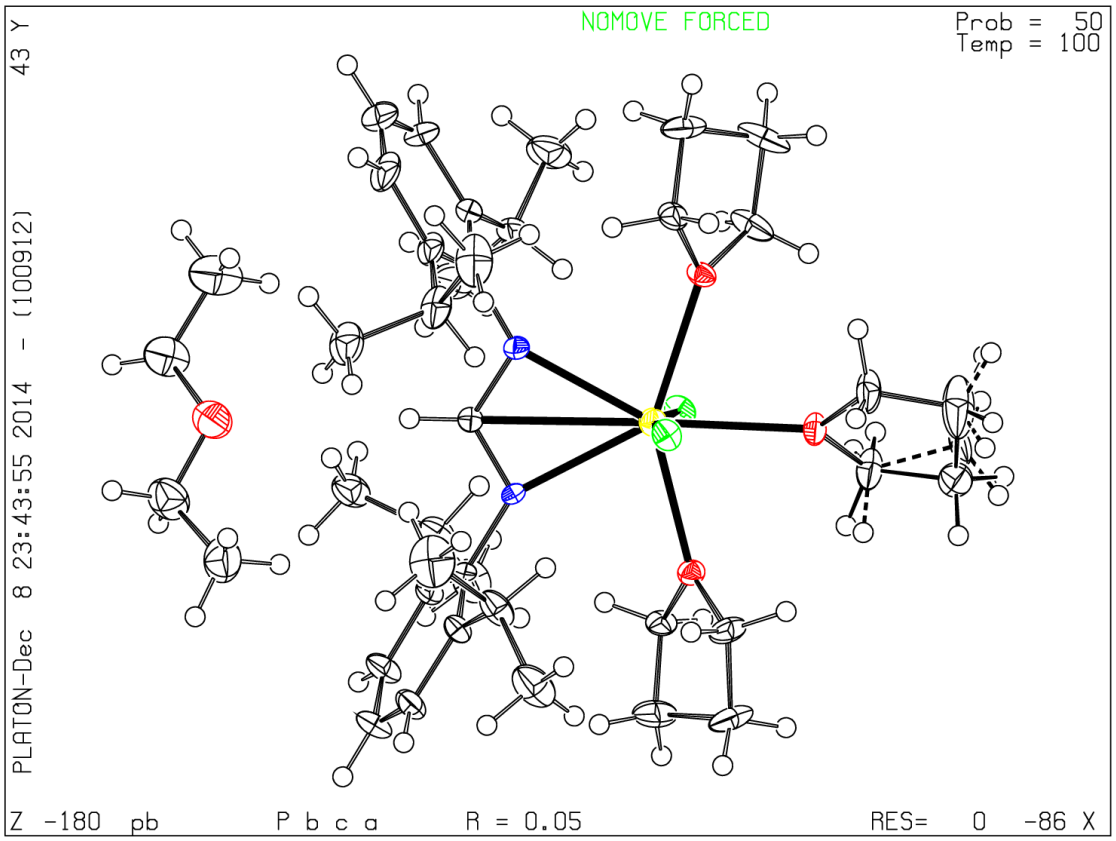
PLATON version of 20/08/2014; check.def file version of 18/08/2014

[Yb(DippForm)I2(thf)3]Et2O (6b)

Datablock pb - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: p1

Bond precision: C-C = 0.0069 A Wavelength=0.71090

Cell: **a=15.901(3) b=21.705(4) c=23.788(5)**
alpha=100.60(3) beta=106.37(3) gamma=100.24(3)
Temperature: 100 K

	Calculated	Reported
Volume	7510(3)	7510(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C138.50 H180.50 N8 O5 Sm2), 0.5(C12 H27), C6 H14 O3, C6 H14,	C139 H182 N8 O5 Sm2, 0.75(C6 H14), 0.5(C6 H14 O3), 0.25(C6 H13)
Sum formula	C296 H405.50 N16 O13 Sm4	C148 H202.75 N8 O6.50 Sm2
Mr	4997.32	2498.62
Dx,g cm-3	1.105	1.105
Z	1	2
Mu (mm-1)	0.825	0.826
F000	2645.5	2646.0
F000'	2645.65	
h,k,lmax	22,30,33	22,30,33
Nref	43939	39845
Tmin,Tmax	0.952,0.992	0.367,0.433
Tmin'	0.848	

Correction method= # Reported T Limits: Tmin=0.367 Tmax=0.433
AbsCorr = MULTI-SCAN

Data completeness= 0.907 Theta(max)= 30.035

R(reflections)= 0.0717(33219) wR2(reflections)= 0.2251(39845)

S = 1.042 Npar= 1638

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low ..... 0.932 Note

---

Alert level B

```
PLAT220_ALERT_2_B Large Non-Solvent  C     Ueq(max)/Ueq(min) Range        6.4 Ratio
PLAT222_ALERT_3_B Large Non-Solvent  H     Uiso(max)/Uiso(min) ...        8.0 Ratio
PLAT601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of .        173 Ang3
```

Alert level C

```
RADNW01_ALERT_1_C  The radiation wavelength lies outside the expected range
           for the supplied radiation type. Expected range 0.71065-0.71075
           Wavelength given =    0.71090
PLAT220_ALERT_2_C Large Non-Solvent  O     Ueq(max)/Ueq(min) Range        5.8 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference O115   --  C116    ..        0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C73    --  C81     ..        0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C107   --  C108    ..        0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C113   --  C114    ..        0.20 Ang.
PLAT241_ALERT_2_C High      Ueq as Compared to Neighbors for .....       O115 Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....       C113 Check
PLAT411_ALERT_2_C Short Inter H...H Contact  H19    ..  H9JB    ..        2.12 Ang.
PLAT413_ALERT_2_C Short Inter XH3 .. XHn     H8AA   ..  H95A    ..        2.13 Ang.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          8 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          8 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by .............      0.50 Ratio
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT Unusually Large.       0.15 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.       7.12 Why ?
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..........    0.03000 Degree
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          7 Report
PLAT300_ALERT_4_G Atom Site Occupancy of *C9A    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C74    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C75    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C75B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C76    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C76B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C77    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C77B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C78    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C78B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C79    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C79B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C80    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C80B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C81    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C81B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C82B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C84    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C84B   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C108   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C109   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C2J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C3J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C4J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C5J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C6J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C7J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C8J    is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C9J    is Constrained at      0.250 Check
```

```
PLAT300_ALERT_4_G Atom Site Occupancy of <C10J   is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C11J   is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C12J   is Constrained at      0.250 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *O6     is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *O7     is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *O8     is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C9AA   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C7BA   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C8BA   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C3BA   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C0AA   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C29C   is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1S    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C2S    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C3S    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C4S    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C5S    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C6S    is Constrained at      0.500 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C8A    is Constrained at      0.500 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =          9 Note
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =        100 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   9.75) in Resd. #          2 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (  11.50) in Resd. #          3 Check
PLAT335_ALERT_2_G Check Large C6 Ring    C-C Range C73    -C81          0.20 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  C8A    ..  C107    ..       1.81 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  C8A    ..  C106    ..       2.63 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          55 Note
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C107   --  C8A     .       1.81 Ang.
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #          23 Check
PLAT793_ALERT_4_G The Model has Chirality at C53     (Centro SPGR)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .....          55 Note
```

```
  1 ALERT level A = Most likely a serious problem - resolve or explain
  3 ALERT level B = A potentially serious problem, consider carefully
 10 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 70 ALERT level G = General information/check it is not something unexpected

  5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 15 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
 60 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

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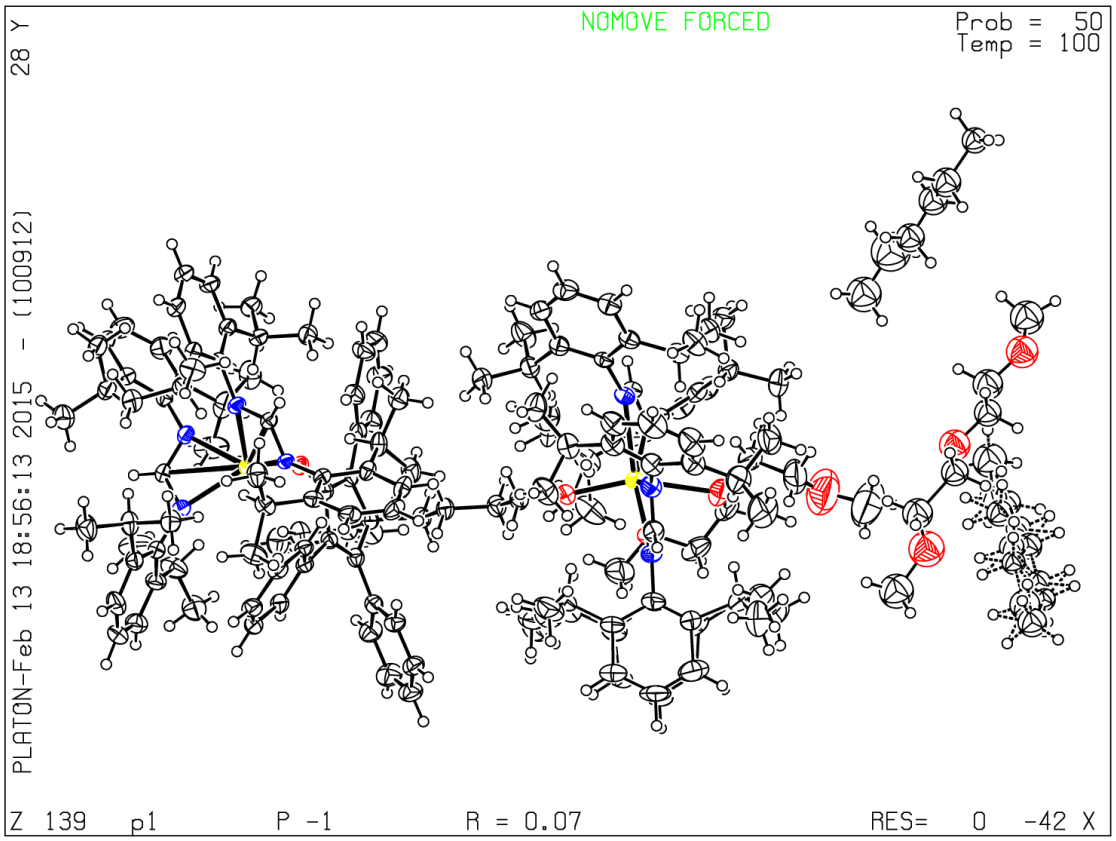
PLATON version of 29/01/2015; check.def file version of 29/01/2015

Datablock p1 - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: p-1

```
Bond precision:  C-C = 0.0055 A          Wavelength=0.71090

Cell:           a=12.077(2)       b=12.403(3)      c=23.208(5)
                alpha=88.29(3)    beta=75.89(3)    gamma=65.73(3)
Temperature:    100 K
```

	Calculated	Reported
Volume	3063.7(14)	3063.8(13)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C66 H84 N4 O3 Yb, C4 H8 O	C66 H84 N4 O3 Yb, C4 H8 O
Sum formula	C70 H92 N4 O4 Yb	C70 H92 N4 O4 Yb
Mr	1226.52	1226.51
Dx,g cm-3	1.330	1.330
Z	2	2
Mu (mm-1)	1.578	1.578
F000	1284.0	1284.0
F000’	1283.63	
h,k,lmax	14,14,27	14,14,27
Nref	10786	10467
Tmin,Tmax	0.854,0.984	0.000,0.000
Tmin’	0.854	

```
Correction method= # Reported T Limits: Tmin=0.000 Tmax=0.000
AbsCorr = MULTI-SCAN

Data completeness= 0.970          Theta(max)= 25.000

R(reflections)= 0.0301( 9994)     wR2(reflections)= 0.0773( 10467)

S = 1.075                 Npar= 728
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT184_ALERT_1_A Missing _cell_measurement_theta_min value ..... Please Do !
PLAT185_ALERT_1_A Missing _cell_measurement_theta_max value ..... Please Do !

Alert level C

RADNW01_ALERT_1_C The radiation wavelength lies outside the expected range
for the supplied radiation type. Expected range 0.71065-0.71075
Wavelength given = 0.71090
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.7 Ratio
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb1 -- O2 .. 5.2 s.u.

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 5.76 Why ?
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.03 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact C6 .. C59 .. 3.19 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 2 Note

2 **ALERT level A** = Most likely a serious problem - resolve or explain
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3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

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Publication of your CIF in other journals

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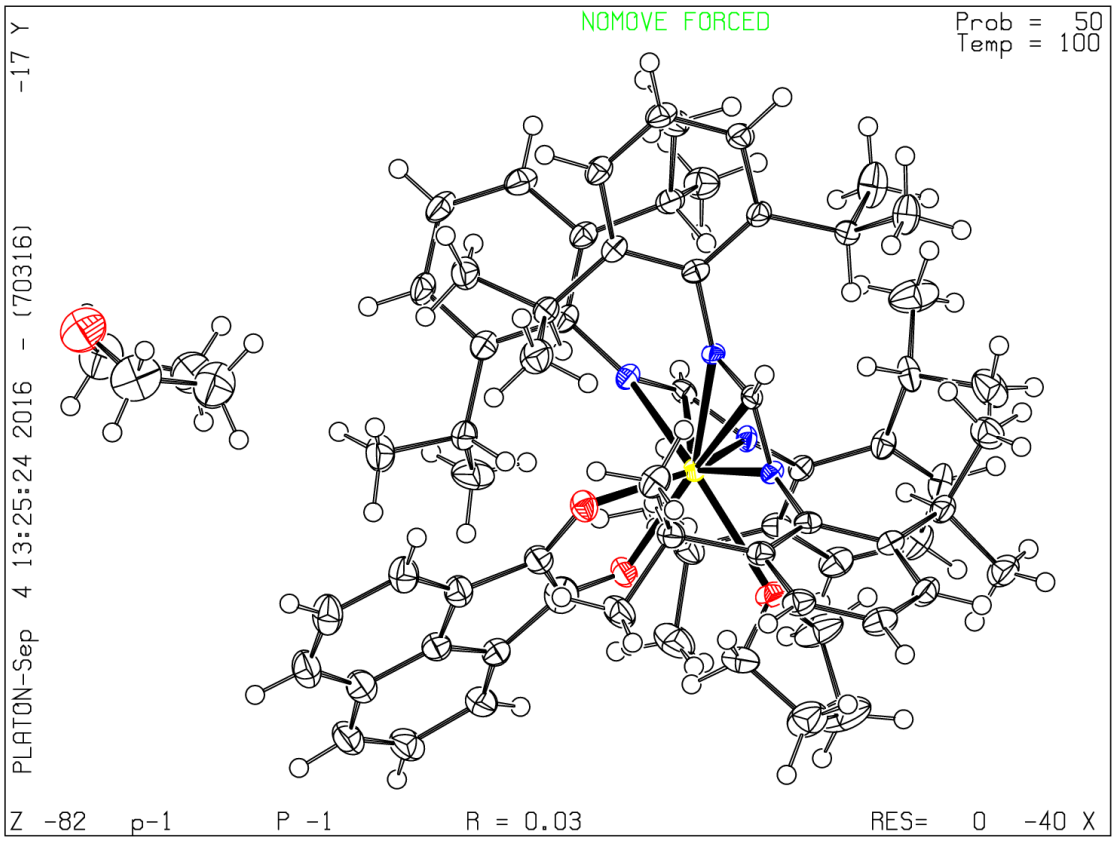
PLATON version of 11/08/2016; check.def file version of 04/08/2016

[Yb(Dipp)2(ace)(thf)](THF)(9)

Datablock p-1 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) p21n1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: p21n1

Bond precision: C-C = 0.0072 A Wavelength=0.71073

Cell: a=18.334(3) b=24.603(4) c=21.647(3)
alpha=90 beta=93.874(5) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	9742(3)	9742(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C100 H136 N8 Se2 Yb2, 0.5(C12)	C100 H136 N8 Se2 Yb2, 0.5(C12)
Sum formula	C106 H136 N8 Se2 Yb2	C106 H136 N8 Se2 Yb2
Mr	2026.24	2026.22
Dx,g cm-3	1.382	1.381
Z	4	4
Mu (mm-1)	2.705	2.705
F000	4144.0	4144.0
F000’	4141.33	
h,k,lmax	21,29,25	21,29,25
Nref	17161	17146
Tmin,Tmax	0.528,0.582	0.616,0.746
Tmin’	0.440	

Correction method= # Reported T Limits: Tmin=0.616 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.000

R(reflections)= 0.0356(13392) wR2(reflections)= 0.1019(17146)

S = 0.941 Npar= 1089

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Th(Min) ... 12 Report

---

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.94 Report
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 4.0 Ratio
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 4.3 Ratio
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb1 -- Se1 .. 5.7 s.u.
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb1 -- Se2 .. 6.7 s.u.
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb1 -- C38 .. 6.0 s.u.
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb2 -- Se1 .. 8.0 s.u.
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb2 -- Se2 .. 9.3 s.u.
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Yb2 -- C63 .. 6.5 s.u.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.595 4 Report
PLAT971_ALERT_2_C Check Calcd Residual Density 1.06A From Se1 1.75 eA-3

Alert level G

PLAT300_ALERT_4_G Atom Site Occupancy of *C2AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C4BA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C0AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C5AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C6AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C7AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C8AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C9AA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C0BA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C1BA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C3BA is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C3AA is Constrained at 0.5 Check
PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 5 Note
PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C13 Check
PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C38 Check
PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C63 Check
PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C88 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 12 Note
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C2AA -- C1BA . 1.94 Ang.
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C6AA -- C9AA . 1.71 Ang.
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C8AA -- C1BA . 1.80 Ang.
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C0BA -- C3BA . 1.73 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 245 Check
C3BA -C2AA -C1BA 1.555 1.555 1.555 42.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 248 Check
C9AA -C4BA -C8AA 1.555 1.555 1.555 35.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 259 Check
C4BA -C8AA -C1BA 1.555 1.555 1.555 37.90 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 269 Check
C3BA -C1BA -C2AA 1.555 1.555 1.555 21.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 276 Check
C4BA -C3BA -C1BA 1.555 1.555 1.555 44.60 Deg.
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still 64 %

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully

```
 11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 28 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 18 ALERT type 2 Indicator that the structure model may be wrong or deficient
  4 ALERT type 3 Indicator that the structure quality may be low
 18 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

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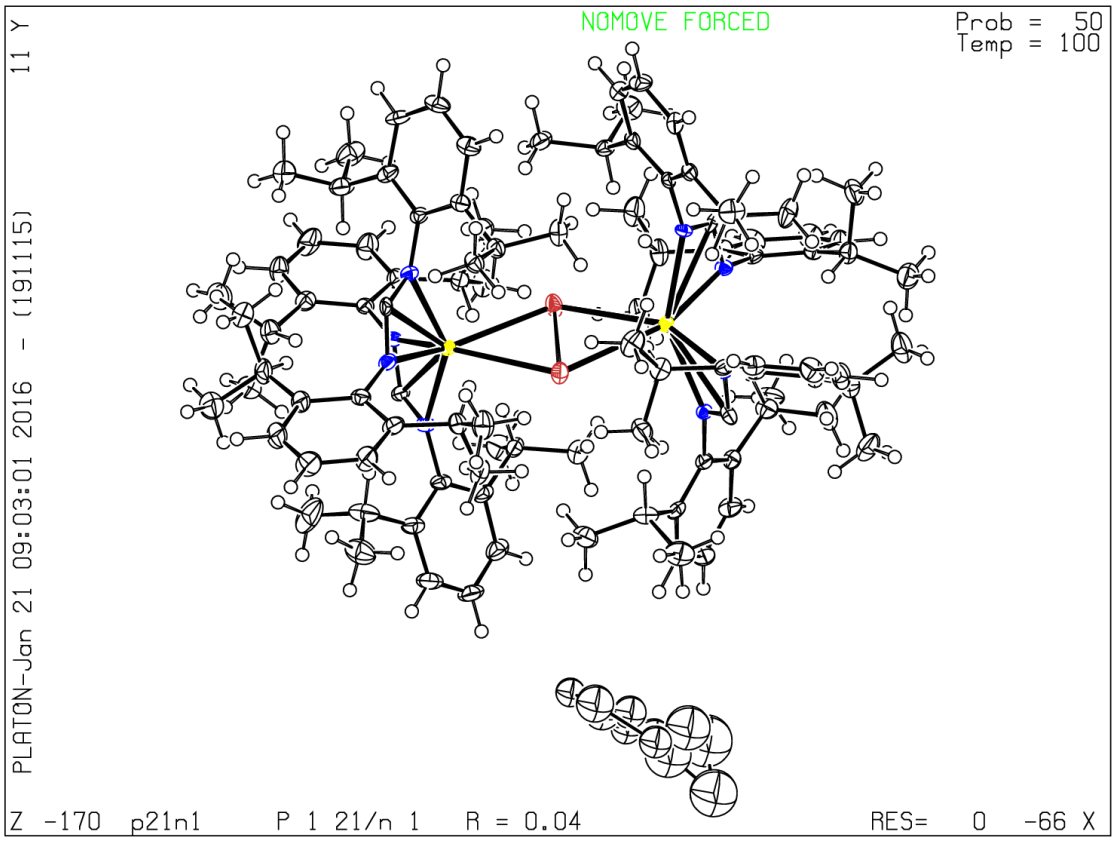
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

[{Yb(DippForm)2}2{Se}2]PhMe (5)-Danslaptopold

Datablock p21n1 - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: dw205

Bond precision: C-C = 0.0089 A Wavelength=0.71073

Cell: **a=20.554(4) b=12.1596(16) c=21.568(3)**
alpha=90 beta=110.316(17) gamma=90
Temperature: 123 K

	Calculated	Reported
Volume	5055.1(15)	5055.1(13)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C54 H78 F N4 O Yb	C54 H78 F N4 O Yb
Sum formula	C54 H78 F N4 O Yb	C54 H78 F N4 O Yb
Mr	991.24	991.24
Dx,g cm-3	1.303	1.302
Z	4	4
Mu (mm-1)	1.894	1.894
F000	2068.0	2068.0
F000'	2067.08	
h,k,lmax	24,14,25	24,14,25
Nref	8924	8922
Tmin,Tmax	0.797,0.827	0.871,1.000
Tmin'	0.685	

Correction method= # Reported T Limits: Tmin=0.871 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 25.000

R(reflections)= 0.0468(5862) wR2(reflections)= 0.0789(8922)

S = 0.942 Npar= 577

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.05 Report
PLAT213_ALERT_2_C Atom C6 has ADP max/min Ratio ..... 3.2 prolat
PLAT213_ALERT_2_C Atom C45 has ADP max/min Ratio ..... 3.3 prolat
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 4.2 Ratio
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) ... 5.3 Ratio

```
PLAT234_ALERT_4_C Large Hirshfeld Difference C1A    --  C2      ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C2     --  C1      ..       0.19 Ang.
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0089 Ang.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         2 Report
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...         2 Units
PLAT300_ALERT_4_G Atom Site Occupancy of >C1A    is Constrained at     0.530 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <C1     is Constrained at     0.470 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =          2 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .....          3 Note
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C2     --  C1      .      1.72 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #       107 Check
              C1A  -C2   -C1      1.555   1.555   1.555            21.90 Deg.
PLAT860_ALERT_3_G Number of Least-Squares Restraints .....          24 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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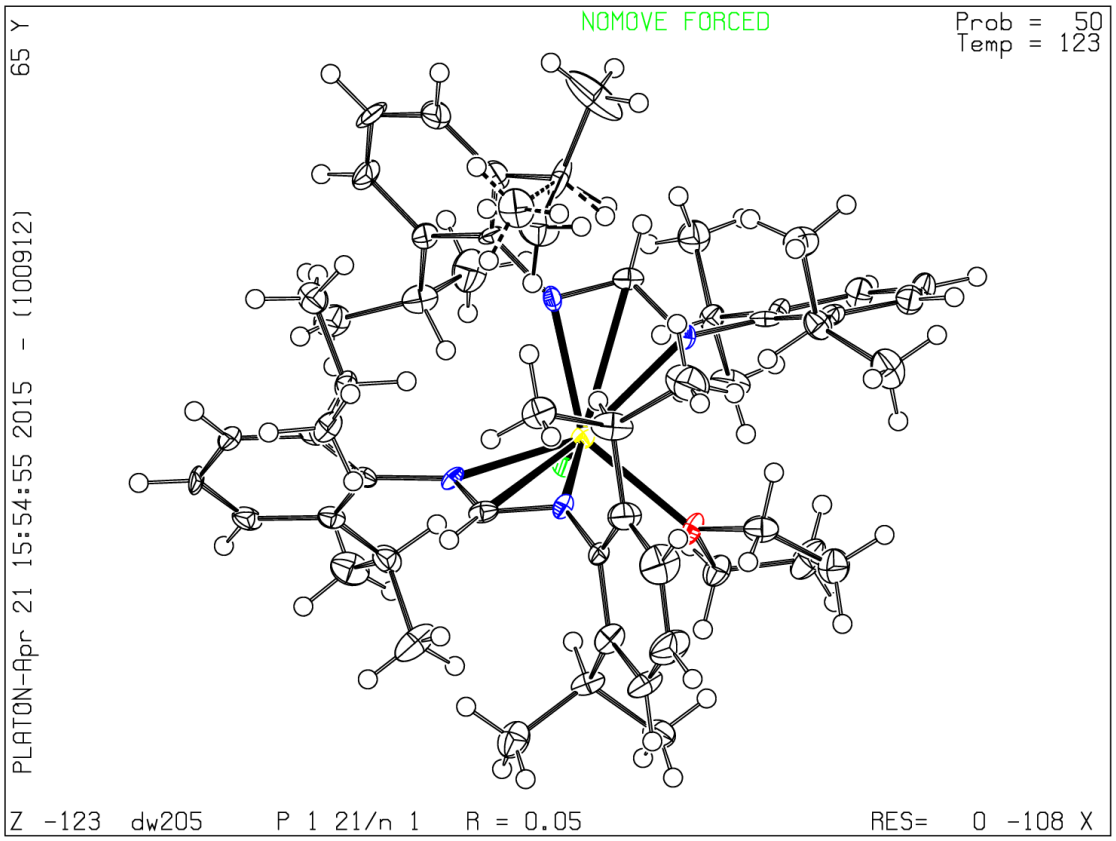
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 29/01/2015; check.def file version of 29/01/2015

[Yb(DippForm)2F(THF)] (3a)

Datablock dw205 - ellipsoid plot

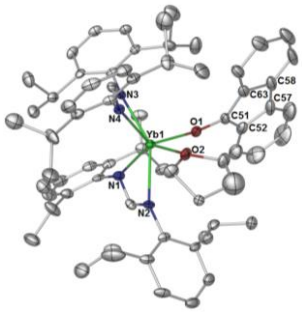


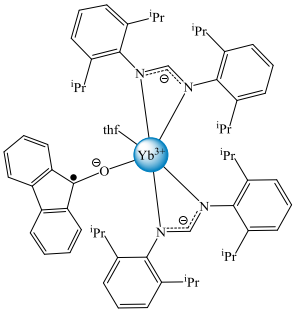
graphical abstract

Bulky Ytterbium Formamidinates Stabilise Complexes with Radical Ligands

Daniel Werner, Xuefei Zhao, Stephen P. Best, Laurent Maron, Peter C. Junk, and Glen B. Deacon

Divalent [Yb(DippForm)$_2$(thf)$_n$] (n = 2 (**1a**), or 1 (**1b**); DippForm = *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate) complexes were treated with a range of ketones and in several cases rare stabilised ketyl radical complexes were isolated, while in others unusual reactivity was noted. To investigate the reactivity of the 2,3,4,5-tetraphenylcyclopentadienone-*O ketyl* radical, we report the outcomes upon treatment with oxidants (CS_2, Se) and reducing agents (Mg^0, [$SmI_2(thf)_2$] and KH).





checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: p-1

```
Bond precision:  C-C = 0.0045 A          Wavelength=0.71090

Cell:          a=13.177(3)       b=13.338(3)      c=17.293(4)
               alpha=94.18(3)    beta=93.44(3)    gamma=109.39(3)
Temperature:   100 K

                Calculated                Reported
Volume          2847.8(13)                2847.8(11)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C64 H78 N4 O2 Yb          C64 H78 N4 O2 Yb
Sum formula     C64 H78 N4 O2 Yb          C64 H78 N4 O2 Yb
Mr              1108.35                   1108.34
Dx,g cm-3       1.293                     1.293
Z               2                         2
Mu (mm-1)       1.687                     1.687
F000            1152.0                    1152.0
F000'           1151.57
h,k,lmax        15,15,20                  15,15,20
Nref            10020                     9929
Tmin,Tmax       0.980,0.983               0.000,0.000
Tmin'           0.951

Correction method= # Reported T Limits: Tmin=0.000 Tmax=0.000
AbsCorr = MULTI-SCAN

Data completeness= 0.991          Theta(max)= 25.000

R(reflections)= 0.0271( 9776)     wR2(reflections)= 0.0667( 9929)

S = 1.049                 Npar= 685
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

```
PLAT184_ALERT_1_A Missing _cell_measurement_theta_min value ......     Please Do !
PLAT185_ALERT_1_A Missing _cell_measurement_theta_max value ......     Please Do !
```

Alert level C

```
RADNW01_ALERT_1_C  The radiation wavelength lies outside the expected range
            for the supplied radiation type. Expected range 0.71065-0.71075
            Wavelength given =    0.71090
```

Alert level G

```
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...         2 Units
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.03 Degree
PLAT300_ALERT_4_G Atom Site Occupancy of *C48    is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C48A   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C49    is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C49A   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C50    is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *C50A   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H48    is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H48A   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H49A   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H49B   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H49C   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H49D   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H49E   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H49F   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H50A   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H50B   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H50C   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H50D   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H50E   is Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of *H50F   is Constrained at        0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =          4 Note
PLAT333_ALERT_2_G Check Large Av C6-Ring C-C Dist. C51    -C64          1.44 Ang.
```

```
   2 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
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```

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PLATON version of 11/08/2016; check.def file version of 04/08/2016

Datablock p-1 - ellipsoid plot