$[Yb(THF)_3(C_5H_4PPh_2)_2W(CO)_4]\cdot 0.5THF$ and ${}^{1}_{\infty}[Yb(THF)(C_5H_4PPh_2)_2(\mu\text{-}OC)W(CO)_3]$: Two New Heterobimetallic Complexes Containing Yb^{II} and W^{0}

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Keywords: Heterometallic complexes / Ytterbium / Tungsten / Carbonyl ligands

The reaction of bis(diphenylphosphanylcyclopentadienyl)ytterbium(II) with tungsten hexacarbonyl in tetrahydrofuran yields $[Yb(THF)_3(C_5H_4PPh_2)_2W(CO)_4]\cdot 0.5THF$ (**1**), whilst $[Yb(THF)(C_5H_4PPh_2)_2(\mu\text{-}OC)W(CO)_3]$ (**2**) is obtained from toluene. Complex **1** contains nine-coordinate bis(η^5-diphenylphosphanylcyclopentadienyl)tris(tetrahydrofuran)ytterbium(II) units. Complex **2** has eight-coordinate ytterbium(II) with one carbonyl group showing an *iso*-carbonyl linkage to ytterbium (W–C≡O–Yb), thereby forming a structure of infinite chains. The $Yb(\eta^5\text{-}C_5H_4PPh_2)_2$ units in both **1** and **2** bind to tungsten through the phosphorus atoms giving an octahedral *cis*-$W(CO)_4P_2$ arrangements.
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Introduction

Early lanthanoid-d-block bimetallic complexes such as $[Yb(THF)(C_5Me_5)_2Co(CO)_4]$[1] and $[Yb(C_5Me_5)_2Fe_3(CO)_{11}]$[2] involve the coordination of a transition metal carbonylate to the lanthanoid through a carbonyl oxygen. The introduction of the diphenylphosphanylcyclopentadienyl ligand ($CpPPh_2$) into organolanthanoid chemistry with $Yb(CpPPh_2)_2$ [3] enabled the preparation of the first lanthanoid-d-block bimetallic complex with the f-block element in the donor part of the molecule. Subsequently, other divalent[4−7] and trivalent[8−14] (diphenylphosphanylcyclopentadienyl)lanthanoid complexes have been prepared, including a Sm^{III} complex with four different ligands,[15] and a limited number of further bimetallics.[4,9,12] Crystallographically characterized derivatives are relatively scarce (see also the related $[Yb(THF)_2(C_4Me_4P)_2Ru(H)_2(PPh_3)_2]$[16]). $[Yb(THF)_2(CpPPh_2)_2Mo(CO)_4]\cdot THF$ and $[Yb(THF)(CpPPh_2)_2Mo(CO)_4]\cdot PhMe$ were prepared with carbonyls of Group 6 transition metals, and the latter was proposed to contain an *iso*-carbonyl−Yb linkage, although no crystal structures were determined.[4] By preparing the tungsten carbonyl analogs, we have succeeded in crystallizing the key complexes $[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot 0.5THF$ (**1**) and $[Yb(THF)(CpPPh_2)_2(\mu\text{-}OC)W(CO)_3]$ (**2**) whose structures illuminate the nature of the $Yb(CpPPh_2)_2$/Group 6 tetracarbonyl bimetallics.

Results and Discussion

Reaction of $[Yb(THF)(CpPPh_2)_2]$[4] with $W(CO)_6$ in THF initially at room temperature and then at elevated temperatures yielded $[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot 0.5THF$ (**1**) [Equation (1)]. Single crystals were also obtained from the same solvent, and readily underwent decomposition when taken out of the mother liquor precluding opportunity for microanalysis.

$$[Yb(thf)(CpPPh_2)_2] + W(CO)_6 \xrightarrow{THF} [Yb(thf)_3(CpPPh_2)_2W(CO)_4]\cdot 0.5THF\ (\mathbf{1}) + 2\ CO \qquad (1)$$

The infrared spectra of the product in Nujol and in THF show four ν(CO) absorptions consistent with a *cis*-$W(CO)_4$ moiety, with values quite similar to those (2010, 1900, 1880, 1845 cm^{-1})[4] for the proposed complex $[Yb(THF)_2(CpPPh_2)_2Mo(CO)_4]\cdot THF$ in Nujol. Although the complex is almost insoluble in toluene (see below) the spectrum of the light green solution shows ν(CO) absorptions similar to the values for the complex in THF, suggesting dissolution of some of the complex as unchanged **1**. The ^1H NMR spectrum in $[D_8]THF$ confirmed the presence of the diphenylphosphanylcyclopentadienyl ligand. A similar ^{31}P resonance was observed for **1** in $[D_8]THF$ and in C_6D_6 (sparing solubility at room temperature) consistent with the similar IR spectra for the compound in THF and toluene. As expected for a P−W coordination, a major shift of the ^{31}P resonance to higher frequencies ($\delta = 9-10$ ppm) than the value for $[Yb(THF)_2(CpPPh_2)_2]$ ($\delta = -20.5$ ppm[4]) is observed, although this change is not as marked as that seen upon coordination of the $Yb(CpPPh_2)_2$ ligand to $Ni(CO)_2$, $PtMe_2$, or $Mo(CO)_4$ (δ =

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17−20 ppm).[4] Further evidence for P−W bonding comes from observation of W−P coupling (see Exp. Sect.) within the usual range for $^1J_{W,P}$.[17,18]

Complex **2** can be obtained as single crystals from the same reactants as **1** but by heating in toluene. Its identity was established as a Yb−O≡C−W-bridged complex [Equation (2)]. Although some **1** dissolves in toluene, the bulk gives dark colored insoluble [Yb(THF)($CpPPh_2$)$_2$(μ-OC)W(CO)$_3$] (**2**) [Equation (3)].

$$[Yb(THF)(CpPPh_2)_2] + W(CO)_6 \xrightarrow{\text{toluene}} [Yb(THF)(CpPPh_2)_2(\mu\text{-}OC)W(CO)_3]\ (\mathbf{2}) + 2\ CO \qquad (2)$$

$$[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot 0.5THF\ (\mathbf{1}) \xrightarrow{\text{toluene}} [Yb(THF)(CpPPh_2)_2(\mu\text{-}OC)W(CO)_3]\ (\mathbf{2}) + 2\ THF \qquad (3)$$

The formation of **2** releases THF into toluene enabling the resulting solution to dissolve a little of **1** unchanged. The IR spectrum of solid **2** also displays four carbonyl absorptions indicative of a *cis*-W(CO)$_4$ arrangement. One of these bands (1758 cm^{-1}) is in the region for a bridging or *iso*-carbonyl group, and even lower than the corresponding value (1790 cm^{-1}) for the related molybdenum complex [Yb(THF)($CpPPh_2$)$_2$Mo(CO)$_4$]·PhMe.[4] Crystals of **2** are extremely unstable outside the mother liquor making a fast characterization by a low temperature X-ray determination necessary and precluding elemental analysis.

Although the compositions of **1** and **2** differ only in their THF content, the structures are very different. In complex **1** a formally nine-coordinate ytterbium atom is surrounded by three THF oxygen atoms and two η^5-bonded $CpPPh_2$ ligands, which chelate through the phosphorus atoms to a W(CO)$_4$ moiety in *cis* positions (Figure 1). The resulting nine-coordination is extremely unusual for Ln^{II}(Cp′)$_2$-thf complexes which are normally eight-coordinate [Ln(Cp′)$_2$(THF)$_2$],[19−21] apart from [Sm(ind)$_2$(THF)$_3$] (ind = indenyl).[22] It may be considered that **1** is more remarkable than the Sm^{II} complex[22] since the nine-coordinate ionic radius is 0.12 Å smaller for Yb^{2+} than Sm^{2+}.[23] It is possible that the electron-withdrawing effect of the $CpPPh_2$ ligands[24] more than compensates for the bulkiness of the PPh_2 substituent. The best-fit polyhedron[25] for the three oxygen donors and the centroids (cent) of the $CpPPh_2$ ligands around ytterbium is a distorted square-based pyramid with O(6) apical. The difference from a trigonal bipyramidal arrangement is best seen in the angle difference of a best-fit polyhedron calculation,[26] which is Δ = 14.4°. For a trigonal bipyramidal arrangement the expected value would be 60° and 0° for an undistorted square-based pyramid. However, describing spherical phenomena such as Cp rings by single points representing the centroids of those rings has to be viewed cautiously. Tungsten shows a slightly distorted octahedron of two *cis* phosphorus and four carbon donor atoms.

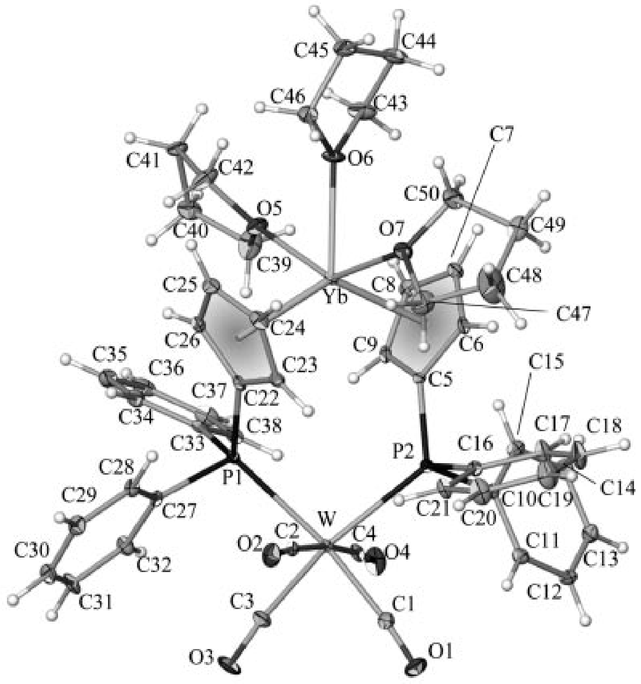

Figure 1. The molecular structure of [Yb(THF)$_3$($CpPPh_2$)$_2$W(CO)$_4$]·0.5THF (**1**); η^5-interactions between Yb and Cp are represented by bonds towards centroids of shaded Cp rings; the thermal ellipsoids here and in Figure 2 are scaled to a probability density of 50%

In complex **2** each ytterbium is eight-coordinate and surrounded by two η^5-$CpPPh_2$ ligands, a THF oxygen and a carbonyl oxygen, with the two phosphorus atoms chelating (*cis*) to a W(CO)$_4$ unit, one oxygen of which bridges to the adjacent ytterbium. The best-fit polyhedron[25] for the disparate oxygen donors and the $CpPPh_2$ centroids is a tetrahedron, whilst tungsten again shows a slightly distorted octahedral geometry (Figure 2). Only one other structure of a Ln−O≡C−W arrangement could be found in a search of the Cambridge Crystallographic Data Base, viz. [Ce(Cp′)$_2$(μ-OC)$_2$W(CO)Cp] [Cp′ = $C_5H_3(SiMe_3)_2$-1,3, Cp = C_5H_5],[27] although analogous molybdenum complexes are more numerous and include Mo−C≡O−Yb-bonded systems.[28−31]

Whilst complex **1** is molecular, complex **2** shows a one-dimensional chain structure running along [100] with neighbouring molecules connected via iso-carbonyl bridges (Figure 3). Complex **2** can therefore be described by the Niggli formula $^1_\infty$[Yb(THF)($C_5H_4PPh_2$)$_2$(μ-OC)W(CO)$_3$].

Selected bond lengths and angles for **1** and **2** are given in Table 1. The average Yb−C distances (276 pm and 270 pm for **1** and **2** respectively) differ, as expected, for eight- and nine-coordinate Yb^{2+}.[23] In addition, the value for **2** corresponds to the average Yb−C bond length (271 pm) of eight-coordinate [Yb(THF)$_2$($CpPPh_2$)$_2$Z]·thf {*Z* = Ni(CO)$_2$, PtMe$_2$}.[4] Although different methods for the calculation of ionic radii are present in the literature, subtraction of ionic radii from distances offers valuable data for comparison. Based on the values[23] for eight- and nine-coordinate Yb^{2+} the subtraction from[32,33] <Yb−C> distances gives a value of 156 pm, which is similar to values for analogous bimetallic complexes.[4] The attached $CpPPh_2$ ligands in **1** show a slight tilt associated with a difference in Yb−C distances of

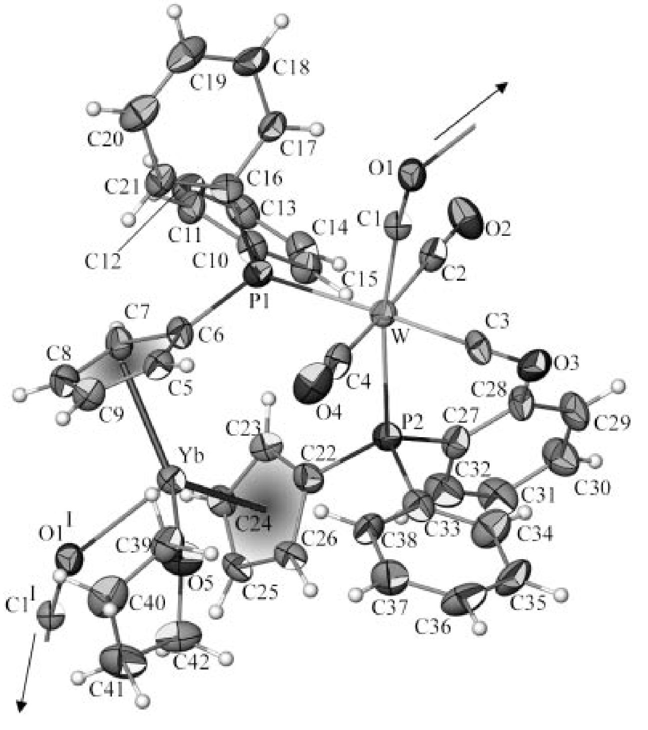

Figure 2. The molecular structure of $^{1}_{\infty}[Yb(THF)(C_5H_4PPh_2)_2(\mu\text{-}OC)W(CO)_3]$ (**2**); η^5-interactions between Yb and Cp are represented by bonds towards centroids of shaded Cp rings; the *iso*-carbonyl-bridging to a neighbouring molecule is indicated by arrows

only 12 pm. Thus, there is no significant trend towards η^3-attachment, as subtraction of the ionic radius from the longest Yb−C distance gives a normal value[32,33] of 162 pm. The Ln−C distance variation is much less than that of $[Er(\eta^5\text{-}CpPPh_2)_3(OPPh_3)]$.[7] The Yb−O(THF) distance of **2** corresponds well with those of $[Yb(THF)_2(CpPPh_2)_2Ni(CO)_2]$ [242.4(4), 242.9(4) pm][4] and is marginally longer than <Yb−O> of the $PtMe_2$ analog (240 pm).[4] On the other hand the Yb−O distances of **1** show a wide variation. One is as short as that of eight-coordinate **2**, and two are much longer so that the average (253 pm) exceeds the value for **2** by more than the expected amount for the coordination number variation. As the shortest distance, Yb−O(6), is for the ligand that is apical in the $Yb(cent)_2O_3$ square pyramid (as best-fit polyhedron) whilst the other two THF ligands are *transoid* to each other, a *trans* influence may be invoked for the lengthening of Yb−O(5,7). Such influences are now well established in lanthanoid chemistry despite the ionic nature of the bonding.[34−37] Subtraction of an appropriate Yb^{2+} ionic radius from the Yb−O distances gives a value of 130 pm for **2**, which is at the short end of the range 134 ± 5 pm for ether complexes of organolanthanoids,[38] whilst the longer Yb−O distances of **1** give a value of 138−141 pm, which is at the higher end and greater than the expected ionic radius difference of about 6 pm due to the variation in coordination number. In contrast the shortest Yb−O distance of **1** gives a value of 124 pm, which is well below the normal range, reflecting the absence of any ligand *transoid* to oxygen. In addition, the $CpPPh_2$ ligand is electron withdrawing[24] and is known to cause bond-shortening upon attachment of coligands.[7] Unfortunately the precision of the $[Sm(ind)_2(THF)_3]$ structure determination[22] is insufficient to be able to compare the Sm−O bond lengths with the present Yb−O bond lengths. Thus **1** provides currently unique data. The Yb−O(C) distances in **2** lie within the range 238−256 pm reported for recent *iso*-carbonyl-bonded ytterbium complexes[30,31,39−41] (cf. 225 pm for ytterbium(III) in two earlier structures[1,2]).

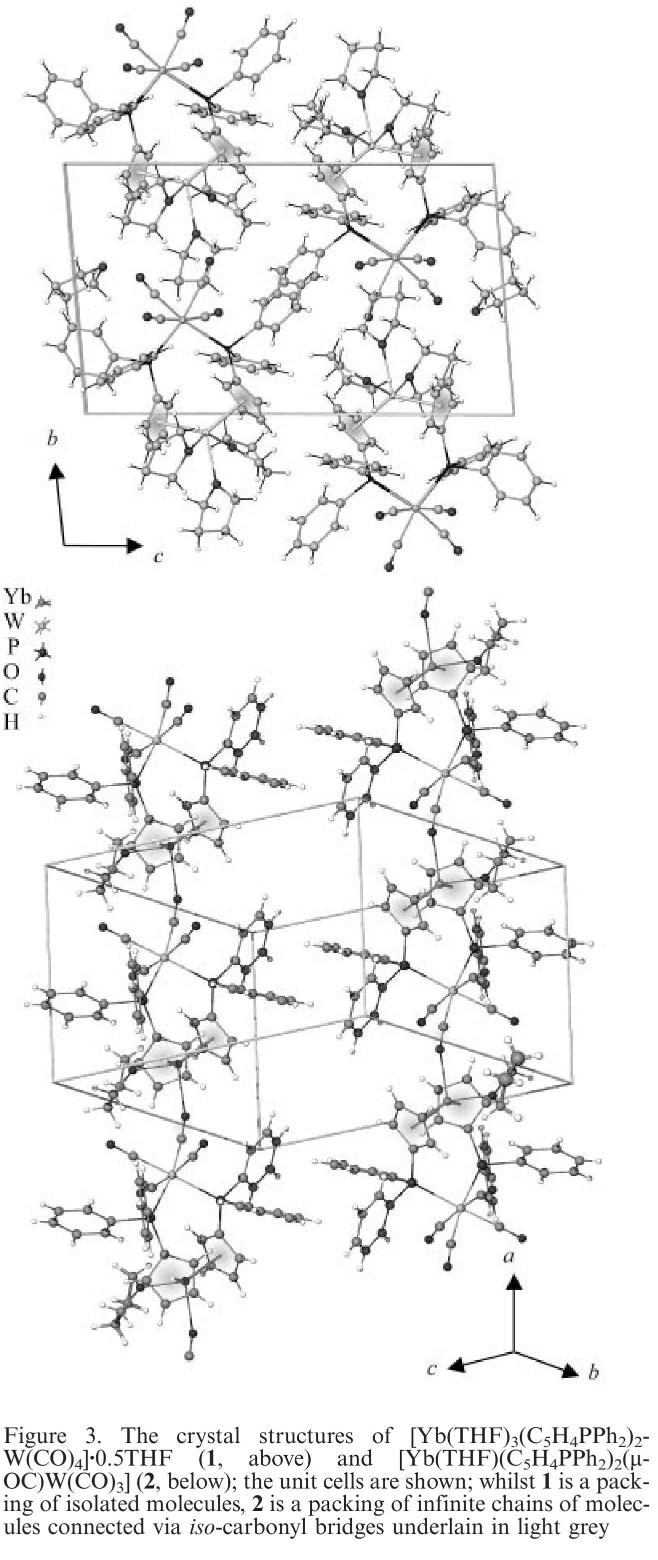

Figure 3. The crystal structures of $[Yb(THF)_3(C_5H_4PPh_2)_2W(CO)_4]\cdot0.5THF$ (**1**, above) and $[Yb(THF)(C_5H_4PPh_2)_2(\mu\text{-}OC)W(CO)_3]$ (**2**, below); the unit cells are shown; whilst **1** is a packing of isolated molecules, **2** is a packing of infinite chains of molecules connected via *iso*-carbonyl bridges underlain in light grey

Table 1. Selected distances (pm) and angles(°) for $[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot0.5THF$ (**1**) and $[Yb(THF)(CpPPh_2)_2(\mu\text{-}OC)W(CO)_3]$ (**2**); standard deviations are given in brackets

$[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot0.5THF$ (**1**)			
Yb−C [range C(22−26)]	270.4(4)−282.2(4)	W−P(2)	256.3(1)
Yb−C [range C(5−9)]	271.6(4)−280.7(4)	W−P(1)	256.7(1)
Yb−C [average C(22−26)]	276.2(4)	W−C(3)	197.5(4)
Yb−C [average C(5−9)]	276.3(4)	W−C(1)	198.5(4)
Yb−O(6)	243.0(3)	W−C(4)	202.3(4)
Yb−O(5)	258.4(3)	W−C(2)	203.8(4)
Yb−O(7)	261.0(3)	P(1)−C(range)	180.7(4)−184.4(4)
Yb−W	534.0(2)	P(2)−C(range)	179.1(4)−185.1(4)
C−O (carbonyl, range)	114.6(5)−115.3(4)		
cent(1)−Yb-cent(2) [a]	130.1	P(1)−W−P(2)	98.31(3)
cent(1)−Yb−O(5)	99.0	P(1)−W−C(1)	91.1(2)
cent(1)−Yb−O(7)	95.0	P(1)−W−C(2)	101.9(2)
cent(1)−Yb−O(6)	117.1	P(2)−W−C(2)	83.0(2)
cent(2)−Yb−O(7) [b]	100.6	P(2)−W−C(3)	88.8(2)
cent(2)−Yb−O(5)	95.0	P(1)−W−C(4)	80.6(1)
cent(2)−Yb−O(6)	112.9	P(2)−W−C(4)	102.6(2)
O(5)−Yb−O(6)	73.30(9)	P(1)−W−C(3)	165.5(2)
O(5)−Yb−O(7)	144.47(8)	P(2)−W−C(2)	167.8(2)
O(6)−Yb−O(7)	71.24(9)	W−C(1)−O(1)	173.8(4)
C(2)−W−C(4)	174.1(2)	W−C(3)−O(3)	173.9(3)
		W−C(2)−O(2)	175.5(4)

$[Yb(THF)(CpPPh_2)_2(\mu\text{-}OC)\ W(CO)_3]$ (**2**)			
Yb−C [range C(5−9)]	268(2)−273(2)	W−P(1)	258.0(4)
Yb−C [range C(22−26)]	268(2)−273(2)	W−P(2)	259.4(4)
Yb−C [average C(5−9)]	270(2)	W−C(1)	199(1)
Yb−C [average C(22−26)]	270(2)	W−C(3)	201(2)
Yb−O(5)	244.1(9)	W−C(4)	203(2)
Yb−$O(1)^{I}$ [c]	248(1)	W−C(2)	204(2)
Yb−W	506.0(6)	P(1)−C(range)	181(2)−185(2)
Yb^{II}−W [d]	525.5(6)	P(2)−C(range)	178(2)−188(2)
C−O(carbonyl, range)	113(2)−116(2)	O(1)−C(1)	113(2)
cent(1)−Yb-cent(2)	131.3	P(1)−W−P(2)	95.5(1)
cent(1)−Yb−$O(1)^{I}$ [c]	108.8	P(1)−W−C(1)	94.8(4)
cent(1)−Yb−O(5)	108.6	P(1)−W−C(2)	89.7(4)
cent(2)−Yb−$O(1)^{I}$ [c]	102.4	P(2)−W−C(2)	94.6(4)
cent(2)−Yb−O(5)	110.1	P(2)−W−C(3)	83.7(4)
$O(1)^{I}$−Yb−O(5) [c]	85.8(3)	P(1)−W−C(4)	92.1(4)
C(2)−W−C(4)	173.0(5)	P(2)−W−C(4)	91.9(4)
W−C(2)−O(2)	173(2)	P(2)−W−C(1)	169.6(4)
W−C(3)−O(3)	178(2)	P(1)−W−C(3)	177.4(4)
W−C(1)−O(1)−Yb^{II} [d]	143(2)	Yb^{II}−O(1)−C(1) [d]	143.0(9)

[a] cent1 = centroid of the $CpPPh_2$ rings with the C atoms C(5)−C(9). [b] cent2 = centroid of the $CpPPh_2$ rings with the C atoms C(22)−C(26). [c] I: $x - 1, y, z$. [d] II: $x + 1, y, z$.

The coordination sphere around tungsten shows the expected features. Opening of the P−W−P angles of **1** and **2** by up to 12° from the normal value of 90° in response to the bulky substituents on phosphorus parallels a similar behavior in recently reported $WP_2(CO)_4$ complexes,[42−44] but is less than the 18.35° observed with bulky *cis*-PPh_2(*o*-$MeOC_6H_4$) ligands.[42] On the other hand the W−P distances are close to those (256, 257 pm) with this bulky phosphane, and larger than those (247, 251 pm) of the less crowded [*cis*-$W(CO)_4(Ph_2PH)_2$].[43] Although the shorter W−C bonds in both **1** and **2** are located *trans* to phosphorus, consistent with a greater *trans* influence of CO than R_3P in W^0 complexes,[45] the differences are within a three esd range and hence are of limited significance. Coordination of the carbonyl group to Yb in **2** has no significant effect within error limits on the W−C bond lengths or W−C−O angles (Table 1), in contrast to $[Ce(Cp')_2(\mu\text{-}CO)_2WCp(CO)_2]$ [$Cp' = C_5H_3(SiMe_3)_2$-1,3, $Cp = C_5H_5$] for which $W{-}C{-}O_{ter}$ is bent relative to near linear $W{-}C{-}O_{br}$.[27] The Yb−O−C angle is at the lower end for *iso*-carbonylytterbium complexes and is close to that of $[Yb(NCMe)_3(\mu\text{-}CO)_3Fe(CO)]_n$ (145.75°)[38] and quite different from the Ce−O−C angles (174.8, 154.4°) of $[Ce(Cp')_2(\mu\text{-}CO)_2WCp(CO)_2]$ [$Cp' = C_5H_3(SiMe_3)_2$-1,3, $Cp = C_5H_5$].[27] Overall the W−C distances (bridging or terminal) of the cerium complex are much shorter than those of **1** and **2**, consistent with a weaker trans influence of Cp than R_3P or CO in W^0 complexes.[45]

Conclusions

Observation of nine-coordinate ytterbium in $[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot0.5THF$ (**1**) is a major surprise in view of the ubiquitous nature of eight-coordinate $[Yb(THF)_2(Cp')_2]$ complexes[19−21] and the presence of eight-coordinate Yb in $[Yb(THF)_2(CpPPh_2)_2PtMe_2]\cdot THF$ and $[Yb(THF)_2(CpPPh_2)_2Ni(CO)_2]$.[4] Accordingly, the proposal[4] that the analytically similar $[Yb(THF)_2(CpPPh_2)_2Mo(CO)_4]\cdot THF$ contains eight-coordinate $Yb(THF)_2(CpPPh_2)_2$ units may be questioned and it is likely that this complex also contains nine-coordinate $Yb(THF)_3(CpPPh_2)_2$ moieties. A single-crystal structure determination is therefore desirable. The only prior example of a nine-coordinate $[Ln(THF)_3(Cp')_2]$ complex, $[Sm(ind)_2(THF)_3]$,[22] is also unexpected given the bulky indenyl ligands, although lack of bond length data frustrates examination of possible slippage towards η^3 coordination

On the other hand, the structure of **2** with the *iso*-carbonyl−Yb linkage provides validation of the proposal of similar bonding in $[Yb(THF)(CpPPh_2)_2Mo(CO)_4]\cdot PhMe$ and indeed in $[Yb(THF)(CpPPh_2)_2Ni(CO)_2]$.[4] Accordingly, the structures of **1** and **2** are of strategic importance in understanding the behavior of $Yb(CpPPh_2)_2$ derived bimetallic complexes.

Experimental Section

All reactions were carried out under dry nitrogen using dry box and standard Schlenk techniques due to the air- and moisture-sensitivity of **1** and **2**. Solvents were dried by distillation from sodium wire/benzophenone. IR data (4000−650 cm^{-1}) were recorded either for Nujol mulls sandwiched between NaCl plates or as THF or PhMe solutions in a solution cell with AgBr plates using a Perkin−Elmer 1600 Fourier transform infrared spectrometer. NMR spectra were obtained on a Bruker AC300 instrument. ^{31}P spectra are referenced to external 85% H_3PO_4. Deuterated solvents were degassed and distilled from Na/K alloy prior to use. $W(CO)_6$ was purchased from Aldrich and used as received whilst $[Yb(THF)(CpPPh_2)_2]$ was prepared according to the literature procedure.[3]

$[Yb(THF)_3(CpPPh_2)_2W(CO)_4]\cdot0.5THF$ (1): A Schlenk flask was charged with $W(CO)_6$ (1.2 mmol), $[Yb(THF)(CpPPh_2)_2]$ (0.7 mmol) and THF (40 mL) giving an intense dark red solution. The reaction mixture was stirred and heated to 60 °C for 48 h and then stirred for a further 48 h at room temperature. Hexane was added until a permanent precipitate formed. Upon heating, the solid re-dissolved and slow cooling to −20 °C gave dark red crystals of **1** and some colorless crystals of $W(CO)_6$. Subsequent warming to room temperature dissolved the colorless material and the remaining red crystals were collected by filtration and dried under vacuum at room temperature for 1 h to give a yield of 0.3 g (45%). Rapid decomposition outside the mother liquor, however, made it preferable to collect the product from solution. IR (Nujol): $\tilde{\nu}$ = 2005vs, 1894vs, 1872vs, 1849vs [all ν(CO)], 1570w, 1440s, 1204w, 1177m, 1153w, 1087m, 1045s, 1031s, 917w, 881m, 742m, 695m; (THF) ν(CO): 2015s, 1914s, 1893s, 1880sh, (PhMe) ν(CO) 2015s, 1917s, 1892s(br), 1868sh cm^{-1}. ^1H NMR (300 MHz, $[D_8]THF$): δ = 5.93 (br s, 4 H, β-C_5H_4), 6.17 (br s, 4 H, α-C_5H_4,), 7.37 [br s, 12 H, *m*-,*p*-*H*(Ph)], 7.59 [br s, 8 H, *o*-*H*(Ph)] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_8]THF$): δ = 9.67 ($^1J_{W,P}$ = 237 Hz); (C_6D_6): 9.00 ($^1J_{W,P}$ = 232 Hz) ppm.

$[Yb(THF)(CpPPh_2)_2(\mu\text{-}OC)W(CO)_3]$ (2): (a) A glass ampoule was charged with $W(CO)_6$ (0.14 mmol), $[Yb(THF/DME)(CpPPh_2)_2]$ (0.14 mmol), and PhMe (1.5 mL) and then degassed and sealed under vacuum. Heating at 130 °C for 127 h gave a dark red solution. Upon cooling, very dark red crystals of **2** deposited, together with $W(CO)_6$ and some green crystals which disappeared on subsequent heating. Several of the dark red crystals were mounted for X-ray crystallography. The remaining material decomposed within hours in the inert drybox atmosphere also indicating instability outside the mother liquor.

(b) Red crystals of **1** were washed with successive amounts of PhMe (3 × 5 mL) until the washings were colorless. The remaining dark colored powder was dried under vacuum at room temperature for 1 h. IR (Nujol): $\tilde{\nu}$ = 2016vs, 1910vs, 1883vs [all $\nu(CO)_{ter}$], 1758vs [$\nu(CO)_{br}$], 1305w, 1177m, 1156w, 1085m, 1036s, 1027m, 894w, 756s, 737s, 694s, cm^{-1}.

X-ray Crystal Structure Determination: The data collection for single crystal X-ray determination of **1** was carried out on a κ-CCD diffractometer (Enraf Nonius), and the data collection for **2** on an IPDS-I diffractometer (STOE). Structure solution: SHELXS-86;[46] structure refinement: SHELXL-97.[47] Integrity of symmetry and geometry: PLATON.[48] All non-hydrogen atoms were refined anisotropically. Some hydrogen atoms of **1** were deduced from the Fourier map while most hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 1.2-times the size of the isotropic displacement parameter of the parent carbon atom. Two THF molecules of **1** show a split position of the carbon atom opposite to the oxygen atom of the THF rings in a ratio of about 2:1. In addition the free THF molecule is split by centers of symmetry.

Crystallographic Data for $C_{52}H_{56}O_{7.5}P_2WYb$ (1): Triclinic, $P\bar{1}$, Z = 2, T = 123(2) K, a = 1024.76(1) pm, b = 1255.72(1) pm, c = 2054.38(3) pm, α = 89.154(1)°, β = 75.803(1)°, γ = 68.069(1)°, V = 2368.7(5)·10^6 pm^3, μ = 45.1 cm^{-1}, Mo-K_α, $5.16 \leq 2\theta \leq 56.56°$, $-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-24 \leq l \leq 27$, $F(000)$ = 1204, R_1 = 0.0340 for 9407 reflections [$I > 2\sigma(I)$], R_1 = 0.0482 and wR_2 = 0.0805 for 11547 unique reflections, GOOF on F^2 = 1.042.

Crystallographic Data for $C_{42}H_{36}O_5PWYb$ (2): Triclinic, $P\bar{1}$, Z = 2, T = 170(1) K, a = 1008.2(4) pm, b = 1195.0(5) pm, c = 1750.4(8) pm, α = 105.06(5)°, β = 97.98(5)°, γ = 106.18(5)°, V = 1904(2)·10^6 pm^3, μ = 55.9 cm^{-1}, Mo-K_α, $4.46 \leq 2\theta \leq 50.0°$, $-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$, $F(000)$ = 1004, R_1 = 0.0564 for 3960 reflections [$I > 2\sigma(I)$], R_1 = 0.0868 and wR_2 = 0.1399 for 6299 unique reflections, GOOF on F^2 = 0.924. CCDC-177663 (**1**) and CCDC-177664 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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