

**THE LANTHANIDE-HYDROGEN-TRANSITION METAL
 COMPOUNDS: $[\{(\text{PMe}_3)_3\text{WH}_5\}_2\text{Yb}\cdot\text{L}_3]$ AND
 $[\{(\eta\text{-C}_5\text{H}_5)_2\text{NbH}_2\}_2\text{Yb}\cdot\text{L}_3]$ WHERE $\text{L}_3 = (\text{MeOCH}_2\text{CH}_2)_2\text{O}$, AND
 RELATED STUDIES***

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Abstract—The preparation of lanthanide–hydrogen–transition metal compounds $[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb}\cdot\text{diglyme}]$ and $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\}_2\text{Yb}\cdot\text{diglyme}]$ from the potassium salts $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ and “ $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2][\text{K}]$ ” and YbI_2 are described. Their X-ray crystal structures and NMR data indicate the presence of $\text{W}(\mu\text{-H}_3)\text{Yb}$ or $\text{W}(\mu\text{-H})_2\text{Nb}$ groups, respectively. The related Group IV metallocene compounds $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$, $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$, $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$ and $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2\text{Cl}_2\text{W}(\text{PMe}_3)_3\text{H}_5]$ have been prepared and the crystal structure of $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2\text{Cl}_2\text{W}(\text{PMe}_3)_3\text{H}_5]$ has been determined.

Compounds containing transition metal–hydrogen–alkali metal bonds $\text{M—H—M}'$ have been described for a variety of different *d*-block transition metals M, where M' may be Li,¹ Na² or K.² An example of particular relevance to this study is the potassium–hydrogen–tungsten compound $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]^2$ which has been used as a precursor to analogous $\text{M—H—M}'$ systems where M' is a lanthanide element. Further, $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ has been reacted with metallocene derivatives of zirconium and hafnium to give new heterobimetallic species. Part of this work has been reported in a preliminary communication.³

RESULTS AND DISCUSSION

Treatment of a suspension of YbI_2 in 1,2-dimethoxyethane (dme) with two equivalents of $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ gave orange crystals that were found to be $[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb}\cdot\text{diglyme}]$ (**1**) by single-crystal X-ray analysis. The presence of the diglyme ligand in the molecular structure was unex-

pected. The source of the diglyme was as a trace impurity in the dme solvent. Thus, a sample of dme was evaporated under reduced pressure at room temperature and the proton NMR spectrum of the residual oil showed bands characteristic for diglyme $[(\text{MeOCH}_2\text{CH}_2)_2\text{O}]$.

The molecular structure of **1** is shown in Fig. 1, and bond lengths and angles are given in Table 1. The molecule has a central W—Yb—W core, with W—Yb distances of 3.23 and 3.26 Å, and an angle W—Yb—W of 133.0°. The three oxygens of the diglyme ligand lie in a plane which is approximately at right angles to the W—Yb—W plane. Each tungsten bears three PMe_3 groups. The hydrogen atoms were not located in the crystal structure.

The average tungsten–ytterbium distance of 3.24 Å is longer than the sum of atomic radii given by Slater⁴ ($\text{W } 1.35 \text{ Å} + \text{Yb } 1.75 \text{ Å} = 3.10 \text{ Å}$), but is shorter than the sum of metallic radii⁵ ($\text{W}_{12\text{-coord}} 1.39 \text{ Å} + \text{Yb}_{6\text{-coord}} 1.93 \text{ Å} = 3.32 \text{ Å}$). This latter distance may be compared to 2.995 Å for the unsupported Lu—Ru bond in the recently reported compound $[\text{Lu}(\eta\text{-C}_5\text{H}_5)_2(\text{thf})\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$;⁶ the sum of atomic radii $\text{Lu } 1.75 \text{ Å} + \text{Ru } 1.30 \text{ Å} = 3.05 \text{ Å}$ and the sum of metallic radii $\text{Lu } 1.74 \text{ Å} + \text{Ru } 1.35 \text{ Å} = 3.09 \text{ Å}$. In contrast, the recently reported⁷ compound $[(\eta\text{-C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-}\eta^1, \eta^5\text{-C}_5\text{H}_4)(\mu\text{-H})_2\text{W}(\eta\text{-C}_5\text{H}_5)]$ has a Sm—W distance of 3.402 Å

* Dedicated to Professor E. W. Abel on the occasion of his retirement.

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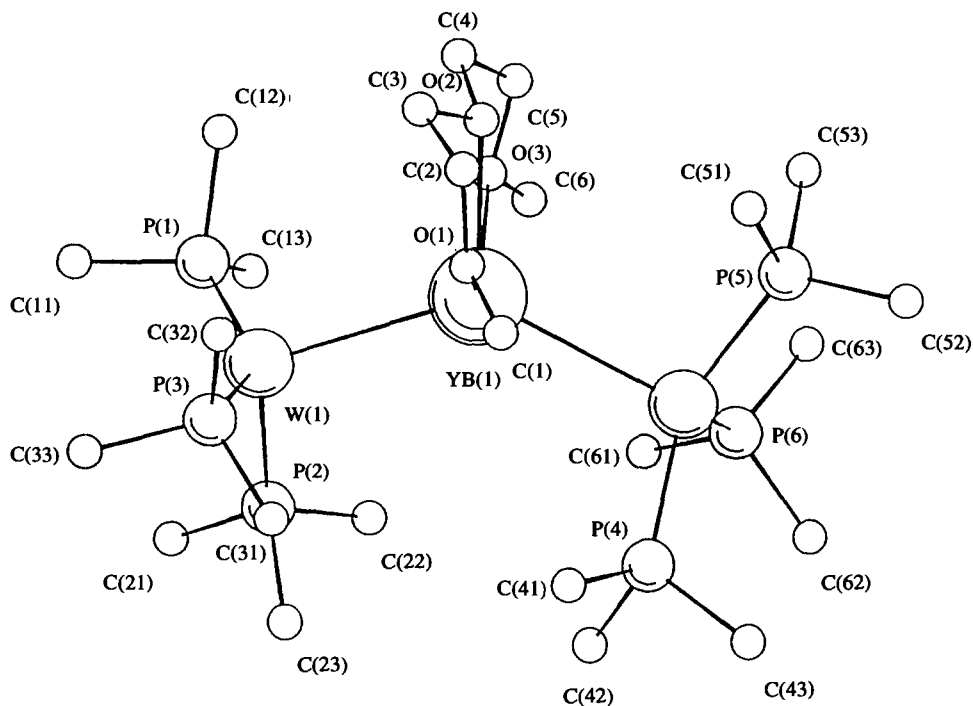
Fig. 1. The molecular structure of $[\{W(PMe_3)_3H_5\}_2Yb \cdot diglyme]$, **1**.

Table 1. Selected interatomic distances (Å) and and interbond angles (°) with estimated standard deviations (e.s.d.s) in parentheses

(a) $[\{W(PMe_3)_3H_5\}_2Yb \cdot diglyme]$, **1**

| | | | |
|--------------|-----------|-----------------|-----------|
| W(1)···Yb(1) | 3.2253(5) | W(1)—P(1) | 2.399(3) |
| W(2)···Yb(1) | 3.2595(5) | W(1)—P(2) | 2.407(3) |
| Yb(1)—O(1) | 2.536(7) | W(1)—P(3) | 2.409(3) |
| Yb(1)—O(2) | 2.571(7) | W(2)—P(4) | 2.401(3) |
| Yb(1)—O(3) | 2.519(7) | W(2)—P(5) | 2.407(3) |
| W(2)—P(6) | 2.410(3) | W(1)—Yb(1)—W(2) | 133.02(2) |

(b) $[\{Nb(\eta-C_5H_5)_2H_2\}_2Yb \cdot diglyme]$, **2**

| | | | |
|--------------------|-----------|--|-----------|
| Yb(1)···Nb(1) | 3.3305(5) | Yb(1)—O(1) | 2.463(9) |
| Yb(1)—H(1) | 2.32(8) | Yb(1)—O(2) | 2.512(4) |
| Yb(1)—H(2) | 2.33(7) | Nb(1)—C _{pcent(1)} | 2.04 |
| Nb(1)—H(1) | 1.77(7) | Nb(1)—C _{pcent(2)} | 2.04 |
| Nb(1)—H(2) | 1.71(7) | H(1)—Nb(1)—H(2) | 82.6(35) |
| Nb(1)—Yb(1)—Nb(1B) | 126.64(2) | H(1)—Yb(1)—H(2B) | 105.7(25) |
| H(1)—Yb(1)—H(2) | 59.1(26) | Yb(1)—H(2)—Nb(1) | 110.0(34) |
| Yb(1)—H(1)—Nb(1) | 108.1(33) | C _{pcent(1)} —Nb(1)—C _{pcent(2)} | 144.0 |
| H(2)—Yb(1)—H(2B) | 158.1(34) | | |

(C_{pcent(1)} and C_{pcent(2)} refer to the computed ring centroids for C(1) to C(5) and C(6) to C(10) respectively)

(c) $[Zr(\eta-C_5Me_5)Cl_2W(PMe_3)_3H_5]$, **6**

| | | | |
|---------------------------|-----------|--------------------------------|----------|
| W(1)—Zr(1) | 2.9430(4) | W(1)—P(1) | 2.446(1) |
| Zr(1)—Cl(1) | 2.439(1) | W(1)—P(2) | 2.448(1) |
| Zr(1)—Cl(2) | 2.427(1) | W(1)—P(3) | 2.431(1) |
| C _{pcent} —Zr(1) | 2.223 | C _{pcent} —Zr(1)—W(1) | 129.0 |

(C_{pcent} refers to the computed ring centroid for C(1) to C(5))

which is longer than the sum of atomic radii 3.20 Å and this suggests the absence of a metal–metal bond.

The internal bond lengths and angles of the diglyme ligand are close to those found in compounds $[\text{TiCl}_3(\text{diglyme})]^8$ and $[\text{K}(\text{diglyme})][\text{Ce}(\text{COT})_2]^9$. All three oxygen atoms are within bonding distance of the Yb, in contrast to the recently reported structures of the compounds $[\text{M}(\text{O})_2\text{Cl}_2(\text{diglyme})]$ ($\text{M} = \text{Mo}, \text{W}$),¹⁰ where only two of the diglyme oxygens are ligated. The average Yb–O distance of 2.54 Å in **1** is slightly longer than other reported Yb–O bonds, to thf, Et₂O and dme, which are typically in the range 2.39–2.50 Å (Yb^{II})^{11–17} or 2.31–2.43 Å (Yb^{III}).^{18–23} The structurally characterized samarium–diglyme compound $[\text{SmI}_2(\text{diglyme})_2]^{24}$ has Sm–O bond lengths that are also slightly longer than samarium bonds to thf and dme.^{25–32}

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in thf-*d*₈ consists of a band centred at –20.0 ppm with two sets of satellites ($J = 175$ and 72 Hz), and a low intensity singlet at –20.6 ppm. The second signal can be readily assigned to the presence of a trace of adventitious $[\text{W}(\text{PMe}_3)_3\text{H}_6]$. The singlet at –20.6 ppm is assignable to the ^{31}P nuclei of the PMe_3 groups. The two sets of satellites are due to the coupling of ^{31}P to both the ^{183}W (spin 1/2, abundance 14.41%) and ^{171}Yb nuclei (spin 1/2, abundance 14.27%). The inner set of satellites may be assigned to coupling with the ^{183}W nuclei from consideration of the $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectrum of **1**, *vide infra*.

The room temperature ^1H NMR spectrum of a sample of **1** prepared *in situ* in thf-*d*₈ consists of a doublet at 1.56 ppm and several bands in the high field region –3.0 and –5.5 ppm. Integration shows a ratio of doublet : high field peaks of intensity ratio 27 : 5. The high field signals include a sharp quartet at –3.2 [$J(\text{H}–^{31}\text{P}) = 38$ Hz] and a broad asymmetric resonance centred at –3.6 ppm. The quartet is assignable to the trace of $[\text{W}(\text{PMe}_3)_3\text{H}_6]$ formed by adventitious hydrolysis. Variable temperature ^1H NMR spectra of **1** are shown in Fig. 2. At 253 K two relatively sharp quartets are observed at –3.63 [$J(\text{H}–^{31}\text{P}) = 20$ Hz] and –4.75 with [$J(\text{H}–^{31}\text{P}) = 37$ Hz] ppm. The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum at 253 K showed two singlets which integrated in the ratio 3 : 2. On cooling to *ca* 213 K the band at –4.75 ppm resolved into two resonances whilst the resonance at –3.63 ppm remained sharp. Further cooling below 213 K caused the two resonances derived from the –4.75 ppm to sharpen giving rise to a broad five-line signal at –6.0 ppm and a broad signal around –4.0 ppm which is partially obscured. As the temperature descends below 193 K the resonance at –3.63 ppm broadens but it was

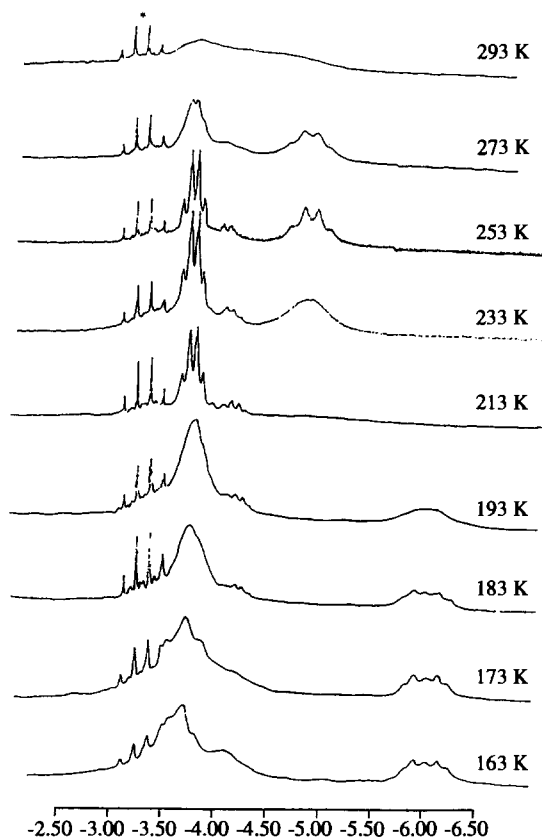


Fig. 2. The variable temperature ^1H NMR spectra of $[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb}]$, **2**, in thf-*d*₈. * indicates $[\text{W}(\text{PMe}_3)_3\text{H}_6]$.

not possible to observe a low-temperature limit as the sample froze at 163 K.

The variable temperature ^1H NMR spectra may be interpreted as follows: at 253 K the two hydride resonances with a ratio 3 : 2 have different $J(\text{H}–\text{P})$ coupling constants and, by analogy with the structurally characterized (neutron diffraction) $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}(18\text{-crown-6})]^2$, these resonances may be assigned to $\text{W}–(\mu\text{-H})_3–\text{Yb}$ and two terminal $\text{W}–\text{H}$ protons, respectively. At temperatures above 253 K these resonances broaden and coalesce due to exchange. The further decoalescences observed on cooling below 253 K are due to attainment of the slow exchange limit for the two terminal hydrides. It may be noted that the chemical shift of the terminal hydrides is close to that found for $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{Na}]^2$ (–4.7 vs. –5.0 ppm), whereas the bridged hydrides have very different chemical shifts (–3.6 in $[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb}]$ and –6.0 ppm in $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{Na}]$), as might be expected from the relative electron affinities of Yb as compared to Na.

A sample of **1** was prepared *in situ* in an 8 mm NMR tube and placed inside a 10 mm tube containing deuterated acetone as an external lock. The

$^{171}\text{Yb}\{^1\text{H}\}$ NMR spectrum, shown in Fig. 3, consists of a single multiplet centred at 1462.3 ppm, relative to $[\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$, with a splitting of 73 Hz. Five lines can be clearly observed from the multiplet, in a ratio consistent with them being the central peaks of a septet (theoretical ratio 1:6:15:20:15:6:1) due to coupling of the ^{171}Yb nucleus to six ^{31}P nuclei. The $^2J(^{171}\text{Yb}\text{---}^{31}\text{P})$ coupling constant of 73 Hz is comparable to that recently reported for the compound $[\text{Yb}\{\text{Ph}_2\text{P}(\text{NSiMe}_3)_2\}_2(\text{thf})_2]$ [$^2J(^{171}\text{Yb}\text{---}^{31}\text{P}) = 67$ Hz].³³ Satellite peaks due to coupling to tungsten (^{183}W abundance 14.41%, spin 1/2) were not observed.

On the basis of the structural and spectroscopic evidence and in the light of the close analogy with the structure and spectroscopic properties of $[\text{W}(\text{PMe}_3)_3\text{H}_2(\mu\text{-H})_3\text{K}(18\text{-C-6})]$ we conclude that each tungsten atom of **1** is bonded to the central yttrium atom by three hydrogens via two-electron three-centre bonds, with possibly a small contribution from direct W—Yb interaction. We note, however, that the data do not rule out an alternative formulation with two hydrogen bridging systems, e.g. $[(\text{PMe}_3)_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Yb}(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3]$, as is found in the compound $[(\text{PMe}_3)_3\text{H}_3\text{W}(\mu\text{-H})_2\text{Al}(\text{H})(\mu\text{-H})_2\text{WH}_3(\text{PMe}_3)_3]$.³⁴ Our preferred formulation for **1** with the W—($\mu\text{-H}$)₃—Yb moieties gives a coordination number of nine for the ytterbium centre and this is more likely than seven.⁵ As noted above, the $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectrum of

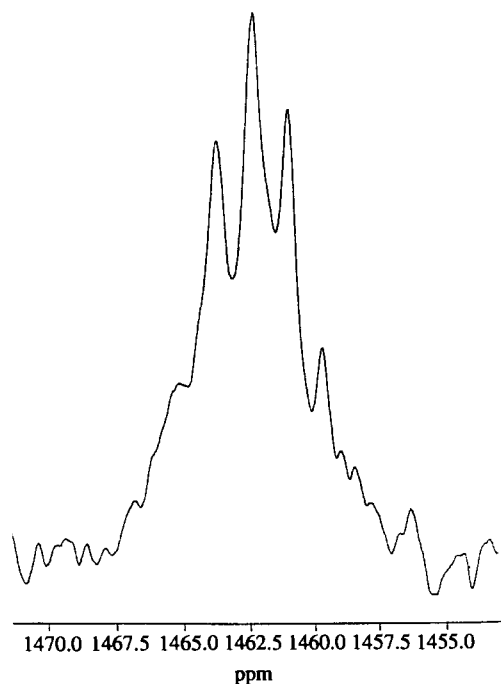


Fig. 3. The $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectrum of $[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb}]$ in thf.

$[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb}]$, **1**, showed coupling of the Yb to the ^{31}P nuclei and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** showed both Yb and W satellites. This is evidence for a covalent interaction between Yb and W. This interaction could arise from Yb—W bonding or from the presence of covalent bridging W—($\mu\text{-H}$)—Yb bonds or a combination of both. The W—Yb distance of 3.24 Å is within the range for a direct interaction.

The compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ in tetrahydrofuran was treated with potassium hydride for three days at room temperature giving an orange precipitate. This was presumed to be $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2][\text{K}]$, by analogy with the preparation of $[\text{K}(18\text{-crown-6})][\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}]$.² The orange precipitate was treated with a suspension of ytterbium diiodide in 1,2-dimethoxyethane, which contains a trace of diglyme (NMR), at room temperature for 12 h. Red crystals were isolated in *ca* 30% yield. A crystal structure determination showed the compound to be $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\}_2\text{Yb}\cdot\text{diglyme}]$ (**2**). The molecular structure of **2** is shown in Fig. 4 and selected bond lengths and angles are given in Table 1.

The compound **2** has a central Nb—Yb—Nb core, with a Nb—Yb distance of 3.33 Å and a Nb—Yb—Nb angle of 126.64°. Two bridging hydrogens were located symmetrically on each side of the Nb—Yb vector and the two bridging hydrogens and the Yb and Nb atoms lie in a plane (the sum of internal angles is 359.9°). The triply coordinated diglyme ligand completes the Yb coordination sphere. Each Nb bears two ($\eta\text{-C}_5\text{H}_5$) groups, bent away from the Yb. The complete molecule has two-fold rotational symmetry about the Yb—O(CH₂CH₂OCH₃)₂ bond. The distance Yb—Nb of 3.33 Å lies between the sum of Slater atomic radii⁴ (Yb 1.75 + Nb 1.45 = 3.20 Å) and the sum of the metallic radii⁵ (Yb_{8-coord} 1.93 + Nb_{12-coord} 1.46 = 3.39 Å) as was found for **1**. The Yb—H distances of 2.32–2.33 Å are comparable with those of 2.2(1) and 2.4(1) Å in $[\text{Yb}(\text{MeCN})_6(\mu\text{-H})_2\text{B}_{10}\text{H}_{12}]$.³⁵ Shorter Yb—H distances of 1.64 and 1.67 Å were calculated for the compound $[\text{Ph}_3\text{Ge}(\mu\text{-H})\text{Yb}(\text{thf})_4(\mu\text{-H})\text{GePh}_3]$.³⁶ The average Nb—H distance of 1.74(6) Å is close to those found in other niobium hydrides (1.69–1.70 Å).^{37–39}

The Nb—C_{pcent} distance of 2.04 Å is in the range for other bis- η -cyclopentadienyl compounds^{40–42} (e.g. $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ 2.09 Å), whereas the C_{pcent(1)}—Nb(1)—C_{pcent(2)} angle of 144.0° is slightly larger than for the niobium metallocene derivatives $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)_2]^-$, 141.2°,⁴³ $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$, 141.6°,³⁸ $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_2\text{H}_4)\text{Et}]$, 132.4°⁴⁴ and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, 130.2°.⁴⁰

The orientation of the ($\eta\text{-C}_5\text{H}_5$)₂Nb groups is

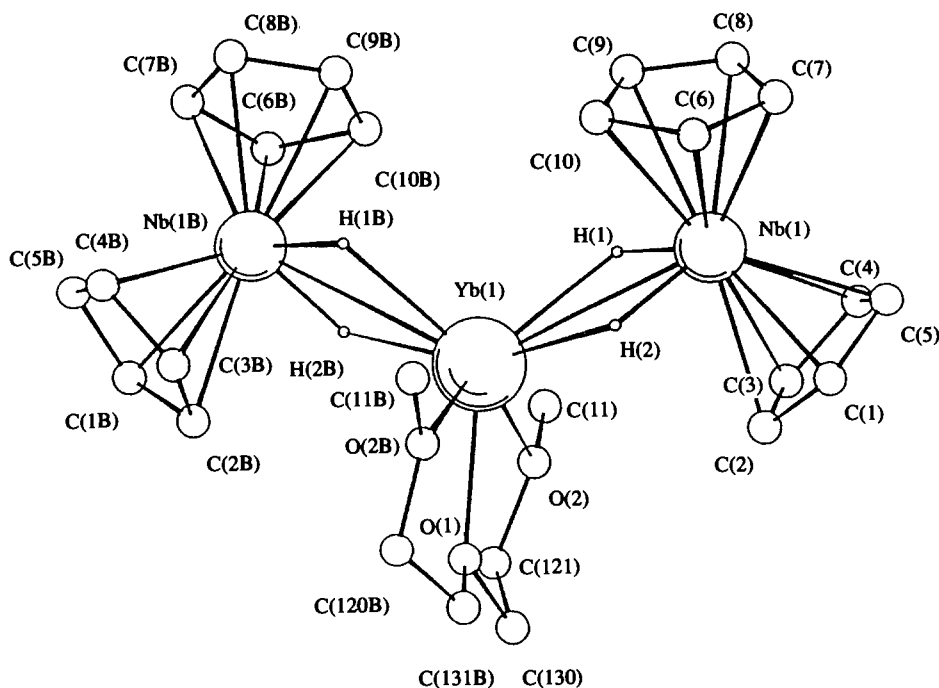


Fig. 4. The molecular structure of $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\}_2\text{Yb}\cdot\text{diglyme}]$, **2**, the atoms labelled with "B" are generated from the asymmetric unit using a two-fold axis.

such that the complete molecule forms a propeller-like arrangement, with the diglyme central O—Yb bond as the shaft, and the blades of the propeller being the $\text{Yb}(\mu\text{-H})_2\text{Nb}$ planes. This is a sterically favoured arrangement, allowing the $(\eta\text{-C}_5\text{H}_5)$ rings to be partially eclipsed both with regard to the other $(\eta\text{-C}_5\text{H}_5)_2\text{Nb}$ group on one side and the diglyme on the other. The Nb—Yb—Nb angle in **2** (126.64°) may be compared to the W—Yb—W angle in **1** of 133.02° . This indicates that the $\text{W}(\text{PMe}_3)_3\text{H}_5$ group has a larger bite angle than the moiety $\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$.

The NMR data for **2** are consistent with the molecular structure found in the crystal. The ^1H NMR spectrum of **2** in $\text{thf-}d_6$ showed a singlet assignable to the $(\eta\text{-C}_5\text{H}_5)$ rings and a broad resonance at -9.3 ppm due to the hydrogens directly bound to the niobium. The bands of the diglyme hydrogen were partially obscured by the solvent thf . The $^{31}\text{C}\{^1\text{H}\}$ nmr spectrum shows a singlet at 79.5 ppm which can be assigned to the $(\eta\text{-C}_5\text{H}_5)$ rings and three other singlets assigned to the three carbon environments expected for the coordinated diglyme solvent. The chemical shifts are comparable to those reported for the compounds $[\text{MO}_2\text{Cl}_2(\text{diglyme})]$ ($\text{M} = \text{Mo}, \text{W}$).¹⁰ A variable temperature ^1H NMR study of **2** in $\text{thf-}d_6$ showed that as the temperature was lowered the band at -9.3 ppm assignable to Nb-hydrogens became sharper, apparently a manifestation of thermal

decoupling^{45,46} due to the quadrupolar nucleus (^{93}Nb , spin $9/2$, 100%). On lowering the temperature to 250 K satellite peaks were observed and these may be assigned to coupling of the Nb-hydrogens with the ^{171}Yb nucleus [$J(^{171}\text{Yb}\text{-H}) = 170$ Hz]. The low temperature NMR data are consistent with a formulation of three Yb—H—Nb bonds analogous to those found in the compound $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$. Since the low temperature ^1H NMR spectrum of **2** shows satellites due to coupling of the hydride ligands to the Yb nucleus and the Yb—Nb distance of 3.33 Å it may be that the hydrogen-bridged bonds are supported by a degree of direct metal—metal bonding. Preliminary studies of the reaction between $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ and samarium diiodide gave a green microcrystalline compound which is tentatively formulated as $[\{\text{W}(\text{PMe}_3)_3\text{H}_2(\mu\text{-H})_3\}_2\text{Sm}]$ (**7**) on the basis of the NMR and analytical data given in Table 2.

Two reactions have been described in the literature where the $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ salt was reacted with $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ or $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{HCl}]$ to give the heterobimetallic tungsten zirconium compounds $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$ and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{HW}(\text{PMe}_3)_3\text{H}_5]$.² We have prepared closely related compounds. Thus, treatment of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ with one equivalent of $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ in thf gave a deep red solution from which red crystals of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$ (**3**)

Table 2. Analytical and spectroscopic data

| Compound, colour and analysis (%) ^a | Spectroscopic data ^b |
|--|---|
| 1 Orange C: 25.15 (25.25) H: 6.5 (6.9) | ¹ H: 1.58 [d, 54 H, <i>J</i> (H—P) 5, 6PMe ₃], 3.3–3.7 [partially obscured, (CH ₃ OCH ₂ CH ₂) ₂ O], –3.6 [br s, 10 H, 10 (W—H)] ^c ; ³¹ P{ ¹ H}: –20.0 [s, <i>J</i> (P—W) 175, <i>J</i> (P—Yb) 72, PMe ₃] ^c ; ³¹ P{ ¹ H—Me}: –20.0 [sxt, <i>J</i> (P—H) 26] ^c ; ¹³ C{ ¹ H}: 72.7 [s, (CH ₃ OCH ₂ CH ₂) ₂ O], 71.2 [s, (CH ₃ OCH ₂ CH ₂) ₂ O], 58.9 [s, (CH ₃ OCH ₂ CH ₂) ₂ O], 34.6 [m, PMe ₃] ^c |
| 2 Red C: 38.6 (41.2) H: 5.0 (5.1) | ¹ H: 4.41 [s, 20H, 4C ₅ H ₅], 3.3–3.7 [partially obscured, (CH ₃ OCH ₂ CH ₂) ₂ O], –9.34 [br s, 4 H, 4(Nb—H)] ^c ; ¹³ C{ ¹ H}: 79.5 [s, C ₅ H ₅], 72.3 [s, (CH ₃ OCH ₂ CH ₂) ₂ O], 71.1 [s, CH ₃ OCH ₂ CH ₂ O], 59.6 [s, (CH ₃ OCH ₂ CH ₂) ₂ O] ^c |
| 3 Red C: 29.7 (30.0) H: 5.6 (5.6) | ¹ H: 6.05 [s, 10 H, 2C ₅ H ₅], 1.52 [d, 27 H, <i>J</i> (H—P) 7.3, 3PMe ₃], –1.67 [q, 5 H, <i>J</i> (H—P) 25.2, <i>J</i> (H—W) 32.6, 5(W—H)] ^d ; ³¹ P{ ¹ H}: –19.9 [s, <i>J</i> (P—W) 206, PMe ₃] ^d ; ³¹ P{ ¹ H—Me}: –19.9 [sxt, <i>J</i> (P—H) 18] ^d Mass spectrum (E.I.): <i>m/z</i> 759 M ⁺ |
| 4 Red C: 31.8 (32.0) H: 5.9 (5.9) | ¹ H: 6.29 (q _{app} , 2 H, 2C ₅ H ₄ Me), 6.16 (q _{app} , 2 H, 2C ₅ H ₄ Me), 5.57 (q _{app} , 2 H, 2C ₅ H ₄ Me), 5.52 (q _{app} , 2 H, 2C ₅ H ₄ Me), 2.40 (s, 6 H, 2C ₅ H ₄ Me), 1.53 [d, 27 H, <i>J</i> (H—P) 7.3, 3PMe ₃], –1.81 [q, 5 H, <i>J</i> (H—P) 25.0, <i>J</i> (H—W) 32.8, 5(W—H)] ^e ; ³¹ P{ ¹ H}: –20.6 [s, <i>J</i> (P—W) 203, PMe ₃] ^e ; ¹³ C{ ¹ H}: 124.0 [s, C, C ₅ H ₄ Me], 116.1 [s, CH, C ₅ H ₄ Me], 113.5 [s, CH, C ₅ H ₄ Me], 109.4, [s, CH, C ₅ H ₄ Me], 106.4 [s, CH, C ₅ H ₄ Me], 29.9 [d, <i>J</i> (C—P) 28, PMe ₃], 16.2 [s, C ₅ H ₄ Me] ^e Mass spectrum (E.I.): <i>m/z</i> 790 M ⁺ IR: 1746 m, 1419m, 1297m, 1278s, 1261m, 1094m, 1020m, 946s, 852w, 725m |
| 5 Dark green C: 36.1 (35.9) H: 6.45 (6.6) | ¹ H: 6.41 (m, 2 H, 2C ₅ H ₄ Me), 6.24 (m, 2 H, 2C ₅ H ₄ Me), 5.60 (m, 2 H, 2C ₅ H ₄ Me), 5.51 (m, 2 H, 2C ₅ H ₄ Me), 2.35 (s, 6 H, 2C ₅ H ₄ Me), 1.55 [d, 27 H, <i>J</i> (H—P) 7.2, 3PMe ₃], –2.43 [q, 5 H, <i>J</i> (H—P) 25.1, <i>J</i> (H—W) 34.2, 5(W—H)] ^e ; ³¹ P{ ¹ H}: –22.7 [s, <i>J</i> (P—W) 199, PMe ₃] ^e ; ³¹ P{Me— ¹ H}: –22.7 [sxt, <i>J</i> (P—H) 23] ^e ; ¹³ C{ ¹ H}: 125.6 [s, C, C ₅ H ₄ Me], 116.8 [s, CH, C ₅ H ₄ Me], 113.9 [s, CH, C ₅ H ₄ Me], 110.4, [s, CH, C ₅ H ₄ Me], 107.2 [s, CH, C ₅ H ₄ Me], 30.0 [d, <i>J</i> (C—P) 28, PMe ₃], 16.3 [s, C ₅ H ₄ Me] ^e Mass spectrum (E.I.): <i>m/z</i> 699 M ⁺ |
| 6 Deep red C: 32.15 (31.9) H: 6.7 (6.6) | ¹ H: 2.19 (s, 15 H, C ₅ Me ₅), 1.59 [d, 27 H, <i>J</i> (H—P) 7.7, 3PMe ₃], –2.24 [q, 5 H, <i>J</i> (H—P) 25.3, <i>J</i> (H—W) 40.4, 5(W—H)] ^e ; ³¹ P{ ¹ H}: –21.8 [s, <i>J</i> (P—W) 187, PMe ₃] ^e ; ³¹ P{Me— ¹ H}: –21.8 [sxt, <i>J</i> (P—H) 19] ^e ; ¹³ C{ ¹ H}: 124.7 [s, C ₅ Me ₅], 29.9 [d, <i>J</i> (C—P) 29, PMe ₃], 13.6 (s, C ₅ Me ₅) ^e Mass spectrum (E.I.): <i>m/z</i> 713 M ⁺ IR: 1808m, 1748w, 1693m, 1594m, 1418m, 1298m, 1279s, 1190m, 1102w, 941s, 722s, 672s. |
| 7 Green C: 20.6 (22.0) H: 6.0 (6.55) | ¹ H: –1.67 (br s, 54 H, 6PMe ₃), –10.21 [br s, 10 H, 10(W—H)] ^e ; ¹³ C{ ¹ H}: 38.3 [d, <i>J</i> (C—P) 24, PMe ₃] ^e |

^a Analytical data given as: found (required) (%).

^b Data given as chemical shift (δ) [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), relative intensity, coupling constant *J* in Hz, assignment].

^c In [²H₈]tetrahydrofuran.

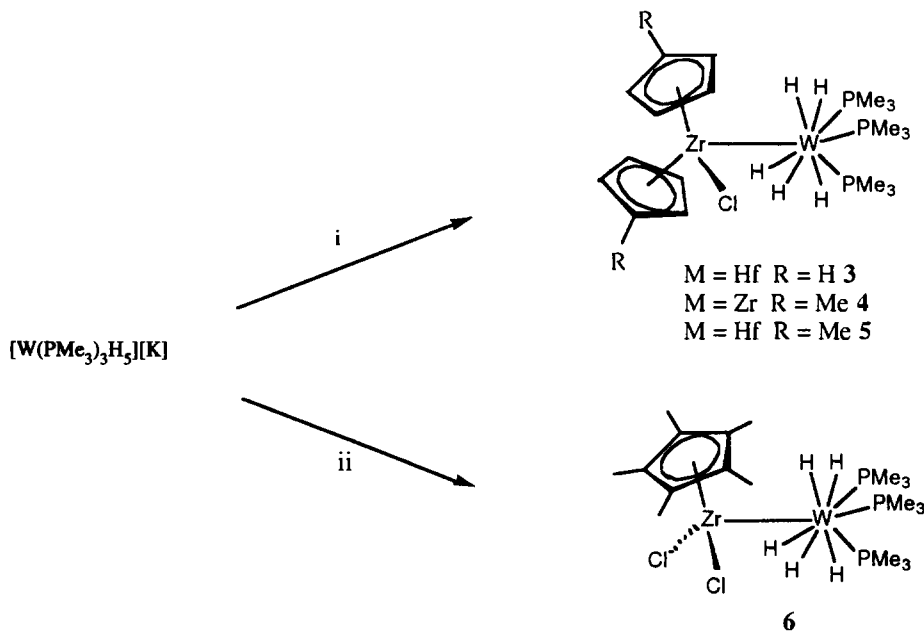
^d In [²H₈]toluene.

^e In [²H₆]benzene.

^f Selected infra-red data, CsI or Nujol (cm⁻¹), w = weak, m = medium, s = strong.

could be isolated. The compounds [Hf(η-C₅H₄Me)₂ClW(PMe₃)₃H₅] (**4**) and [Zr(η-C₅H₄Me)₂ClW(PMe₃)₃H₅] (**5**) have been prepared in a similar manner, see the Scheme. Treatment of [Zr(η-C₅Me₅)Cl₃·2thf] with the salt [W(PMe₃)₃H₅] [K] gave the monocyclopentadienyl compound [Zr(η-C₅Me₅)Cl₂W(PMe₃)₃H₅] (**6**). The analytical,

¹H NMR and ³¹P NMR data for the compounds **3–6** are given with assignments in Table 2. The values for *J*(H—³¹P) were about 25 Hz and for *J*(H—¹⁸³W) lie in the range 32.6–40.4 Hz. At room temperature the ¹H NMR spectra of **3–6** each showed a quartet (–1.67 to –2.43 ppm) assignable to the five tungsten hydrides, together with a low



Scheme. (i) $[\text{M}(\eta\text{-C}_5\text{R}_5)\text{Cl}_2]$ in thf at -78°C , warm to room temperature for 2–5 h, $\text{M} = \text{Hf}$, $\text{R} = \text{H}$, 22%; $\text{M} = \text{Hf}$, $\text{R} = \text{Me}$, 27%; $\text{M} = \text{Zr}$, $\text{R} = \text{Me}$, 27%. (ii) $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3 \cdot 2\text{thf}]$ in thf at room temperature for 5 h, 55%.

intensity quartet assignable to the inevitable hydrolysis product $[\text{W}(\text{PMe}_3)_3\text{H}_6]$. Low temperature ^1H NMR spectra for **4** are shown in Fig. 5. At 253 K the quartet begins to broaden and this process continues until decoalescence is reached (below 223 K). By 203 K, two broad resonances are observed, at -1.35 and at -2.55 ppm. These integrate approximately in the ratio 3:2 (cut and weighed peaks, after removing hydrolysis product signal). Further cooling below this temperature does not cause further sharpening of these peaks before the sample freezes at *ca* 183 K. The ^1H NMR behaviour of the hydrides in **4** is therefore similar to that observed for the case of **1**, showing two different hydride environments at low temperatures which may be explained in terms of bridging and terminal hydrogen ligands.

The variable low temperature ^1H NMR spectra for **6** were similar to those for **4**. Thus, at room temperature a quartet integrating as 5 H is observed at -2.26 ppm. On cooling, this broadens near 233 K, undergoes decoalescence at approximately 203 K and separates into two broad peaks (-1.8 and -2.55 ppm) at 183 K, below which temperature the sample froze. In this case, the substantial overlap of the peaks at the lowest temperature obtainable precluded their separate integration.

The crystal structure of the violet-black crystals of **6** has been determined. The molecular structure is shown in Fig. 6 and selected bond lengths and

angles are given in Table 1. The Zr–W distance of 2.94 \AA is close to the sum of the Slater atomic radii⁴ of W and Zr of 2.90 \AA (W $1.35 + \text{Zr } 1.55 \text{ \AA}$), and less than the sum of metallic radii⁵ of 2.99 \AA (W $1.39 + \text{Zr } 1.60 \text{ \AA}$). The compound $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-PPh}_2)_2\text{W}(\text{CO})_4]$ has a longer Zr–W distance of 3.289 \AA ;⁴⁷ a donor–acceptor bond from W(0) to electron deficient Zr(IV) was proposed. The molybdenum atom has effectively the same metallic radius as that of tungsten. Thus, the compound $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-OC})(\text{Me})(\mu\text{-CO})\text{Mo}(\text{CO})(\eta\text{-C}_5\text{H}_5)]$ which has a Zr–Mo distance of 3.297 \AA ⁴⁸ was described as “unambiguously a 34-electron dimer with a Zr–Mo bond”. Therefore, on the basis of the above evidence, the presence of a Zr–W bond in **6** is reasonable.

Hydrogen atoms bonded directly to the tungsten centre in **6** were not located. However, as for **1** it is probable that there are bridging hydrogens between the two metals. In the structure of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{ClOs}(\text{PMe}_2\text{Ph})_3\text{H}_3]$ ⁴⁹ it was argued that the three bridging hydrogens supported the Zr–Os bond, although they were not located in the crystal structure. The low temperature ^1H NMR spectrum of **6** showed that the five hydrogens bound to W are divided into two sets. As was the case for **1** it is not possible to say if two or three hydrogens are bridging the metals. The Cl(1)–Zr–W and Cl(2)–Zr–W angles for $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\text{W}(\text{PMe}_3)_3\text{H}_5]$ are 104.47° and 104.32° respectively

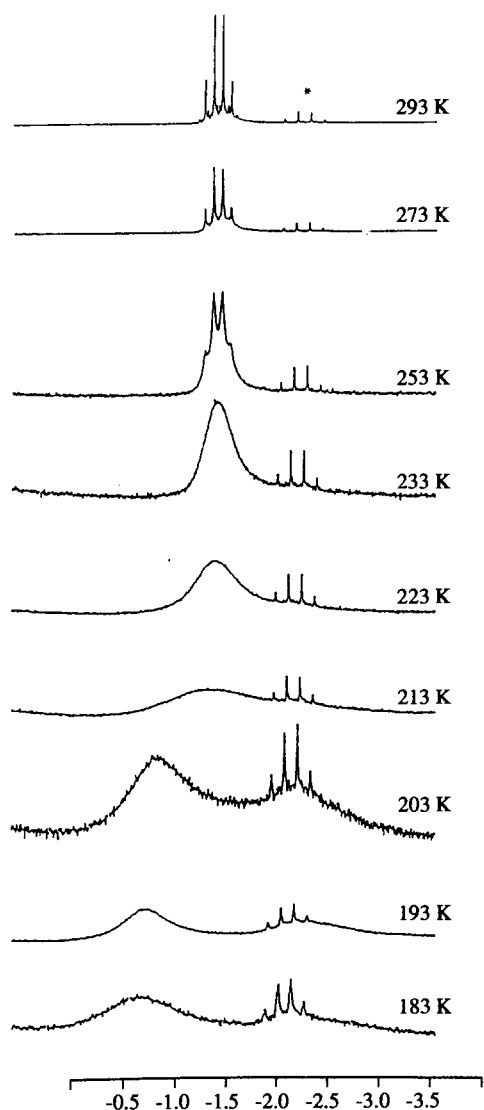


Fig. 5. The variable temperature ^1H NMR spectra of $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$, **4** in toluene- d_8 . * indicates $[\text{W}(\text{PMe}_3)_3\text{H}_6]$.

and the W—Cl distances [namely W...Cl(1) 4.266 and W...Cl(2) 4.253 Å] preclude these chlorides acting as bridging atoms between the two metals.

The average W—P distance of 2.44 Å in **6** is slightly longer than the average W(1)—P distance of 2.40 and W(2)—P distance of 2.41 Å found in the structure of **1**. The average P—W—Zr angle of 103.14° is comparable and slightly smaller than the average P—W(1)—Yb angle of 104.7° and P—W(2)—Yb of 105.8°.

Electron impact mass spectra at typically 350–450°C for **3–6** showed the parent ions M^+ . At lower temperatures, all six compounds gave essentially identical spectra ascribable to $\text{W}(\text{PMe}_3)_3$ and its breakdown products.

EXPERIMENTAL

All preparations and reactions described were carried out under an atmosphere of argon or dinitrogen (<10 ppm oxygen or water) using standard Schlenk and vacuum-line techniques or in a dry-box. Argon and nitrogen were purified by passage through a gas-drying column containing MnO catalyst and 4 Å molecular sieves.

Solvents were pre-dried over activated molecular sieves and then distilled from sodium (toluene), sodium–potassium alloy (tetrahydrofuran, diethyl ether, light petroleum ether) or calcium hydride (dichloromethane) under an inert atmosphere of nitrogen. Deuterated solvents for NMR samples were stored in ampoules over sodium–potassium alloy and transferred by vacuum distillation.

Elemental analyses were performed by Analytische Laboratorien, Elbach, Germany, or the Analytical Laboratory in this Department.

NMR spectra were recorded using a Bruker AM300 instrument (^1H 300 MHz, ^{13}C 75.5 MHz, ^{31}P 121.6 MHz, ^{171}Yb 52.5 MHz). Spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane ($\delta = 0$ ppm), or externally using trimethylphosphate in D_2O (^{31}P) and $[\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2(\text{thf})]$ in thf (^{171}Yb).

Mass spectra were obtained on an AEI MS 302 mass spectrometer (E.I.), updated by a data-handling system supplied by Mass Spectrometry Services Ltd, and further updated and renovated. Masses were calibrated using polyfluorokerosine (up to *ca* 900 mass units) or heptacosafuorotributylamine.

The compounds YbI_2 , SmI_2 ,⁵⁰ SmI_2 ,⁵¹ $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$,² $[\text{NbCl}_4(\text{thf})_2]$,^{52,53} $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$,⁵⁴ $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Cl}_2]$ ⁵⁵ (M = Zr, Hf; R = H, Me), $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3 \cdot 2\text{thf}]$ ⁵⁶ were prepared as described.

Preparation of $[\{\text{W}(\text{PMe}_3)_3\text{H}_5\}_2\text{Yb} \cdot \text{diglyme}]$, **1**

A white suspension of YbI_2 (0.401 g, 0.94 mmol) in dme (50 ml) was treated with an orange solution of $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ (0.857 g, 1.9 mmol) in dme (50 ml). The reaction mixture became green and a white precipitate (KI) separated. After stirring for a further 2 h the mixture was filtered and the volume of the filtrate was reduced to 25 ml. Orange crystals were formed overnight by cooling the solution to -25°C . Yield: 0.360 g, 34%.

Preparation of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2][\text{K}]$

A mixture of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ (2.75 g, 12.2 mmol) in thf (100 ml) and KH (0.486 g, 12.1 mmol)

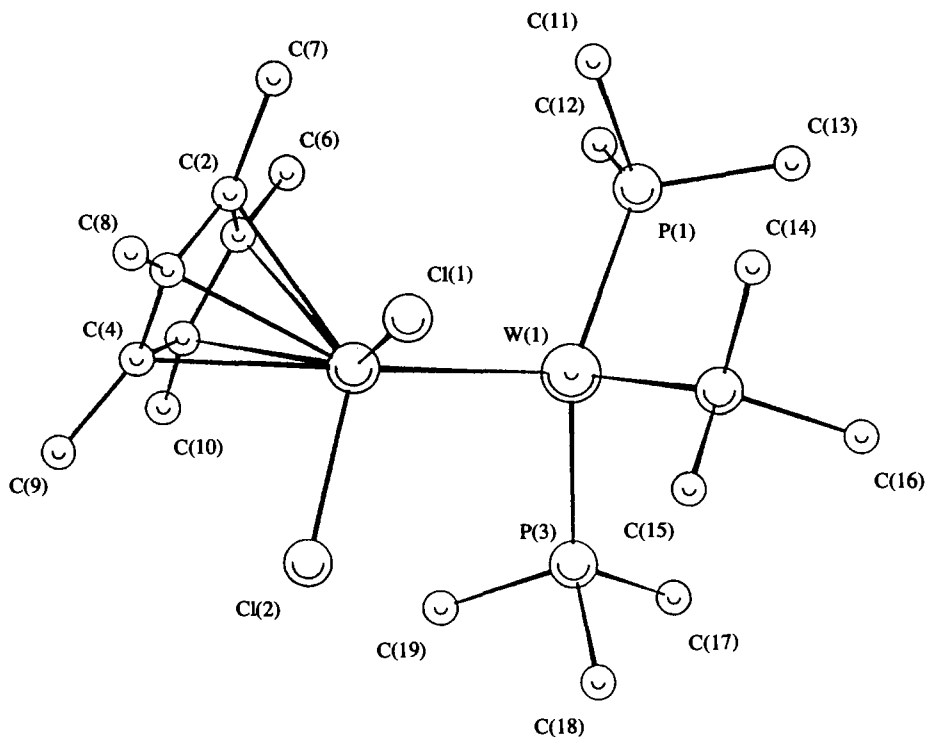


Fig. 6. The molecular structure of $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\text{W}(\text{PMe}_3)_3\text{H}_5]$, **6**.

was stirred for 3 days giving an orange suspension. The thf was removed under reduced pressure and the resulting orange powder was washed with toluene (1×50 ml), with petroleum ether (3×30 ml) and was dried *in vacuo* to give 2.5 g of an orange compound believed to be $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2][\text{K}]$ on the basis of subsequent reactions. Yield: 2.5 g, 78%.

Preparation of $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\}_2\text{Yb} \cdot \text{diglyme}]$ **2**

A white suspension of YbI_2 (570 mg, 13 mmol) in dme (50 ml) was added to an orange suspension of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2][\text{K}]$ (706 mg, 27 mmol) in dme (50 ml) with rapid stirring. The reaction mixture became red and a white precipitate was observed. After stirring for 12 h the red solution was filtered. The filtrate was reduced in volume to 25 ml under reduced pressure and cooled to -25°C overnight giving red crystals of $[\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2\}_2\text{Yb} \cdot \text{diglyme}]$. Yield: 0.350 g, 30%.

Preparation of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$, **3**

An orange solution of $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ (0.4 g, 8.8 mmol) in thf (20 ml) was added slowly to a colourless solution of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (0.333 g, 8.8 mmol) in thf (30 ml) at -78°C . The reaction mixture turned first green and then red. After warming to room temperature, the mixture was stirred for 1 h, after which the solvent was removed under

reduced pressure. The residue was extracted with petroleum ether (4×15 ml) and filtered. The filtrate was cooled to -25°C overnight giving red needles. Yield: 0.150 g, 22%.

Preparation of $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$, **4**

An orange solution of $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ (0.426 g, 9.3 mmol) in thf (20 ml) was added slowly to a colourless solution of $[\text{Hf}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$ (0.380 g, 9.3 mmol) at room temperature. The reaction mixture turned red during the addition. The mixture was stirred for 2 h, after which the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (4×15 ml). The extract was filtered and the filtrate was cooled to -25°C overnight giving red crystals. Yield: 0.2 g, 27%.

Preparation of $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{ClW}(\text{PMe}_3)_3\text{H}_5]$, **5**

An orange solution of $[\text{W}(\text{PMe}_3)_3\text{H}_5][\text{K}]$ (0.598 g, 1.3 mmol) in thf (20 ml) was slowly added to a colourless solution of $[\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$ (0.420 g, 1.3 mmol) in thf at room temperature. The reaction mixture turned green during the addition. After addition was complete, the mixture was stirred for a further 5 h, after which the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (4×15 ml), filtered, and

Table 3 Crystal data and some details of experimental conditions

| | 1 | 2 | 6 |
|---|---|---|--|
| Formula | C ₂₄ H ₇₈ O ₃ P ₆ W ₂ Yb | C ₂₆ H ₃₈ O ₃ Nb ₂ Yb | C ₁₉ H ₄₇ Cl ₂ P ₃ WZr |
| Formula weight | 1141.4 | 757.44 | 714.48 |
| Crystal size (mm) | 0.40 × 0.50 × 0.80 | 0.20 × 0.20 × 0.40 | 0.10 × 0.40 × 0.62 |
| Crystal system | Monoclinic | Orthorhombic | Triclinic |
| Space group | <i>P2₁/n</i> | <i>Fddd</i> | <i>P1</i> |
| <i>a</i> (Å) | 14.976(7) | 14.017(4) | 9.9858(7) |
| <i>b</i> (Å) | 16.117(7) | 26.278(16) | 12.2278(8) |
| <i>c</i> (Å) | 19.648(1) | 33.404(16) | 12.533(1) |
| α (°) | | | 75.37(1) |
| β (°) | 107.09(3) | | 86.42(1) |
| γ (°) | | | 85.08(1) |
| Cell volume (Å ³) | 4532.7 | 12306.3 | 1474.0 |
| <i>Z</i> | 4 | 16 | 2 |
| <i>D_c</i> (g cm ⁻³) | 1.67 | 1.635 | 1.61 |
| μ (cm ⁻¹) | 74.44 | 37.28 | 46.81 |
| <i>F</i> (000) | 2216 | 5920 | 708 |
| Radiation ($\lambda/\text{Å}$) | Mo- <i>K_{\alpha}</i> | Mo- <i>K_{\alpha}</i> | Mo- <i>K_{\alpha}</i> |
| 2 θ limits (°) | 3–48 | 2–44 | 2–55 |
| Zone | $-l-h, -l-k, -l-l$ | 0- <i>hkl</i> | $-h h, -k k, -l l$ |
| Scan mode | $\omega-2\theta$ | ω | $\omega-2\theta$ |
| Total data collected | 8115 | 2566 | 7322 |
| Total unique data | 7081 | 1892 | 6462 |
| No. of observations (<i>I</i> > 3 σ (<i>I</i>)) | 4524 | 1462 | 5524 |
| R(merge) | 0.061 | 0.012 | 0.013 |
| No. of variables | 326 | 176 | 235 |
| Obs./variables | 13.9 | 8.3 | 19.3 |
| Weighting scheme | Chebyshev | Chebyshev | Chebyshev |
| Weighting coefficients | 8.63, -10.4, 6.71, -1.63 | 14.8, 0.703, 11.6, 4.25 | 24.8, -34.3, 21.4, -7.9 |
| Max peak in final diff. map (eÅ ⁻³) | 0.99 | 1.83 | 1.2 |
| r.m.s. shift/e.s.d. in final 1.s. cycle | 0.073 | 0.249 | 0.007 |
| <i>R</i> | 0.031 | 0.032 | 0.030 |
| <i>R_w</i> | 0.034 | 0.031 | 0.034 |
| $R = \Sigma(F_0 - F_o)/\Sigma F_o $; $R_w = [\Sigma w(F_0 - F_o)^2/\Sigma w F_o ^2]^{1/2}$ | | | |

stored at -25°C overnight, giving green crystals. Yield: 0.25 g, 27%.

Preparation of [Zr(η -C₅Me₅)Cl₂W(PMe₃)₃H₅], 6

An orange solution of [W(PMe₃)₃H₅][K] (0.327 g, 0.7 mmol) in thf (20 ml) was slowly added to a colourless solution of [Zr(η -C₅Me₅)Cl₃·2thf] (0.350 g, 0.7 mmol) in thf at room temperature. The reaction mixture turned red during the addition. After the addition was finished, the mixture was stirred for a further 5 h, after which the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (4 × 15 ml), filtered and stored at -25°C overnight, giving deep red crystals. Yield: 0.280 g, 55%.

Preparation of [{W(PMe₃)₃H₅]₂Sm], 7

SmI₂ (0.200 g, 0.49 mmol) was dissolved in thf (50 ml) giving a blue solution. To this was added an orange solution of [W(PMe₃)₃H₅][K] (0.450 g, 0.99 mmol) in thf (50 ml). The reaction mixture became red and a white precipitate (KI) was observed. After stirring for a further 4 h, the reaction solution was filtered and the solvent removed under reduced pressure giving a green oil. Petroleum ether (100 ml) was added and the resulting green solution filtered. The filtrate was concentrated under reduced pressure and the solution was cooled to -25°C overnight. Green microcrystals precipitated in low yield and were isolated by decantation and dried *in vacuo*.

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|---|------------|------------|------------|
| (a) [$\{W(PMe_3)_3H_3\}_2Yb \cdot diglyme]$ 1 | | | |
| W(1) | 0.86467(2) | 0.27218(2) | 0.43395(2) |
| W(2) | 0.58698(2) | 0.27446(2) | 0.59678(2) |
| Yb(1) | 0.77117(3) | 0.33369(2) | 0.55354(2) |
| P(1) | 1.0167(2) | 0.2213(2) | 0.4980(2) |
| P(2) | 0.7952(2) | 0.1404(2) | 0.3906(2) |
| P(3) | 0.7926(2) | 0.3647(2) | 0.3371(2) |
| P(4) | 0.4793(2) | 0.2327(2) | 0.4854(1) |
| P(5) | 0.6012(2) | 0.3665(2) | 0.6959(1) |
| P(6) | 0.6003(2) | 0.1405(2) | 0.6534(2) |
| O(1) | 0.7290(5) | 0.4813(4) | 0.5117(4) |
| O(2) | 0.8696(5) | 0.4498(5) | 0.6295(4) |
| O(3) | 0.9007(5) | 0.2876(5) | 0.6607(4) |
| C(1) | 0.6356(9) | 0.5056(9) | 0.4715(8) |
| C(2) | 0.7840(9) | 0.5487(7) | 0.5487(7) |
| C(3) | 0.879(1) | 0.5179(8) | 0.5824(7) |
| C(4) | 0.9564(8) | 0.4215(9) | 0.6746(7) |
| C(5) | 0.9413(9) | 0.3451(9) | 0.7130(6) |
| C(6) | 0.8965(9) | 0.2079(9) | 0.6923(7) |
| C(11) | 1.0989(8) | 0.202(1) | 0.4477(8) |
| C(12) | 1.0900(8) | 0.288(1) | 0.5674(7) |
| C(13) | 1.031(1) | 0.125(1) | 0.5508(9) |
| C(21) | 0.859(1) | 0.0661(8) | 0.3544(7) |
| C(22) | 0.765(1) | 0.0701(9) | 0.4563(8) |
| C(23) | 0.684(1) | 0.1352(9) | 0.3219(8) |
| C(31) | 0.6652(8) | 0.3666(9) | 0.2948(7) |
| C(32) | 0.808(1) | 0.4754(8) | 0.3559(8) |
| C(33) | 0.835(1) | 0.362(1) | 0.2594(7) |
| C(41) | 0.472(1) | 0.299(1) | 0.4094(6) |
| C(42) | 0.492(1) | 0.1356(8) | 0.4433(7) |
| C(43) | 0.3555(8) | 0.230(1) | 0.4804(7) |
| C(51) | 0.624(1) | 0.4752(7) | 0.6807(7) |
| C(52) | 0.4995(9) | 0.380(1) | 0.7272(7) |
| C(53) | 0.6915(9) | 0.3518(9) | 0.7806(6) |
| C(61) | 0.6754(9) | 0.0630(7) | 0.6291(8) |
| C(62) | 0.4944(9) | 0.0767(8) | 0.6401(7) |
| C(63) | 0.646(1) | 0.1315(9) | 0.7507(6) |

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--|------------|------------|-------------|
| (b) [$\{Nb(\eta-C_3H_5)_2H_2\}_2Yb \cdot diglyme]$ 2 | | | |
| Yb(1) | 0.6250 | 0.1250 | 0.291847(9) |
| Nb(1) | 0.42128(4) | 0.09323(2) | 0.24708(1) |
| O(1) | 0.636(1) | 0.1298(7) | 0.3654(3) |
| O(2) | 0.5755(4) | 0.2068(2) | 0.3248(1) |
| C(1) | 0.3141(9) | 0.0693(4) | 0.2969(3) |
| C(2) | 0.3716(7) | 0.1077(4) | 0.3141(2) |
| C(3) | 0.3532(7) | 0.1522(4) | 0.2950(3) |
| C(4) | 0.2899(7) | 0.1439(4) | 0.2649(3) |
| C(5) | 0.2644(6) | 0.0922(5) | 0.2660(3) |
| C(6) | 0.4364(8) | 0.0215(3) | 0.2074(2) |
| C(7) | 0.3650(6) | 0.0519(3) | 0.1920(2) |
| C(8) | 0.4029(8) | 0.0956(4) | 0.1768(2) |
| C(9) | 0.4959(9) | 0.0952(4) | 0.1821(3) |
| C(10) | 0.5222(8) | 0.0506(5) | 0.2006(3) |
| C(11) | 0.5663(8) | 0.2518(3) | 0.3022(3) |
| C(120) | 0.553(1) | 0.2073(8) | 0.3655(2) |
| C(121) | 0.611(2) | 0.2125(6) | 0.3636(3) |

Table 4—continued.

| C(130) | 0.594(1) | 0.1683(6) | 0.3896(6) |
|---|------------|------------|------------|
| C(131) | 0.612(1) | 0.1681(8) | 0.3851(6) |
| H(1) | 0.503(6) | 0.145(3) | 0.247(2) |
| H(2) | 0.504(5) | 0.067(3) | 0.279(2) |
| (c) [$Zr(\eta-C_5Me_5)Cl_2W(PMe_3)_3H_3]$ 6 | | | |
| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
| W(1) | 0.71028(2) | 0.31983(1) | 0.31170(1) |
| Zr(1) | 0.75892(4) | 0.16930(3) | 0.1613(3) |
| Cl(1) | 0.8532(2) | −0.0087(1) | 0.2768(1) |
| Cl(2) | 0.9610(2) | 0.2331(2) | 0.0540(1) |
| P(1) | 0.4996(1) | 0.2960(1) | 0.4228(1) |
| P(2) | 0.8493(1) | 0.2351(1) | 0.46987(9) |
| P(3) | 0.8462(1) | 0.4753(1) | 0.2209(1) |
| C(1) | 0.5312(6) | 0.1834(5) | 0.0840(5) |
| C(2) | 0.5678(6) | 0.0668(5) | 0.1225(4) |
| C(3) | 0.6758(7) | 0.0379(6) | 0.0550(6) |
| C(4) | 0.7039(7) | 0.1384(8) | −0.0247(5) |
| C(5) | 0.6181(7) | 0.2259(6) | −0.0038(5) |
| C(6) | 0.4101(8) | 0.2460(8) | 0.1236(8) |
| C(7) | 0.4936(9) | −0.0133(8) | 0.2147(7) |
| C(8) | 0.736(1) | −0.0803(9) | 0.063(1) |
| C(9) | 0.806(1) | 0.143(2) | −0.1193(8) |
| C(10) | 0.610(1) | 0.3466(9) | −0.0752(9) |
| C(11) | 0.4314(6) | 0.1564(5) | 0.4552(6) |
| C(12) | 0.3532(6) | 0.3882(6) | 0.3700(6) |
| C(13) | 0.4940(7) | 0.3205(6) | 0.5609(5) |
| C(14) | 0.7966(6) | 0.1074(5) | 0.5684(5) |
| C(15) | 1.0184(6) | 0.1818(6) | 0.4353(5) |
| C(16) | 0.8871(8) | 0.3211(6) | 0.5613(6) |
| C(17) | 0.8149(8) | 0.6062(5) | 0.2643(7) |
| C(18) | 1.0284(6) | 0.4578(6) | 0.2216(6) |
| C(19) | 0.8222(6) | 0.5260(5) | 0.0732(5) |

Crystal structure determinations

The crystal data and experimental details are given in Table 3. Atomic parameters are given in Table 4 and selected interatomic distances and interbond angles in Table 1. Data were collected on an Enraf–Nonius CAD4 diffractometer. An empirical absorption correction based on azimuthal scan data was applied and the data were corrected for Lp effects. Systematically absent reflections were rejected and equivalent reflections were merged. The heavy-atom positions were determined from the SIR88 program.⁵⁷ Subsequent difference syntheses revealed the positions of all other non-hydrogen atoms. For all structures organic hydrogen atoms were placed in estimated positions (C—H = 0.96 Å) with isotropic thermal parameters equal to 1.3 times that of U_{equiv} of the attached carbon atom. For **2** electron density located at reasonable distances from Nb and Yb was modelled as bridging H atoms. The non-hydro-

gen atoms were refined in anisotropic approximation using a full-matrix least-squares procedure with the hydrogen atoms "riding" on their supporting carbon atoms, with the exception of the Yb—H—Nb hydrogens [i.e. H(1) and H(2)] the fractional atomic coordinates and isotropic temperature factors of which were refined. A weighting scheme was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction in the final stages of refinement.

The molecule **2** lies across a crystallographic two-fold axis and two conformations of the diglyme ligand were modelled as fractional disorder. Crystallographic calculations were carried out using the CRYSTALS⁵⁸ program on a MicroVax 3800 computer in the Chemical Crystallography Laboratory, Oxford, U.K.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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