

**New Lanthanide–Hydrogen–Transition Metal Compounds:  $[\{(PMe_3)_3WH_5\}_2Yb \cdot L_3]$  and  $[\{(\eta-C_5H_5)_2NbH_2\}_2Yb \cdot L_3]$  where  $L_3 = (MeOCH_2CH_2)_2O$** **Malcolm L. H. Green,\* Andrew K. Hughes, Despo M. Michaelidou and Philip Mountford***Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*

The new lanthanide–hydrogen–transition metal compounds  $[\{(PMe_3)_3WH_5\}_2Yb \cdot L_3]$  and  $[\{(\eta-C_5H_5)_2NbH_2\}_2Yb \cdot L_3]$ , where  $L_3 = (MeOCH_2CH_2)_2O$ , are prepared and their crystal structures determined.

Compounds containing transition metal–hydrogen–alkali metal bonds have been described for a variety of different d-block transition metals including M–H–Li,<sup>1</sup> M–H–Na and M–H–K<sup>2</sup> and, in particular, for the potassium–hydrogen–tungsten compound  $[K\{(PMe_3)_3WH_5\}]$ .<sup>2</sup> Here, we report the first examples of analogous lanthanide(II)–hydrogen–transition metal compounds.

Treatment of pure, anhydrous,  $YbI_2$  with 2 equiv. of

$[K\{(PMe_3)_3WH_5\}]$  in 1,2-dimethoxyethane (dme) containing an adventitious trace of diglyme  $[(MeOCH_2CH_2)_2O]$  at room temp. for 12 h gave a green solution from which orange crystals of **1** were obtained in 32% yield on cooling to  $-25^\circ C$ . These were shown to be the trinuclear compound  $[\{(PMe_3)_3WH_5\}_2Yb \cdot diglyme]$  **1**. The presence of diglyme in the dme was shown by <sup>1</sup>H NMR spectroscopy.

The crystal structure of **1** has been determined by X-ray

diffraction† and the molecular structure is shown in Fig. 1 together with selected data. The structure shows a central Yb atom with two adjacent  $W(PMe_3)_3$  units (average  $W-Yb = 3.24$  Å) (Fig. 1). The metal hydride groups, which are detected in the  $^1H$  NMR spectrum, could not be located.

The NMR data for **1**‡ are consistent with the molecular structure and show that the compound is diamagnetic. Specifically, the  $^{31}P\{^1H\}$  NMR spectrum shows coupling to both the  $^{183}W$  (spin 1/2, abundance 14.41%) and  $^{171}Yb$  nuclei (spin 1/2, abundance 14.31%). The  $Yb-P$  coupling constant ( $J$  73 Hz) was determined from the  $^{171}Yb\{-^1H\}$  NMR spectrum (Fig. 3), and is the first to be reported. The room-temperature  $^1H$  NMR spectrum shows a broad high field band at  $\delta -3.6$  assignable to tungsten-hydrogen ligands. Cooling the sample to 253 K causes this band to resolve into two separate quartets at  $\delta -3.63$  and  $-4.75$  integrating in a 3:2 ratio, respectively. Phosphorus decoupling collapses

† Crystal data for **1**:  $C_{24}H_{78}O_3P_6W_2Yb$ ,  $M = 1141.5$ , crystal size = ca.  $0.40 \times 0.50 \times 0.80$  mm, monoclinic, space group  $P2_1/n$ ,  $a = 14.976(7)$ ,  $b = 16.117(7)$ ,  $c = 19.648(1)$  Å,  $\beta = 107.09(3)^\circ$ ,  $V = 4532.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.67$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 74.44$  cm<sup>-1</sup>,  $F(000) = 2216$ , scan type  $\omega-2\theta$ ,  $T = 293$  K,  $2 < 2\theta < 48^\circ$ , total unique data 7081, no. of observations [ $I > 3\sigma(I)$ ] 4524, observations/variables 8.30,  $R_{merge} = 0.061$ ,  $R = 0.031$ ,  $R_w = 0.034$  (Chebyshev parameters 8.63, -10.4, 6.71, -1.63), maximum peak in final Fourier difference synthesis  $0.99$  e Å<sup>-3</sup>.

For **2**:  $C_{26}H_{38}Nb_2O_3Yb$ ,  $M = 757.44$ , crystal size = ca.  $0.20 \times 0.20 \times 0.40$  mm, orthorhombic, space group  $Fddd$ ,  $a = 14.017(4)$ ,  $b = 26.278(16)$ ,  $c = 33.404(16)$  Å,  $V = 12306.3$  Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 1.635$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 37.28$  cm<sup>-1</sup>,  $F(000) = 5920$ , scan type  $\omega$ ,  $T = 293$  K,  $2 < 2\theta < 44^\circ$ , total unique data 2566, no. of observations [ $I > 3\sigma(I)$ ] 1462, observations/variables 8.30,  $R_{merge} = 0.012$ ,  $R = 0.032$ ,  $R_w = 0.031$ , (Chebyshev parameters 14.8, 0.703, 11.6, 4.25), maximum peak in final Fourier difference synthesis  $1.83$  e Å<sup>-3</sup> [in a position remote from the molecule at (0.125, 0.125, 0.125)].

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 programs<sup>11</sup> Subsequent difference syntheses revealed the positions of all other non-hydrogen atoms. For both 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 the  $U_{equiv}$  of the attached carbon atom. For compound **2** electron density located at reasonable distances from Yb and Nb was modelled as bridging H atoms. The non-hydrogen atoms were refined 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 molecules of **2** lie across a crystallographic twofold axis and two conformations of the diglyme ligand were modelled as fractional disorder. Crystallographic calculations were carried out using the CRYSTALS<sup>12</sup> program on a MicroVax 3800 computer in the Chemical Crystallography Laboratory, Oxford, UK.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Selected spectroscopic data: NMR data recorded at room temp. at 300 MHz ( $^1H$ ), 121.5 MHz ( $^{31}P\{^1H\}$ ), 75.5 MHz ( $^{13}C\{^1H\}$ ) or 52.5 MHz ( $^{171}Yb\{^1H\}$ ) and given as  $\delta$  relative to  $SiMe_4$ , ( $^1H$  and  $^{13}C$ ),  $(MeO)_3PO$  ( $^{31}P$ ) or  $(C_5Me_5)_2Yb(thf)$ , ( $^{171}Yb$ ), relative intensity, multiplicity, coupling constant and assignment. The solvent used was [ $^2H_8$ ]tetrahydrofuran.

NMR data for **1**:  $^1H$  NMR:  $\delta$  1.58 (27H, d,  $PCl_3$ ,  $J_{P-H} 5$  Hz),  $-3.6$  (5H, br s, W-H).  $^{31}P\{^1H\}$  NMR:  $-20.0$  (s,  $J_{P-W} 175$  Hz,  $J_{P-Yb} 72$  Hz).  $^{31}P\{Me\}$  NMR:  $-20.0$  (sextet  $J_{P-H} 26$  Hz).  $^{171}Yb\{^1H\}$  NMR: 1462.3 (septet,  $J_{Yb-P} 73$  Hz).

NMR data for **2**:  $^1H$  NMR:  $\delta$  4.41 (10H, s,  $C_5H_5$ ),  $-9.3$  (2H, br s, Nb-H).  $^{13}C$  NMR: 79.5 (s,  $C_5H_5$ ).

these quartets to singlets. The NMR data for **1** closely resemble those of solutions of  $[K(18-crown-6)]\{-[(PMe_3)_3WH_5]\}$ . A neutron structure determination of  $[K(18-crown-6)]\{[(PMe_3)_3WH_5]\}$  showed the presence of two terminal tungsten-hydrogens and the presence of three bridging hydrogens in a  $W-(\mu-H)_3-K$  fragment.<sup>2</sup> Therefore, we propose that there are also three hydrogens bridging from each tungsten to the ytterbium in **1**.

In a second study  $[Nb(\eta-C_5H_5)_2H_3]$  in tetrahydrofuran was treated with potassium hydride for 3 days at room temp. giving an orange precipitate, which was presumed to be  $[K\{Nb(\eta-C_5H_5)_2H_2\}]$  by analogy with the preparation of  $[K(18-crown-6)]\{[Mo(\eta-C_5H_5)_2H]\}$ .<sup>2</sup> The orange potassium-niobium compound was treated with a suspension of ytterbium diiodide in 1,2-dimethoxyethane which contained a trace of diglyme (NMR) at room temp. for 12 h. After filtering and cooling to

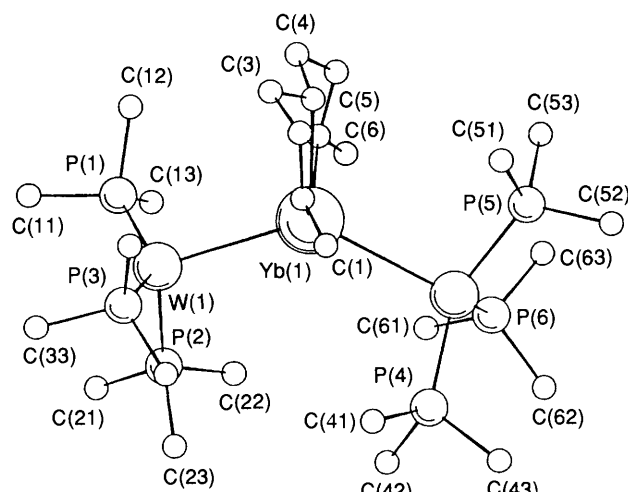


Fig. 1 Molecular structure of  $\{[(PMe_3)_3WH_5]_2Yb\text{-diglyme}\}$  **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) as follows:  $W(1)\cdots Yb(1)$  3.2253(5),  $W(2)\cdots Yb(1)$  3.2595(5),  $Yb(1)-O(1)$  2.536(7),  $Yb(1)-O(2)$  2.571(7),  $Yb(1)-O(3)$  2.2519(7),  $W(1)-Yb(1)-W(2)$  133.02(2).

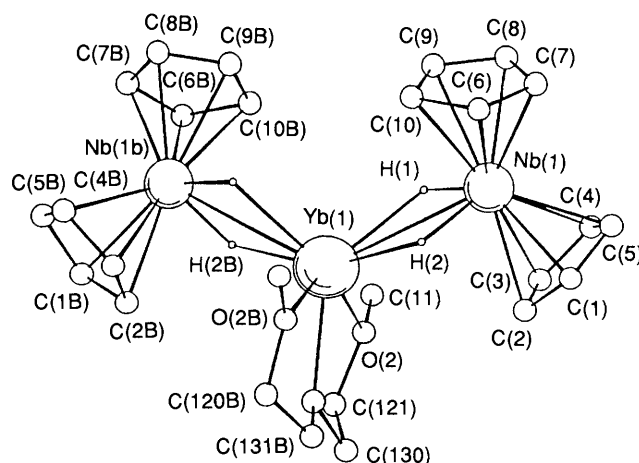


Fig. 2 Molecular structure of  $\{[(\eta-C_5H_5)_2NbH_2]_2Yb\text{-diglyme}\}$  **2**. The molecule lies across a crystallographic twofold axis which relates atoms labelled 'B' to their counterparts. Hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) as follows:  $Yb(1)\cdots Nb(1)$  3.3305(5),  $Yb(1)-H(1)$  2.32(8),  $Yb(1)-H(2)$  2.33(7),  $Nb(1)-H(1)$  1.77(7),  $Nb(1)-H(2)$  1.71(7),  $Yb(1)-O(1)$  2.463(9),  $Yb(1)-O(2)$  2.512(4),  $Nb(1)-C_{Pcent(1)}$  2.04,  $Nb(1)-C_{Pcent(2)}$  2.04,  $Nb(1)-Yb(1)-Nb(1B)$  126.64(2),  $H(1)-Nb(1)-H(2)$  82.6(35),  $H(1)-Yb(1)-H(2)$  105.7(25),  $Yb(1)-H(1)-Nb(1)$  108.1(33),  $Yb(1)-H(2)-Nb(1)$  110.0(34),  $C_{Pcent(1)}-Nb(1)-C_{Pcent(2)}$  144.0 where  $C_{Pcent(1)}$  and  $C_{Pcent(2)}$  refer to the computed ring centroids for C(1) to C(5) and C(6) to C(10), respectively.

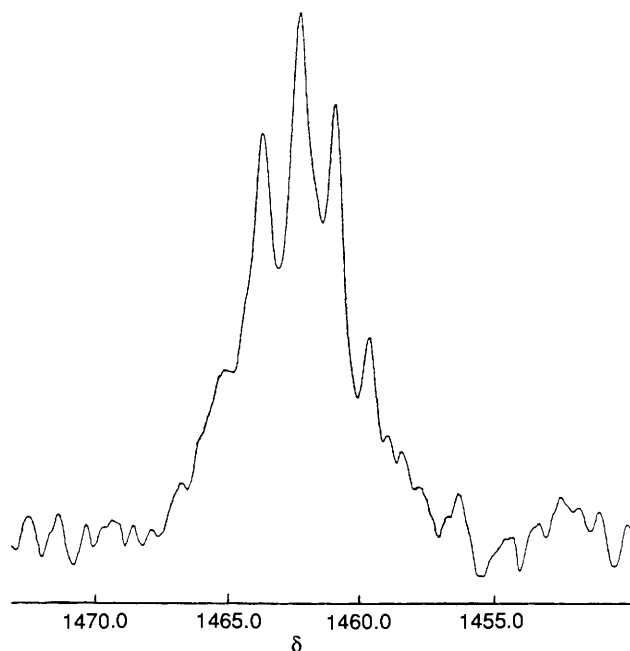


Fig. 3  $^{171}\text{Yb}\{^1\text{H}\}$  NMR spectrum for **1**, at 52.525 MHz at room temp., showing coupling to the six equivalent  $^{31}\text{P}$  nuclei

$-25^\circ\text{C}$ , red crystals separated and these were identified as  $[\{(\eta\text{-C}_5\text{H}_5)_2\text{NbH}_2\}_2\text{Yb}\text{-diglyme}]$  **2**. The yield was ca. 30%.

The crystal structure of **2** has been determined<sup>†</sup> and the molecular structure is shown in Fig. 2, together with selected data. In this case the hydrogen atoms could be located. The average Nb–H distance of 1.74(6) Å is close to those found in other niobium hydrides (1.69–1.70 Å).<sup>3–5</sup> The Yb–H distances of 2.32–2.33 Å are comparable with those of 2.2(1) and 2.4(1) Å in  $[\text{Yb}(\text{MeCN})_6(\mu\text{-H})_2\text{B}_{10}\text{H}_{12}]$ .<sup>6</sup> Shorter Yb–H distances of 1.64 and 1.67 Å were calculated for the compound  $[\text{Ph}_3\text{Ge}(\mu\text{-H})\text{Yb}(\text{thf})_4(\mu\text{-H})\text{GePh}_3]$ .<sup>7</sup>

The  $^1\text{H}$  NMR spectrum of **2** at room temperature shows a band assignable to the  $\eta\text{-C}_5\text{H}_5$ -hydrogens and a broad band at  $\delta = 9.3$  integrating as two H atoms per Nb unit, which may be assigned to the Nb-hydrogens. Lowering the temperature to 250 K causes the latter band to sharpen and satellite peaks to appear. These satellites may be assigned to coupling of the Nb-hydrogens with the  $^{171}\text{Yb}$  nucleus,  $J(^{171}\text{Yb}\text{-H})$  170 Hz. It has not proved possible to observe the  $^{171}\text{Yb}\{^1\text{H}\}$  NMR spectrum of **2**.

The average Yb–W distance of 3.24 Å in **1** and the Nb–Yb

distance of 3.33 Å in **2** are both significantly longer than the sum of the atomic radii<sup>8</sup> of Yb (1.75 Å) and W (1.35 Å) or Nb (1.45 Å), respectively. Such a comparison is tenuous since there is no accepted covalent radius for ytterbium. Nonetheless, it seems unlikely that there is direct covalent W–Yb (or Nb–Yb) bonding. It is more probable that, as postulated for compounds such as  $[\text{K}(18\text{-crown-6})][(\text{PMe}_3)_3\text{WH}_5]^2$  there is a degree of covalency in the W–( $\mu\text{-H}$ )<sub>3</sub>–Yb systems in **1** and similarly in the Nb–( $\mu\text{-H}$ )<sub>2</sub>–Yb units in **2**. In particular, the observation of  $^{31}\text{P}\text{-}^{171}\text{Yb}$  coupling in **1** strongly suggests the presence of covalency between the two nuclei.

In conclusion, the compounds **1** and **2** are the first examples of molecular compounds containing a transition metal and a lanthanide(II) metal within bonding distance and are brought together through novel polyhydride ligand environments. Previously described compounds broadly related to **1** and **2** are  $(\text{C}_5\text{H}_5)_2\text{Y}(\text{thf})\text{Re}_2\text{H}_7(\text{PMe}_2\text{Ph})_4$  and  $(\text{C}_5\text{H}_5)_2\text{LuRe}_2\text{H}_7(\text{PMe}_2\text{Ph})_4$ <sup>9</sup> as well as the yttrium compound  $[\{(\text{C}_5\text{H}_4\text{Me})_2\text{YH}\}_2\{(\text{C}_5\text{H}_4\text{Me})_2\text{ZrH}\}\text{H}]$ . The latter may have Y–H–Zr bonds.<sup>10</sup>

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