Lanthanide–Tungsten Heterobimetallic Complexes *via* σ-Bond Metathesis

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Reactions of [{Ln(C_5Me_5)$_2$H}$_2$] (Ln = Y, Sm) with [W(C_5H_5)$_2$$H_2$] afford the σ-bond metathesis products [(C_5Me_5)$_2$Ln(μ-η^1, η^5-C_5H_4)(μ-H)$_2$W(C_5H_5)], *via* dehydrocoupling between the Ln–H bond and the C–H (but not the weaker W–H) bond of [W(C_5H_5)$_2$$H_2$].

We have recently described efficient σ-bond metathesis reactions that introduce silyl ligands at an early transition metal centre [eqn. (1), R = H, silyl].[1] Related procedures for

$$\text{M-R} + \text{H-SiR}'_3 \rightarrow \text{M-SiR}'_3 + \text{H-R} \qquad (1)$$

preparing germyl and stannyl complexes have also been described.[2] Such reactions are intriguing in that they represent a rare synthetic pathway to bonds between electropositive elements. We have recently extended this chemistry to the synthesis of lanthanide silyls, using σ-bond metathesis reactions of hydrosilanes with both [Ln(C_5Me_5)$_2$CH($SiMe_3$)$_2$] and [{Ln(C_5Me_5)$_2$H}$_2$] complexes.[3] However, we noted that reactions of silanes with the latter hydride species are cleaner and more rapid. For this reason we have begun to explore dehydrocoupling reactions of [{Ln(C_5Me_5)$_2$H}$_2$] complexes with various hydrogen-containing compounds, in search of general routes to new lanthanide–element bonds. Assuming that the best substrates for such reactions would possess relatively weak bonds to hydrogen, we initially focused on a transition-metal hydride, [W(C_5H_5)$_2$$H_2$]. Alvarez *et al.* have previously reported σ-bond metathesis reactions of lanthanide alkyls with transition metal hydrides, which form mixed-metal hydride complexes.[4]

Reaction of [W(C_5H_5)$_2$$H_2$][5] with [{Sm($C_5Me_5$)$_2$H}$_2$][6] in toluene at room temperature (2 h) afforded a red complex (86% yield) which analysed correctly for a dehydrocoupled product. However, the ^{1}H NMR spectrum of this complex revealed a peak for only one intact C_5H_5 ligand [per Sm(C_5Me_5)$_2$ group], paramagnetically shifted to δ 2.48.† The second C_5H_5 ligand gave rise to singlets at δ 6.48 and 12.51, which both integrated as two hydrogens. Subsequent characterization of this product by X-ray crystallography revealed the structure given in Fig. 1. Thus, the reaction proceeds as shown in Scheme 1 to give the metallated cyclopentadienyl derivative [(C_5Me_5)$_2$Sm(μ-η^1,η^5-C_5H_4)(μ-H)$_2$W(C_5H_5)] (**1**). Related activations of aromatic C–H bonds by [{Ln(C_5Me_5)$_2$H}$_2$] compounds (Ln = a lanthanide or group 3 metal) have been described.[7]

The molecular structure of **1**‡ consists of two metallocene fragments linked by a Sm–C(C_5H_4) bond of 2.52(2) Å. This distance is remarkably similar to the Sm–C(Ph) distance of 2.511(8) Å found in [Sm(C_5Me_5)$_2$Ph(thf)][8], and (as expected) significantly shorter than the comparable Sm–C(C_5H_5) distances in [(C_5Me_5)$_2$Sm(μ-η^5,η^2-C_5H_5)Sm(C_5Me_5)$_2$] [av. 2.800(4) Å].[9] The Sm–W distance of 3.402(1) Å is greater than the sum of the atomic radii for Sm (1.85 Å) and W (1.35 Å),[10] suggesting the absence of a direct Sm–W bond. In addition, the overall conformation of the molecule, with close approach of the two metal atoms, implied the presence of bridging hydride ligands. The C_5H_5(centroid)–C_5H_5(centroid) and C_5Me_5(centroid)–C_5Me_5(centroid) vectors are nearly perpendicular (93.4 °).

Hydride ligands in compound **1** could not be located in the X-ray structure, and were not identified by ^{1}H NMR spectroscopy, even at −80 °C. To characterize the nature of metal–hydrogen bonding in this system more definitively, the diamagnetic and isostructural (by IR spectroscopy) yttrium analogue [(C_5Me_5)$_2$Y(μ-η^1,η^5-C_5H_4)(μ-H)$_2$W(C_5H_5)] **2** was prepared as yellow crystals in 77% yield. For this compound, the hydride ligands (two by integration) appear as a well-defined doublet at δ −14.25, with satellite peaks due to ^{183}W–^{1}H coupling (Fig. 2). The observed ^{183}W–^{1}H coupling constant (*J* 78 Hz) is even greater than that found in [W(C_5H_5)$_2$$H_2$] (*J* 73 Hz). This effect was also observed for the related compound [(Et_3P)$_2$(H)Ir(μ-η^1,η^5-C_5H_4)(μ-H)$_2$W(C_5H_5)], which has J_{WH} coupling constants of 92.4 and 95.2 Hz.[11] In

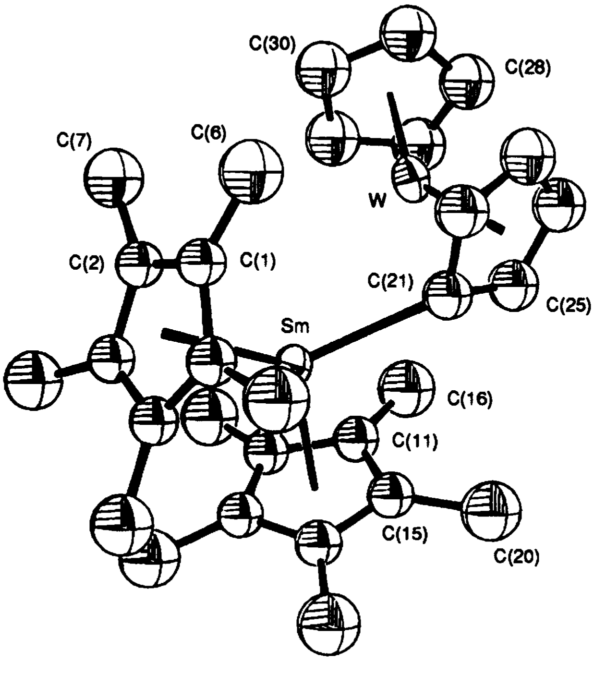
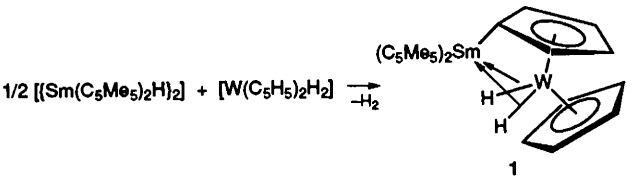
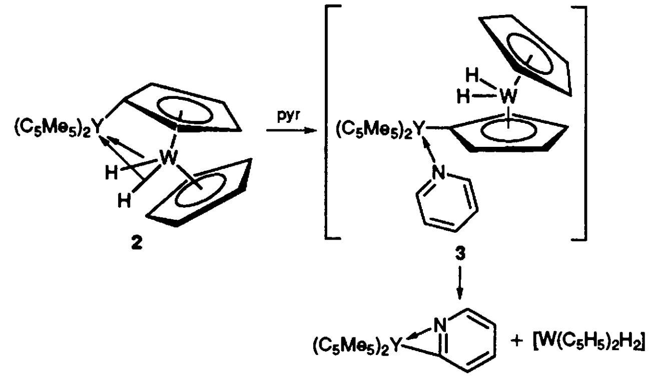


Fig. 1 ORTEP view of compound 1



Scheme 1



Scheme 2

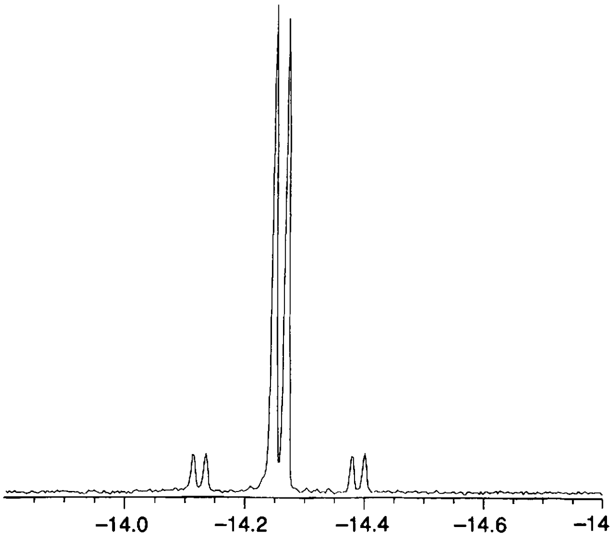


Fig. 2 ^1H NMR signal for the hydride ligands of **2**

contrast, the ^{89}Y–^1H coupling constant (J 6.3 Hz) is low when compared to values reported for normal covalent Y–H bonds {*e.g.* 81.7 Hz in [$Y(C_5Me_5)_2H]\cdot$thf}.[12] Comparable J_{YH} coupling constants have been observed for the mixed-metal hydrides [$(C_5H_5)_2Y$(thf]$H_6Re(PPh_3)_2$] (J 8.3 Hz) and [$(C_5H_5)_2Y$(thf)$H_4Re(PMe_2Ph)_3$] (J 14.7 Hz).[4] The observed coupling constants characterize the bridging hydride ligands as interacting much more strongly with tungsten, as indicated by the resonance structure in Scheme 1. Similar bonding interactions appear to exist in the Y–Re complexes mentioned above,[4] and in the recently reported compounds [$Yb\{H_5W(PMe_3)_3\}_2$(diglyme)] and [$Yb\{H_2Nb(C_5H_5)\}_2$- (diglyme)].[13]

Consistent with depiction of the hydride bridge-bonding as involving coordination of W–H covalent bonds to the lanthanide centre, experiments show that the dative interactions are displaced by Lewis bases. Compound **2** reacts rapidly ($\leq$10 min) with pyridine (15 equiv.) in [$^2H_6$]benzene solution to produce a new complex **3** which has a hydride resonance in the ^1H NMR spectrum (δ −11.90, J_{WH} 73 Hz) that does not exhibit ^{89}Y–^1H coupling. It proved impossible to isolate **3** because of its decomposition ($\tau_{1/2}$ *ca.* 2 h) to the σ-bond metathesis products [$Y(C_5Me_5)_2(\eta^2\text{-}NC_5H_4)$][11] (56%) and [$W(C_5H_5)_2H_2$] (100%), but overall the NMR data for **3**[†] support the proposed structure shown in Scheme 2.

Compound **2** reacts analogously with thf (20 equiv., $\leq$ 1 h) to produce [$W(C_5H_5)_2H_2$] (100%) and [$\{Y(C_5Me_5)_2H\}_2$] (40%). The latter product presumably arises *via* β-H elimination from an initial product of σ-bond metathesis between **2** and thf, $(C_5Me_5)_2\ Y(\overline{CHOCH_2CH_2CH_2})$.

We are currently investigating the synthetic utility of other σ-bond metathesis reactions of lanthanide-silicon and lanthanide-hydrogen bonds, and have noted that the hydrides [$\{Ln(C_5Me_5)_2H\}_2$] (Ln = Y, Sm) do not react with [$Ru(C_5Me_5)(PMe_3)_2H$] over two days at room temp.

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Footnotes

[†] Isolated compounds were characterized by microanalysis and NMR spectroscopy. Selected data: **1**: ^1H NMR (300 MHz, [$^2H_{12}$]cyclohexane): δ 1.07 (s, 30H, C_5Me_5), 2.48 (s, 5H, C_5H_5), 6.48 (s, 2H, C_5H_4), 12.51 (s, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (125.7 MHz, [$^2H_{12}$[cyclohexane): δ 18.27 (C_5Me_5), 71.10 (C_5H_5), 117.65 (C_5Me_5). IR (Nujol): ν(SmHW)/cm^{-1} = 1700 (br). **2**: ^1H NMR (300 MHz, [$^2H_6$]benzene): δ −14.24 (d, J_{YH} 6.3 Hz, J_{WH} 78 Hz, 2H, YH_2W), 2.13 (s, 30H, C_5Me_5), 4.08 (s, 5H, C_5H_5), 4.25 (s, 2H, C_5H_4), 5.57 (s, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (125.7 MHz, [$^2H_6$]benzene): δ 12.55 (C_5Me_5), 72.63 (C_5H_5), 80.58 (C_5H_4), 91.08 (C_5H_4), 118.01 (C_5Me_5). IR (Nujol): ν(YHW)/cm^{-1} = 1730 (br). **3**: ^1H NMR (300 MHz, [$^2H_6$]benzene): δ −11.90 (s, J_{WH} 73 Hz, 2H, H_2W), 1.94 (s, 30H, C_5Me_5), 3.95 (s, 2H, C_5H_4), 4.42 (s, 5H, C_5H_5), 4.61 (s, 2H, C_5H_4).

[‡] *Crystal Data* for **4**: $C_{30}H_{39}SmW$, M = 733.8, crystal size = 0.50 × 0.50 × 0.50 mm, monoclinic, space group $P2_1/c$, a = 9.928(2), b = 18.705(4), c = 15.247(3) Å, β = 104.56(3) °, V = 2741(8) Å^3, Z = 4, D_c = 1.78 g cm^{-3}, μ(Mo–Kα) = 64.30 cm^{-1}, $F(000)$ = 1420, scan type Wyckoff, T = 296 K, 3 < 2θ < 50 °, total unique data 4821, no. of observations [$(F) > 4\sigma(F)$] 2813, observations/variables 39.6, R_{merge} = 0.033, R = 0.065, R_w = 0.070. The structure was solved by heavy atom methods. Carbon-hydrogen atoms were inserted at expected positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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