Interaction of Amido- and Hydrido-derivatives of Metals and Metalloids; a General Synthesis of Compounds having Metal–Metal Bonds

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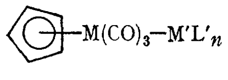
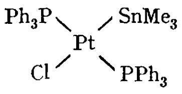
WE report a general synthesis of compounds having metal–metal bonds, as illustrated by the following equation (where L_n and L'_n represent the sum of all the ligands other than NMe_2 or H attached to the metal or metalloid M and M′):

$$L_nM\text{–}NMe_2 + H\text{–}M'L'_n \rightarrow L_nM\text{–}M'L'_n + Me_2NH$$

A selection of the compounds prepared according to this scheme is shown in (I)—(III).



(I) M=W; $M'L'_n = SnMe_3$
(II) M=Mo; $M'L'_n = TiOPr^i_3$



(III)

Compounds (I)—(III) were made from the appropriate transition-metal hydride and the amido-derivative of Sn, Ti, and Sn, respectively. They have been characterised by elemental analyses, molecular weights, and spectral data. Compounds (I) and (II) were obtained in almost quantitative yields when the reactants were refluxed in tetrahydrofuran under an atmosphere of carbon monoxide. (I) is a colourless, crystalline, air-stable solid, m.p. 120°, subliming *in vacuo*, and whose parent ion survived in the mass spectrometer. Except under a blanket of carbon monoxide, both (I) and (II) decomposed rapidly in solution with elimination of carbon monoxide. Compound (III), a yellow–brown solid, m.p. 234°, was obtained after the reactants had been refluxed for several hours in xylene. The $SnMe_3$ protons appear at τ 9·6 ($CDCl_3$) (those of Me_3SnNMe_2 at τ 9·83) and ν_{Pt-Cl} is found at 278 cm.$^{-1}$; $\rho(CH_3)_3Sn$ at 760 and 736 cm.$^{-1}$ (766 and 741 cm.$^{-1}$ in Me_3SnNMe_2). The highly acidic trifluorophosphine hydrides of cobalt and rhodium[1] reacted extremely easily with amido-metal derivatives at room temperature. The reaction of Me_3SnNMe_2 with $(PF_3)_4RhH$ in tetrahydrofuran liberated amine. An Rh–Sn compound was not isolated, presumably because the high value for the heat of formation of crystalline Me_3SnF caused the latter to be formed (99·2%), together with an orange trifluorophosphinerhodium compound. Interaction of $(F_3P)_4CoH$ and Me_3SiNMe_2 was highly exothermal, with evolution of dimethylamine. The liquid residue is believed to be $(F_3P)_4Co\text{–}SiMe_3$, but its characterisation is still incomplete.

The interaction of amido- and hydrido-derivatives of metals and metalloids as a general method for preparing metal–metal bonds offers the following useful features:[2] (i) reaction conditions are mild, (ii) yields are essentially quantitative, (iii) the only other product is gaseous and therefore easily removed, and (iv) alternative methods are sometimes difficult to formulate (as in the case where the L_nM anion cannot be made). We are exploring the system further, especially to include (a) reactions of di- and tri-hydrides with mono-, bis-, and tris-amido-derivatives of metals and metalloids (there are indications that metal clusters may sometimes be formed), and (b) synthesis of heavy transition-metal amido-derivatives.

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