A New Route to Hydride, Carbonyl, and Bis-dinitrogen Complexes of Tungsten

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Summary The types of complexes mentioned in the title are prepared by sodium amalgam reduction of *trans*-$[WCl_4(PR_3)_2]$ (PR_3 = tertiary phosphine) under dihydrogen, carbon monoxide, or dinitrogen, respectively.

It is now evident that the elements which form isolable mononuclear dinitrogen complexes occupy a well-defined area of the transition-metal series in the Periodic Table. This lies about a line joining tungsten to nickel. In general the stabilities of the complexes increase towards tungsten, and bis-dinitrogen complexes are formed only by metals near the tungsten end (Ru, Os, and Mo).[1] Tungsten should therefore form the most stable bis-dinitrogen complexes, and here we describe their preparation by a method which also lends itself to the preparation of hydride and carbonyl complexes.

We find that tungsten(IV) complexes of type *trans*-$[WCl_4(PR_3)_2]$[2] (PR_3 = tertiary phosphine) are reduced in anhydrous tetrahydrofuran by 2% sodium amalgam at 20° under dinitrogen at atmospheric pressure, in the presence of an excess of the phosphine, to yield yellow to orange materials containing strong bands in the 1900—2000 cm^{-1} region of their i.r. spectra. Two have been isolated, which we formulate *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$. The former is yellow and is assigned a *cis*-configuration because it has two strong bands in its i.r. spectrum at 1931 and 1998 cm^{-1} (benzene). The latter complex is orange with only one strong band in the $\nu(N_2)$ region (1953 cm^{-1}, benzene). These complexes provide the first example where a *cis*- and a *trans*-bis-dinitrogen complex have been obtained with the same central element. The two bis-dinitrogen complexes are stable, but the solids deteriorate after a few days at room temperature in air. Other phosphines and diphosphines give materials containing 'nitrogen bands.'

When the reduction of *trans*-$[WCl_4(PMe_2Ph)_2]$[2] is run under carbon monoxide, *fac*-$[W(CO)_3(PMe_2Ph)_3]$[3] is rapidly formed even in the presence of a large excess of the phosphine; similarly were prepared *fac*-$[W(CO)_3(PMePh_2)_3]$,[4] *fac*-$[W(CO)_3(PEtPh_2)_3]$, and *trans*-$[W(CO)_4(PPh_3)_2]$.[5] Under dihydrogen, $[WH_6(PMe_2Ph)_3]$[6] is formed. Since the $[W(CO)_n(PR_3)_{6-n}]$ (n = 3 or 4) type of complex is usually obtained by multistage reactions from tungsten hexacarbonyl and the hydride has been obtained in rather poor yield by sodium borohydride reduction,[6] this method provides a more convenient route to these two types of previously known complexes, as well as a route to the new bis-dinitrogen complexes.

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