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A Convenient Route to Three-valent Bis-π-cyclopentadienyl Niobium Hydrides and Related Derivatives

By C. R. Lucas and M. L. H. Green*

(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary The preparations in good yields of the borohydride $(\pi\text{-}C_5H_5)_2NbBH_4$ and of the hydrides $(\pi\text{-}C_5H_5)_2NbH(PR_3)$, $R_3 = Ph_3$ or $PhMe_2$, are described; the latter hydrides are basic and may be protonated giving the dihydride cations $[(\pi\text{-}C_5H_5)_2NbH_2(PR_3)]^+$.

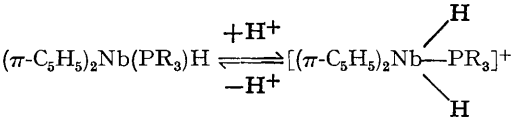
Relatively little is known of the chemistry of trivalent niobium compounds but it is clear that compounds such as $(\pi\text{-}C_5H_5)_2NbHL$, where L = a donor ligand may have interesting reactivity, for example with the activation of aromatic systems.[1,2] Here we describe a convenient synthesis of three-valent niobium derivatives of the type $(\pi\text{-}C_5H_5)_2NbLX$.

Following the method of de Leifde-Meijer[2] niobium pentachloride was treated with dry sodium cyclopentadienide suspension in benzene. The mixture was then added directly to concentrated hydrochloric acid containing an excess of bromine and, after bromide had been evaporated off, excess of stannous chloride was added to the filtered aqueous extract giving brown crystals of the dichloride $(\pi\text{-}C_5H_5)_2NbCl_2$ (I) (75%). Reduction of the dichloride (I) in tetrahydrofuran with sodium borohydride gives dark-green air-sensitive crystals of the borohydride derivative $(\pi\text{-}C_5H_5)_2NbBH_4$ (II) (85%); ν (B–H) 2450 cm^{-1}, *m/e* 238 (M^+).

Treatment of the borohydride (II) with tertiary phosphine R_3P ($R_3 = Ph_3$ or $PhMe_2$) gives the dark red hydrides $(\pi\text{-}C_5H_5)_2NbH(R_3P)$ (III) (60%) [for $R_3 = PhMe_2$; ν(M–H) 1630 cm^{-1}; τ 17·53 (d, $J_{H,P}$ 28·6 Hz); for $R_3 = Ph_3$, ν (M–H) 1625 cm^{-1}: τ 16·65 (d, $J_{H,P}$ 27·0 Hz)].

The hydride (III; $R_3 = PhMe_2$) reacts smoothly with n-butyl bromide in 1:1 molar ratio giving green crystals of the bromide $(\pi\text{-}C_5H_5)_2NbBr(PPhMe_2)$ (IV) (95%).

By analogy with the hydrides $(\pi\text{-}C_5H_5)_2MoH_2$ and $(\pi\text{-}C_5H_5)_2ReH$ the hydrides (III) would be expected to show basic behaviour. In accord with this we have found that the hydrides (III) dissolve in dilute aqueous hydrochloric acid and may be reprecipitated by addition of base. Treatment of the acidic solution of (III; $R_3 = PhMe_2$) with solutions of the anions A^- (BF_4^- or PF_6^-) precipitates the dihydride cation $[(\pi\text{-}C_5H_5)_2NbH_2(PPhMe_2)]^+ A^-$ (V), [for $A = PF_6$, ν (M–H) 1740 cm^{-1}]. The ^1H n.m.r. spectrum of (V) shows a doublet assignable to the NbH_2-hydrogens at τ 13·96 $J_{H,P}$ 31·5 Hz, showing that either there are exchange phenomena or, most likely, that (V) has the symmetrical structure shown in equation (1).



$$(\pi\text{-}C_5H_5)_2Nb(PR_3)H \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} [(\pi\text{-}C_5H_5)_2\underset{H}{\overset{H}{Nb}}\text{—}PR_3]^+ \qquad (1)$$

(III) (V)

All the above compounds have been fully characterised by analysis, and i.r. and ^1H n.m.r. spectroscopy.

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