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Preliminary communication

Pentamethylcyclopentadienyl niobium(III) nitrene complexes containing phosphine, carbonyl, olefin and acetylene ligands

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Abstract

The novel d^2 niobium nitrene complex $(\eta\text{-}C_5Me_5)Nb(NAr)(PMe_3)_2$ ($Ar = 2,6\text{-}{}^iPr_2C_6H_3$) (**1**) is accessible *via* magnesium reduction of $(\eta\text{-}C_5Me_5)Nb(NAr)Cl_2$ in the presence of PMe_3. Compound **1** reacts with carbon monoxide, ethylene and diphenylacetylene to give adducts of the type $(\eta\text{-}C_5Me_5)Nb(NAr)(PMe_3)(L)$ ($L = CO$, C_2H_4, $PhC{\equiv}CPh$) and is oxidised by dihydrogen to $(\eta\text{-}C_5Me_5)Nb(NAr)(PMe_3)(H)_2$.

We report the synthesis and characterisation of a series of pentamethylcyclopentadienylniobium(III) nitrene (or imido) complexes containing π-acid ligands which are not commonly observed in combination with the π-basic nitrene group. These complexes have been prepared *via* a novel bis-phosphine derivative **1** which is obtained in 83% yield upon magnesium reduction of $Cp^*Nb(NAr)Cl_2$ ($Cp^* = \eta\text{-}C_5Me_5$) [1] in the presence of trimethylphosphine (eq. 1).

$$(\eta\text{-}C_5Me_5)Nb(NAr)Cl_2 \xrightarrow[2PMe_3]{Mg,\ THF} \underset{(\mathbf{1})}{(\eta\text{-}C_5Me_5)Nb(NAr)(PMe_3)_2} \qquad (1)$$

The derivative chemistry developed from **1** is summarised in Scheme 1. In all cases the reactions are quantitative by NMR, and the products * may be isolated in very good yields.

The carbonyl and ethylene complexes **2** and **3** are obtained by treatment of **1** with an excess of carbon monoxide and ethylene gas respectively in toluene; the reaction with CO(g) proceeds notably faster. Both compounds may be crystallised from toluene, **2** in the form of red prisms, **3** as a yellow microcrystalline solid. The

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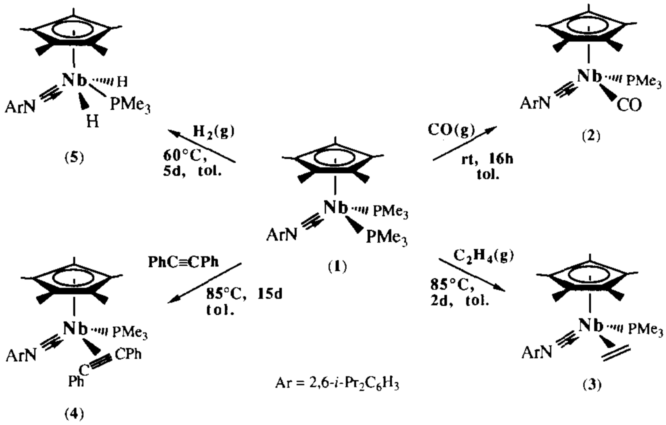

Scheme 1.

CO stretch for **2**, at 1875 cm^{-1}, and the ^{13}C NMR shifts for the niobium-bonded ethylene carbons (δ 33.0 and 37.6 ppm) are consistent with considerable back-donation from the niobium(III) centres of **2** and **3**. We were unable to determine the olefinic C–H coupling constants due to ^{93}Nb quadrupolar broadening of the resonances, although coupling of one of the ethylene carbons to the ^{31}P nucleus of the PMe_3 ligand (*ca.* 12 Hz) is discernable. Diphenylacetylene (1 equiv.) reacts slowly with **1** at 85°C to give **4**; a ^{13}C NMR spectrum shows resonances for the acetylenic carbons at δ 151.7 and 159.6 ppm, in accordance with the acetylene acting as a two electron ligand [2,3]. These shifts are comparable with those found for $Cp^{\star}_2Nb(PhC{\equiv}CPh)(H)$ (δ 150.4 and 156.3 ppm [4]). Both of the acetylenic carbons of **4** also show couplings of *ca.* 24 Hz to the ^{31}P nucleus of the PMe_3 ligand.

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* Satisfactory elemental analyses have been obtained. Selected spectroscopic data for **1**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 1.20 (d, $^2J(PH)$ 5.2 Hz, 18H, PMe_3), 1.33 (d, $^3J(HH)$ 7.2 Hz, 12H, $CHMe_2$), 1.90 (s, 15H, C_5Me_5), 4.75 (sept, 2H, $^3J(HH)$ 7.2 Hz, $CHMe_2$), 7.01 (t, $^3J(HH)$ 7.6 Hz, 1H, p-C_6H_3) and 7.14 (d, 2H, $^3J(HH)$ 7.6 Hz, m-C_6H_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K): δ 19.7 (s(br), PMe_3). For **2**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 0.94 (d, $^3J(HH)$ 7.2 Hz, 12H, $CHMe_2$), 1.36 (d, $^2J(PH)$ 7.0, 9H, PMe_3), 1.87 (s, 15H, C_5Me_5), 4.14 (sept, 2H, $^3J(HH)$ 7.2 Hz, $CHMe_2$), 6.98 (m, 1H, p-C_6H_3) and 7.09 (m, 2H, m-C_6H_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K): δ 10.1 (s(br), PMe_3). IR (CsI, Nujol mull, cm^{-1}): 1875 [ν(CO)]. For **3**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ -0.05 (m, 1H, C_2H_4), 1.06 (d, $^2J(PH)$ 6.8 Hz, 9H, PMe_3), 1.09 (m, 1H, C_2H_4), 1.27 (dd, $J(HH)$ 6.8, 2.8 Hz, 12H, $CHMe_2$), 1.53 (m, 1H, C_2H_4), 1.72 (m, 1H, C_2H_4), 1.77 (s, 15H, C_5Me_5), 3.93 (sept, 2H, $^3J(HH)$ 6.8 Hz, $CHMe_2$), 6.90 (m, 1H, p-C_6H_3) and 7.02 (m, 2H, m-C_6H_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K): δ 10.7 (s(br), PMe_3). For **4**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 0.95 (d, $^2J(PH)$ 8.0 Hz, 9H, PMe_3), 1.14 (d, $^3J(HH)$ 6.8 Hz, 6H, $CHMe_2$), 1.23 (d, $^3J(HH)$ 6.8 Hz, 6H, $CHMe_2$), 1.87 (s, 15H, C_5Me_5), 4.09 (sept, 2H, $^3J(HH)$ 6.8 Hz, $CHMe_2$), 6.9–7.3 (m, 9H, aromatic H's) and 7.76 (m, 4H, o-C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K); δ 2.8 (s(br), PMe_3). IR (CsI, Nujol mull, cm^{-1}): 1695, 1670 [ν(C≡C)]. For **5**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 1.10 (d, $^2J(PH)$ 7.6 Hz, 9H, PMe_3), 1.39 (d, $^3J(HH)$ 6.8 Hz, 6H, $CHMe_2$), 2.05 (s, 15H, C_5Me_5), 3.36 (d, $^2J(PH)$ 74 Hz, 2H, Nb–H), 4.47 (sept, 2H, $^3J(HH)$ 6.8 Hz, $CHMe_2$), 6.97 (m, 1H, p-C_6H_3) and 7.09 (m, 2H, m-C_6H_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K): δ -4.5 (s(br), PMe_3). IR (CsI, Nujol mull, cm^{-1}): 1640, 1605 [ν(Nb–H)].

In its reaction with dihydrogen at 60°C, **1** affords the colourless niobium(V) dihydride (**5**). This complex is analogous to the tantalum complex $Cp^{\star}Ta(N^{t}Bu)(PMe_3)(H)_2$ described previously by Mayer *et al.* [5]. The hydride ligands are found to be equivalent by ^1H NMR, resonating as a severely broadened doublet resonance at δ 3.36 ppm [$J(PH) = 74$ Hz]. They are thus presumed to be disposed symmetrically either side of the P–Nb–N plane, as illustrated in Scheme 1.

Finally, it is worth noting the close relationship between the frontier orbitals of the [$Cp^{\star}Nb(NAr)$] fragment with those of the bent metallocene moiety [Cp_2M] [1] of the Group 4 metals, allowing a direct analogy to be drawn between **1** and the synthetically versatile titanocene complex $Cp_2Ti(PMe_3)_2$ [6], and between **2**–**4** and derivatives of the type $Cp_2M(PMe_3)(L)$ where M = Ti [6] or Zr [7] and L = CO, olefin or acetylene.

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