Low-valent Niobium Aryloxide Chemistry

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Reduction of niobium penta-aryloxides in the presence of bis(dimethylphosphino)ethane allows the isolation and study of a number of low-valent niobium aryloxides.

Over the past few years there has been considerable research interest in the chemistry of the heavier group 5 elements (Nb, Ta) in their lower oxidation states.[1—3] This effort has been prompted by the demonstrated high reactivity exhibited by low-valent niobium and tantalum complexes.[4—6] Typical synthetic strategies have involved the reduction of the high-valent halides, MCl_5, in the presence of co-ordinating ligands such as tertiary phosphines.[1—6] We report here our initial findings concerning the synthesis and reactivity of low-valent niobium aryloxides formed by reduction of the penta-aryloxides $Nb(OAr)_5$.

The yellow aryloxides $Nb(OArMe\text{-}4)_5$ and $Nb(OArMe_2\text{-}3,5)_5$ (OArMe-4 = 4-methylphenoxide, $OArMe_2$-3,5 = 3,5-dimethylphenoxide) are slowly reduced by sodium amalgam

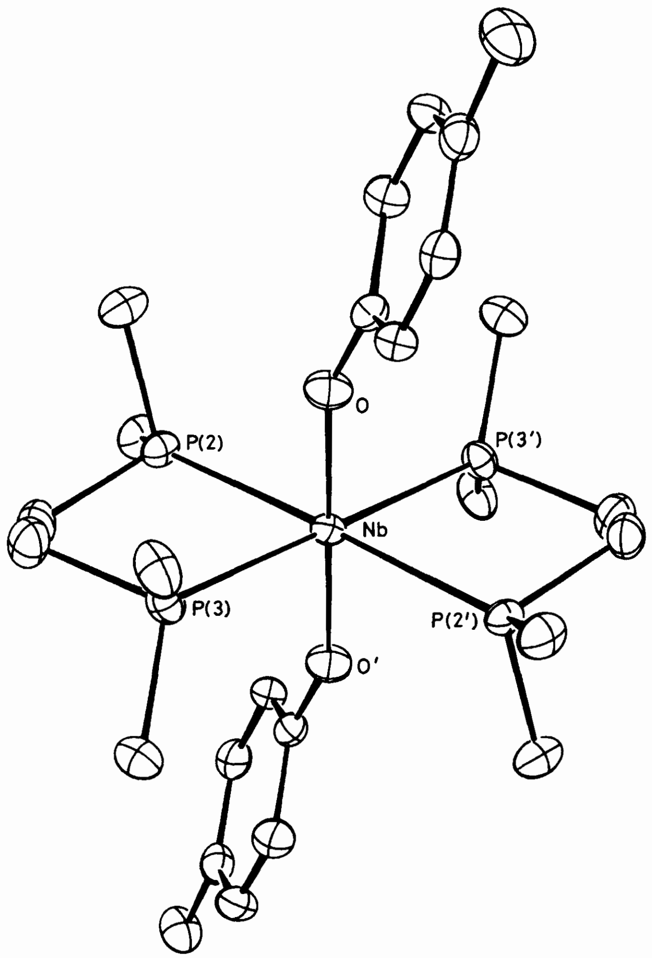

Figure 1. Molecular structure of $Nb(OArMe\text{-}4)_2(dmpe)_2$ (**1a**), molecule B. Selected distances (Å) and angles (°) are: Nb–O 2.023(3), Nb–P(2) 2.562(2), Nb–P(3) 2.555(1), P(2)–Nb–P(3) 76.58(5), Nb–O–C 156.4(3).

at 25 °C over 24 h in toluene solution containing $\geqslant$2 equiv. of bis(dimethylphosphino)ethane (dmpe) to yield solutions of the niobium(II) complexes $Nb(OArMe\text{-}4)_2(dmpe)_2$ (**1a**) and $Nb(OArMe_2\text{-}3,5)_2(dmpe)_2$ (**1b**) [equation (1)] which can be isolated in 25—30% yield as deep purple crystals from toluene. Both compounds are related to the known dichloride[4] and exhibit a room temperature e.s.r. signal

$$Nb(OAr)_5 + 3Na\text{–}Hg + 2\ dmpe \rightarrow Nb(OAr)_2(dmpe)_2 + 3NaOAr \quad (1)$$

(1)

a; OAr = 4-methylphenoxide
b; OAr = 3,5-dimethylphenoxide

consisting of ten lines due to coupling to Nb ($I = 9/2$) while at lower temperatures each of these lines begins to resolve into pentets due to coupling to four equivalent ^{31}P nuclei. These data coupled with a measured solution magnetic moment[7] of 1.05 μ_B (**1a**) and 1.10 μ_B (**1b**) are consistent with a low spin electronic configuration for these d^3-complexes. The cyclic voltammogram of (**1a**) in tetrahydrofuran (THF)–0.2 M $Bu^n{}_4NPF_6$ (TBAH) at a Pt-disc electrode using an Ag-pseudoreference electrode [$cp_2Fe^{+/0}$ (cp = cyclopentadienyl) couple at +0.47 V] shows two redox couples. The first consists of a very accessible, reversible one electron oxidation at −0.09 V while the second consists of a pseudoreversible one electron reduction at −1.81 V. Addition of $AgPF_6$ to THF solutions of (**1b**) yields black metallic silver and pale green solutions we believe to contain $[Nb(OArMe_2\text{-}3,5)_2(dmpe)_2]PF_6$, but isolation and full characterization of this complex has proved difficult. Oxidation of (**1b**) with 3,5-dimethylphenol ($HOArMe_2\text{-}3,5$) rapidly takes place according to equation (2)

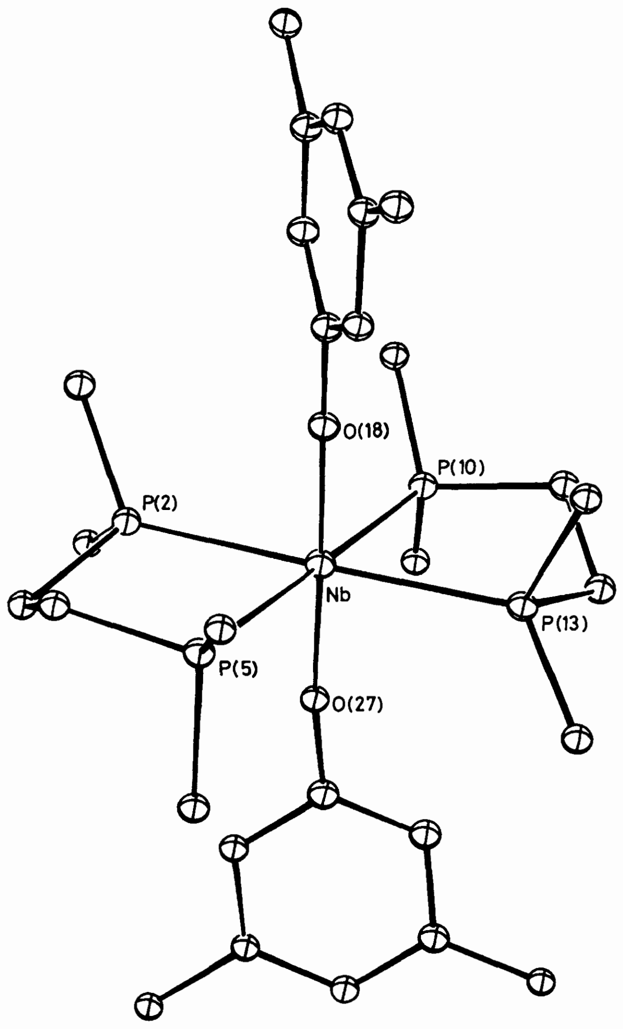

Figure 2. Molecular structure of the cation $[Nb(OArMe_2\text{-}3,5)_2(dmpe)_2]^+$ in complex (**2**). Selected distances (Å) and angles (°) are: Nb–O(18) 1.917(2), Nb–O(27) 1.937(2), Nb–P(2) 2.563(3), Nb–P(5) 2.591(3), Nb–P(10) 2.577(3), Nb–P(13) 2.589(3), P(2)–Nb–P(5) 77.95(8), P(10)–Nb–P(13) 77.61(8), Nb–O(18)–C 176.83(6), Nb–O(27)–C 168.54(6).

$$Nb(OArMe_2\text{-}3,5)_2(dmpe)_2 + 2HOArMe_2\text{-}3,5 \rightarrow \text{‘}Nb(OArMe_2\text{-}3,5)_4(dmpe)\text{’} + H_2 + dmpe \quad (2)$$

(2)

to give a green crystalline material (**2**) of stoicheiometry ‘$Nb(OArMe_2\text{-}3,5)_4(dmpe)$.’ However, this apparently d^1-compound is e.s.r. silent and gives sharp ^1H n.m.r.

Table 1. Comparison of Nb–O and Nb–P distances (in Å) for low-valent niobium aryloxides.

Complex	Nb–O/Å	Nb–P/Å
$Nb(OArMe_2\text{-}3,5)(CO)_2(dmpe)_2$ (**3**)	2.181(4)	2.572(2)—2.608(2)
$Nb(OArMe\text{-}4)_2(dmpe)_2$ (**1a**)	2.023(3)	2.539(2)—2.562(2)
$Nb(OArMe_2\text{-}3,5)_2(dmpe)_2^+$ (**2**)	1.917(2), 1.937(2)	2.563(3)—2.591(3)

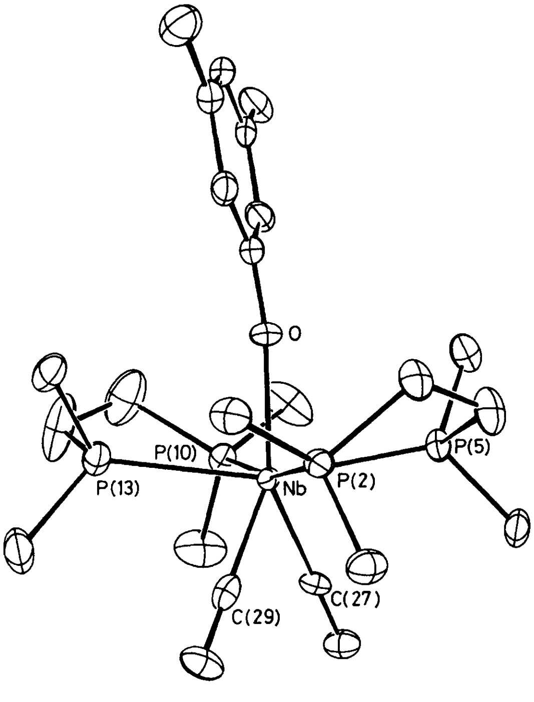

Figure 3. Molecular structure of $Nb(OArMe_2\text{-}3,5)(CO)_2(dmpe)_2$ (**3**). Selected distances (Å) and angles (°) are: Nb–O 2.181(4), Nb–C(27) 2.019(6), Nb–C(29) 2.028(6), Nb–P(2) 2.572(2), Nb–P(5) 2.608(2), Nb–P(10) 2.608(2), Nb–P(13) 2.603(2), P(2)–Nb–P(5) 73.31(6), P(10)–Nb–P(13) 73.24(6), Nb–O–C 159.9(4).

signals.† A single crystal *X*-ray analysis of compound (**2**) showed the compound to be a salt complex of correct formulation $[Nb(OArMe_2\text{-}3,5)_2(dmpe)_2]^+[Nb(OArMe_2\text{-}3,5)_6]^-$ containing the Nb^{III} cation previously discussed as well as Nb^V hexaphenoxide counter-anion (*vide infra*). Attempts to generate the Nb^{IV} complex '$Nb(OArMe_2\text{-}3,5)_4(dmpe)$' by one-electron reduction of $Nb(OArMe_2\text{-}3,5)_5$ in the presence of dmpe has so far yielded the mixed Nb^{III}–Nb^V salt (**2**) as the only characterizable product. Hence it appears that this may be the thermodynamically most stable form of this stoicheiometry.

The neutral compound (**1b**) can also be reduced by simple exposure to an atmosphere of carbon monoxide to give moderate yields of the orange $Nb(OArMe_2\text{-}3,5)(CO)_2(dmpe)_2$ (**3**) an 18-electron complex formally containing an Nb^I metal centre.† This complex is also obtained by Na–Hg reduction of $Nb(OArMe_2\text{-}3,5)_5$ under an atmosphere of CO and represents another example of $MX(CO)_2(dmpe)_2$ type complexes previously reported.[1,8]

In order to more fully characterize the structure and bonding of these new compounds, single crystal *X*-ray diffraction analyses of (**1a**), (**2**), and (**3**) have been carried out.‡ For the complex (**1a**) there are two crystallographically independent but structurally similar molecules in the unit cell. A view of one of these is shown in Figure 1. Each molecule possesses a crystallographically imposed centre of symmetry. It can be seen that the co-ordination about the niobium atom is close to octahedral with *trans*-aryloxides the only significant distortion being the 76.6(5)° 'bite' of the dmpe ligand. The major difference between the two different molecules in the unit cell is the Nb–O–Ar angle [156.4(3) and 171.3(3)°, respectively]. Figure 2 shows a view of the cation $[Nb(OArMe_2\text{-}3,5)_2(dmpe)_2]^+$ in complex (**2**). Again the co-ordination is best described as octahedral with *trans*-aryloxides. The octahedral $[Nb(OArMe_2\text{-}3,5)_6]^-$ counter-anion is unexceptional and is not shown. The structure of the dicarbonyl (**3**) (Figure 3) is best described as a monocapped trigonal prismatic co-ordination with the aryloxide ligand in the capping position. There are similarities between the geometry of (**3**) and that reported for $TaCl(CO)_3(PMe_3)_3$.[9]

An important characteristic of the bonding between alkoxide or aryloxide ligands and high valent transition metal centres is the importance of oxygen-p to metal-d π-bonding.[10] This results in M–O distances significantly shorter than would be expected for a single bond. The complexes (**1a**), (**2**), and (**3**) are of interest in that they allow this effect to be well illustrated, containing as they do aryloxide ligands co-ordinated to a niobium metal centre in the formally +1, +2, +3 oxidation states. Table 1 shows the Nb–O and Nb–P distances found in these three structures. It can be seen that the Nb–P distances remain almost constant, while the Nb–O distance is very sensitive to the metal oxidation state, dropping by 0.27 Å on going from (**1a**), where π-donation would violate the 18-electron rule, to the cation in (**2**). This dramatic change can be compared to the much smaller changes in Ta–Cl bond

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† *Spectroscopic data: g*-values (*a*-Nb); (**1a**): 2.008 (125 G), (**1b**): 2.127 (123 G). ^1H n.m.r. (C_6D_6, 35 °C); (**2**): δ 1.03(m,PCH_3), 1.6(m,PCH_2), 1.98(s), 2.16(s) (intensity ratio of 2:6 $OC_6H_3Me_2$ in cation and anion); (**3**): δ 1.27(m,PCH_3), 1.11(m,PCH_2), 2.25(s,$OC_6H_3Me_2$), 6.21(s), 5.90(s), (aromatic). I.r. (Nujol mull); (**3**): $\bar{\nu}(CO)$, 1805, 1740 cm^{-1}.

‡ *Crystal Data:* $C_{26}H_{46}NbO_2P_4$ (**1a**), M = 607.45, space group $P\bar{1}$, a = 12.646(4), b = 14.016(5), c = 9.707(3) Å, α = 110.87(2), β = 105.83(2), γ = 76.21(2)°, U = 1527.38 Å^3, Z = 2, D_c = 1.321 g cm^{-3}, $\lambda(Mo\text{-}K_\alpha)$ = 0.71069 Å. Of the 4017 unique intensity data measured 3477 with $F_o > 3\sigma(F_o)$ yielded $R(F)$ = 0.0403, $R_w(F)$ = 0.0424. $[NbC_{28}H_{50}O_2P_4][NbC_{48}H_{54}O_6]$ (**2**), M = 1455.36, space group $P2_1/a$, a = 27.967(23), b = 23.496(17), c = 13.319(9) Å, β = 119.72(3)°, U = 7600.92 Å^3, Z = 4, D_c = 1.272 g cm^{-3}. Of the 9914 unique intensities only the 3410 with $F_o > 3\sigma(F_o)$ were used to give $R(F)$ = 0.0754, $R_w(F)$ = 0.0750. $C_{22}H_{41}NbO_3P_4$ (**3**), M = 570.37, space group $Pcab$, a = 16.751(3), b = 12.133(2), c = 27.331(7) Å, U = 5554.68 Å^3, Z = 8, D_c = 1.321 g cm^{-3}. Of the 3633 unique intensities, 2742 with $F_o > 3\sigma(F_o)$ yielded $R(F)$ = 0.0433, $R_w(F)$ = 0.0434. The hydrogen atoms were located in (**1a**) and (**3**) and refined isotropically. All other atoms were refined anisotropically except the non-co-ordinating atoms in structure (**2**). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

lengths that have been reported for complexes containing this function with an even more diverse range of metal oxidation state.[3,4,11]

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