Synthesis, Structure and Reactivity of New Low-valent Mono(η-arene)niobium Compounds†

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The new compounds $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3R]$ (R = H or $SiMe_3$), $[Nb(\eta\text{-}C_6H_5Me)(tmps)]$,† $[Nb(\eta\text{-}C_6H_5Me)(tmps)H]$ [tmps = $MeSi(CH_2PMe_2)_3$], $[Nb(\eta\text{-}C_6H_5Me)(\eta\text{-}C_5H_5)(PMe_3)]$, $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_9H_7)(PMe_3)]$, $[Nb(\eta^5\text{-}C_9H_7)(CO)_3(PMe_3)]$, $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$,† $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$, $[Nb(CO)_3(PMe_3)_4][Nb(CO)_5(PMe_3)]$,† $[Nb(\eta\text{-}C_7H_7)(CO)_2(PMe_3)]$, $[Nb(\eta\text{-}C_6H_5Me)_2X]$ (X = Br, I, Me, Ph or CH_2Ph), $[\{Nb(\eta\text{-}C_6H_5Me)(\mu\text{-}SR)_2\}_2]$ (R = CH_2Ph, Me or Bu) and $[\{Mo(\eta\text{-}C_6H_5Me)(\mu\text{-}SePh)_2\}_2][PF_6]_2$ have been prepared († indicates the crystal structure has been determined). Evidence for the anions $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3]^-$ and $[Nb(\eta\text{-}C_6H_5Me)(tmps)]^-$ is presented.

The chemistry of low-valent or low-oxidation-state compounds of the early transition metals is still a relatively underdeveloped area. We continue to carry out an exploratory synthesis program to discover new low-valent chemistry of these highly electropositive elements.

This paper is concerned primarily with η-arene half-sandwich derivatives of niobium. Previously described half-sandwich η-arene compounds of Group 5 are $[M(\eta\text{-arene})(CO)_4]^+$ (M = V, Nb or Ta), $[V(\eta\text{-}C_6Ph_6)(CO)_3]$, $[V(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_3X]$ (X = I or H), and the trinuclear niobium cation $[Nb_3(\eta\text{-}C_6Me_6)_3Cl_6]^+$.[1-3] Reaction of the tetracarbonyl cation $[M(\eta\text{-arene})(CO)_4]^+$ (M = Nb or Ta) with HCl gas or X_2 gave the halide-bridged dinuclear compounds $[\{M(CO)_4\}_2(\mu\text{-}X)_3]$ (M = Nb or Ta; X = Cl, Br or I).[4] A preliminary account of part of the chemistry described below has been published.[5]

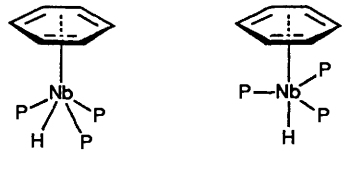
Results and Discussion

The zero-valent compound $[Nb(\eta\text{-}C_6H_5Me)_2]$ **1**[6] was used as the key starting material. We found that 2–3 g of pure, dark red, crystals of **1** could be prepared in a single 4 h co-condensation reaction between niobium atoms and toluene using the metal-vapour synthesis equipment described previously.[7] The analogous reaction using benzene instead of toluene yielded only < 100 mg of $[Nb(\eta\text{-}C_6H_6)_2]$.

Bis(η-arene)molybdenum undergoes displacement of one η-arene ligand when treated with PMe_3 forming the compound $[Mo(\eta\text{-arene})(PMe_3)_3]$.[8] Therefore, by analogy, we explored the η-toluene substitution reactions of $[Nb(\eta\text{-}C_6H_5Me)_2]$. Treatment of $[Nb(\eta\text{-}C_6H_5Me)_2]$ with neat trimethylphosphine gave a deep red solution from which almost black crystals of $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ **2** could be isolated. All the new compounds described in this work are thermally stable at ambient temperatures but they are all highly sensitive to oxygen and/or water. The characterising data for **2**, and for all the other new compounds described below, are given in Table 1. These data will not be discussed further unless interpretation is not straightforward.

The ^1H NMR spectrum of compound **2** has two broad overlapping resonances at δ 3.65 and 3.60 (relative integral *ca.* 4:1) and a quartet at δ 2.28 [integral 3, *J*(PH) 1, toluene Me]; these are assignable to an η-toluene ligand. A broad singlet resonance at δ 1.23 (integral 27) is assignable to three trimethylphosphine ligands, and upon resolution enhancement this resonance showed a virtual triplet structure. Although no high-field peaks are visible at room temperature, at 193 K there was a quartet resonance at δ −0.41 [*J*(PH) 89, integral ≈1] assignable to a NbH moiety coupling to three equivalent phosphorus nuclei. The ^{31}P NMR spectrum at room temperature is broadened into the baseline due to interaction with the quadrupolar ^{93}Nb nucleus (^{93}Nb, 100%, $I = \frac{9}{2}$). However, at 200 K the niobium nuclei becomes partially decoupled and a broad, apparently single resonance is observed at δ −6.5.

In all structurally characterised examples of molecules in the classes $[M(\eta\text{-arene})L_4]$ and $[M(\eta\text{-}C_5H_5)L_4]$ the ML_4 moiety has a square-pyramidal configuration, **A**. If compound **2** has the same arrangement then the apparent presence of only a single ^{31}P NMR resonance may arise either from rapid intramolecular exchange even at 200 K, or the chemical shifts of the *cis* and *trans* phosphorus ligands may be closely similar and as they are broadened by the ^{93}Nb nucleus they could be unresolved. The width at half-height of the ^{31}P NMR resonance of **2** is *ca.* 400 Hz (≈4 ppm) at 200 K. We note that the ^{31}P NMR spectrum of $[W(\eta\text{-}C_5H_5)(PMe_3)_3Cl]$ shows the expected two resonances, in a 2:1 ratio, but which are separated by only 7 ppm.[9] Alternatively, we can envisage a structure **B** with chemically equivalent phosphorus atoms where the hydride ligand is centrally located in a trigonal arrangement of phosphine ligands.



A **B**

3

The ^{31}P NMR spectra of the complexes $[Mo(\eta\text{-arene})(PR_3)_3H]^+X^-$ (arene = C_6H_6, $R_3 = Me_2Ph$ or $MePh_2$;[10] arene = $C_6H_3Me_3$-1,3,5, R = Me[11]) also show three equivalent phosphorus nuclei down to −96 °C. In addition, both *cis* and *trans* isomers have been observed in the ^1H NMR spectrum at −86 °C of the compound $[Mo(\eta\text{-arene})(CO)_2(PR_3)H]^+$ but at room temperature rapid exchange occurred.[12] Further, it has been reported that the three trimethyl phosphite ligands in the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: cal = 4.184 J, atm = 101 325 Pa.

Table 1 Analytical and spectroscopic data[a]

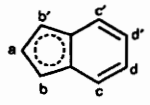
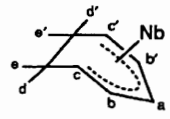
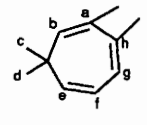
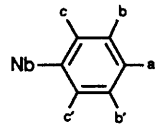
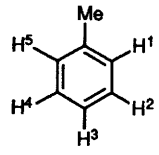
2 [Nb(η-C_6H_5Me)(PMe_3)$_3$H] Dark red C, 46.1 (46.4); H, 8.5 (8.8)	^{1}H:[b] 3.65 (br m, 4 H, $H_{o,o'}$ and $H_{m,m'}$), 3.60 (br m, 1 H, H_p), 2.28 (q, 3 H, Me), 1.23 [d, 27 H, J(PH) 8, 3 PMe_3]; (at 250 MHz)[c] −0.41 [q, 1 H, J(PH) 89, NbH] ^{31}P-{^{1}H}:[d] −6.5 (br s)
4 [Nb(η-C_6H_5Me)(PMe_3)$_3$($SiMe_3$)] Orange[f]	^{1}H at 250 MHz:[e] 3.75 (m, 1 H, H_p), 3.63 (m, 2 H, $H_{o,o'}$ or $H_{m,m'}$), 3.50 (m, 2 H, $H_{m,m'}$ or $H_{o,o'}$), 2.22 (s, 3 H, Me), 1.22 (s, 27 H, 3 PMe_3), 0.35 (s, 9 H, $SiMe_3$) ^{31}P-{^{1}H}:[d] −11.4 (br s)
6 [Nb(η-C_6H_5Me)(tmps)] Dark red[g] C, 44.8 (45.0); H, 7.9 (7.8)	Paramagnetic
7 [Nb(η-C_6H_5Me)(tmps)H] Green[h] C, 44.7 (44.9); H, 7.9 (8.0)	^{1}H:[b] 4.08 (br m, 4 H, $H_{o,o'}$ and $H_{m,m'}$), 3.88 (m, 1 H, H_p), 2.01 [d, 3 H, J(PH) 1, toluene Me], 1.40 [vt, 18 H, J(PH) 2, 3 PMe_2], 0.64 (m, 6 H, 3 CH_2), −0.06 [d, 3 H, J(PH) 1, SiMe], −4.50 [q, 1 H, J(PH) 53, NbH] ^{31}P-{^{1}H}:[c,i] 1.1 (br s) ^{13}C-{^{1}H}:[c,j] 94.8 (s, quaternary), 85.7 (s, η-CH), 79.6 (s, η-CH), 77.7 (s, η-CH), 30.5 (s, CH_2), 24.9 (s, toluene Me), 17.0 (br s, PMe_2), 1.1 (s, SiMe)
8 [Nb(η-C_6H_5Me)(η-C_5H_5)(PMe_3)] Red-brown C, 55.0 (55.2); H, 6.8 (6.8)	^{1}H:[b] 4.61 [d, 5 H, J(PH) 4, η-C_5H_5], 4.48 (m, 1 H, H_p), 3.50 (m, 2 H, $H_{o,o'}$), 3.38 (m, 2 H, $H_{m,m'}$), 2.13 [d, 3 H, J(PH) 1, Me], 0.76 [d, 9 H, J(PH) 6, PMe_3] ^{31}P-{^{1}H}:[c,i] −22.0 (s) ^{13}C-{^{1}H}:[e,j] 83.5 (s, η-C_5H_5), 70.3 (s, η-CH), 68.8 (s, η-CH), 64.9 (s, η-CH), 23.6 (s, Me), 21.4 [d, J(PC) 17, PMe_3]
9 [Nb(η-C_6H_5Me)(η^5-C_9H_7)(PMe_3)] Red-brown C, 60.2 (60.7); H, 6.1 (6.4)  	^{1}H:[c] 7.13 (m, 2 H, $H_{d,d'}$), 6.81 (m, 2 H, $H_{c,c'}$), 5.35 [q, 1 H, $J(H_bH_a)$ = $J(H_aP)$ 3, H_a], 4.62 [dd, 2 H, $J(H_bP)$ 7.3, $J(H_bH_a)$ 3 $H_{b,b'}$], 4.34 (m, 1 H, H_p), 2.90 (m, 4 H, $H_{o,o'}$ and $H_{m,m'}$), 2.25 [d, 3 H, J(PH) 1, Me], 0.85 [d, 9 H, J(PH) 6, PMe_3] ^{31}P-{^{1}H}:[c,i] −21.3 (s) ^{13}C:[e,j] 124.0 [d, J(CH) 160, C_d], 121.0 [d, J(CH) 157, C_c], 108.7 (s, quaternary C), 84.7 [d, J(CH) 179, η-CH], 80.7 [d, J(CH) 172, η-CH], 73.7 [d, J(CH) 164, η-CH], 70.7 [d, J(CH) 167, η-CH], 68.5 [d, J(CH) 179, η-CH], 22.2 [q, J(CH) 120, Me], 21.4 [dq, J(CH) 129, J(PC) 17, PMe_3]
10 [Nb(η^5-C_9H_7)$(CO)_3$(PMe_3)] Dark red[k] C, 48.7 (48.9); H, 4.3 (4.4)	^{1}H:[b] 7.07 (m, 2 H, $H_{d,d'}$), 6.63 (m, 2 H, $H_{c,c'}$), 5.46 [d, 2 H, $J(H_bH_a)$ 3, $H_{b,b'}$], 5.26 [t, 1 H, $J(H_aH_b)$ 3, H_a], 0.71 [d, 9 H, J(PH) 8, PMe_3)] ^{31}P-{^{1}H}:[c,i] 8.6 (s) ^{13}C-{^{1}H}:[e,i] 124.6 (s, C_d), 123.0 (s, C_c), 115.1 (s, quaternary C), 82.8 (s, C_b), 58.9 (s, C_a), 17.5 [d, J(PC) 27, PMe_3]
11 [Nb(η-C_6H_5Me)(η^5-C_7H_9)(PMe_3)] Red-brown C, 57.3 (57.6); H, 7.3 (7.4)  	^{1}H at 300 MHz:[c] 5.16 (5 lines, 1 H, H_a), 4.95 [q, 2 H, $J(H_bH_a)$ = $J(H_bH_c)$ 8, $H_{b,b'}$], 4.26 (m, 1 H, H_p), 3.90 (m, 2 H, $H_{c,c'}$), 3.69 [q, 2 H, $J(H_mH_o)$ = $J(H_mH_p)$ 7, $H_{m,m'}$], 3.58 (m, 2 H, $H_{o,o'}$), 2.16 (s, 3 H, Me), 1.99 (m, 2 H, $H_{d,d'}$ or $H_{e,e'}$), 1.51 (m, 2 H, $H_{e,e'}$ or $H_{d,d'}$) ^{31}P-{^{1}H}:[c,i] −21.9 (s) ^{13}C-{^{1}H}:[c,j] 104.0 (s, C_a), 83.8 (s, C_b), 76.4 (s, η-CH), 72.9 (s, η-CH), 33.4 (s, $C_{d,e}$), 19.0 [d, J(PC) 15, PMe_3]
12 [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] Red-brown  	^{1}H at 300 MHz:[c] 6.12 (m, 1 H, H_f), 4.71 (m, 1 H, H_e), 4.41 [d, 7 H, J(PH) 2, η-C_7H_7)], 3.75 (m, 1 H, H_g), 3.72 (m, 1 H, H_b), ≈3.70 (obscured, 2 H, H_a and H_h), 2.56 (m, 1 H, H_c or H_d), 2.34 (m, 1 H, H_d or H_c), 0.51 [d, 9 H, J(PH) 5, PMe_3]
13 [Nb(η-C_7H_7)$(CO)_2$(PMe_3)] Red-brown[l] C, 45.6 (45.3); H, 5.1 (5.2)	^{1}H:[b] 4.55 [d, 7 H, J(PH) 3, η-C_7H_7], 0.84 [d, J(PH) 7, PMe_3] ^{31}P-{^{1}H}:[c,i] −12.5 (s) ^{13}C-{^{1}H}:[e,j] 87.1 (s, η-C_7H_7), 20.6 [d, J(PC) 21, PMe_3]
14 [Nb(η-C_6H_5Me)$_2$Br] Brown[m] C, 45.3 (47.1); H, 4.3 (4.5)	^{1}H:[b] 4.37 (m, 2 H, $H_{m,m'}$), 4.35 [tt, $J(H_pH_m)$ 7, $J(H_pH_o)$ 1, H_p], 4.15 [t, 2 H, $J(H_oH_m)$ 7, $H_{o,o'}$], 2.00 (s, 3 H, Me) ^{13}C-{^{1}H}:[e,j] 101.7 (s, quaternary C), 88.9 (s, C_m or C_o), 80.6 (s, C_o or C_m), 78.6 (s, C_p), 22.3 (s, Me)
15 [Nb(η-C_6H_5Me)$_2$I] Brown-purple[n] C, 40.0 (41.6); H, 3.8 (4.0)	^{1}H:[b] 4.69 (m, 1 H, H_p), 4.34 (m, 4 H, $H_{o,o'}$ and $H_{m,m'}$), 1.95 (s, 3 H, Me) ^{13}C:[e,j] 98.4 (s, quaternary C), 86.7 [d, J(CH) 172, C_o or C_m], 81.5 [d, J(CH) 172, C_m or C_o], 81.2 [d, J(CH) 173, C_p], 22.8 [q, J(CH) 128, Me]
16 [Nb(η-C_6H_5Me)$_2$Me] Dark red C, 60.9 (61.7); H, 6.3 (6.5)	^{1}H:[b] 4.50 [tt, 2 H, $J(H_pH_m)$ 7, $J(H_pH_o)$ 1, H_p], 3.95 (m, 8 H, $H_{m,m'}$ and $H_{o,o'}$), 1.93 (s, 6 H, toluene Me), −0.22 (s, 3 H, NbMe) ^{13}C-{^{1}H}):[e,j] 97.0 (s, quaternary C), 84.5 (s, C_o or C_m), 80.7 (s, C_m or C_o), 78.9 (s, C_p), 21.8 (s, Me)

Table 1 (*continued*)

17 [Nb(η-$C_6H_5Me)_2Ph$] Dark red C, 67.6 (67.8); H, 5.8 (6.0) 	^1H:[b] 8.05 (m, 2 H, $H_{b,b'}$ or $H_{c,c'}$), ≈7.15 (obscured, 3 H, H_a and $H_{c,c'}$ or $H_{b,b'}$), 4.47 [tt, 2 H, $J(H_pH_m)$ 6, $J(H_pH_o)$ 1, H_p], 4.04 [t, 4 H, $J(H_oH_m)$ 6, H_m], 3.93 [d, 4 H, $J(H_mH_o)$ 6, H_o], 1.77 (s, 6 H, Me) ^{13}C-{^1H}:[e,j] 142.1 (s, C_b or C_c), 125.8 (s, C_c or C_b), 123.1 (s, C_a), 98.6 (s, quaternary C), 83.4 (s, C_o or C_m), 82.5 (s, C_m or C_o), 80.4 (s, C_p), 21.8 (s, Me)
18 [Nb(η-$C_6H_5Me)_2(CH_2Ph)$] Dark red	^1H:[b] 7.26 [t, 2 H, J(HH) 7, $H_{m,m'}$ of CH_2Ph], 7.10 [d, 2 H, J(HH) 7, $H_{o,o'}$ of CH_2Ph], 6.94 [t, 1 H, J(HH) 7, H_p of CH_2Ph], 4.71 [t, 2 H, J(HH) 6, H_p (toluene)], 3.89 [t, 4 H, J(HH) 6, $H_{m,m'}$ (toluene)], 3.61 [d, 4 H, J(HH) 6, $H_{o,o'}$ (toluene)], 1.84 (s, 2 H, CH_2), 1.82 (s, 6 H, toluene Me) ^{13}C-{^1H}:[e,j] 159.1 (s, C of CH_2Ph), 127.1 (s, C of CH_2Ph), 120.0 (s, C of CH_2Ph), 95.2 (s, η-C), 84.3 (s, η-C), 82.6 (s, η-C), 82.1 (s, η-C), 28.5 (br s, CH_2), 21.5 (s, Me)
19 [{Nb(η-C_6H_5Me)(μ-$SCH_2Ph)_2\}_2$] Black[o] C, 57.9 (58.5); H, 5.3 (5.1) 	^1H:[b] 7.28 [d, 4 H, J(HH) 7, $H_{o,o'}$ of CH_2Ph], 7.08 [t, 4 H, J(HH) 7, $H_{m,m'}$ of CH_2Ph], 7.00 (m, 2 H, H_p of CH_2Ph), 4.34 [t, 1 H, J(HH) 7, H^3], 4.28 [t, 1 H, J(HH) 7, H^2], 4.22 [d, 1 H, J(HH) 6, H^5], 3.97 [d, 1 H, J(HH) 6, H^1], 3.87 [t, 1 H, J(HH) 7, H^4], 3.63 [s, 4 H, CH_2], 1.21 (s, 3 H, toluene Me) ^{13}C:[j,p] 143.3 (s, quaternary C of CH_2Ph), 129.3 [d, J(CH) 158, C_o or C_m of CH_2Ph], 127.6 [d, J(CH) 158, C_m or C_o of CH_2Ph], 125.7 [d, J(CH) 158, C_p], 122.4 (s, quaternary C of η-toluene), 110.0 [d, J(CH) 168, η-CH], 98.8 [d, J(CH) 172, η-CH], 98.2 [d, J(CH) 172, η-CH], 93.0 [d, J(CH) 170, η-CH], 91.1 [d, J(CH) 176, η-CH], 33.2 [t, J(CH) 141, CH_2], 21.3 [q, J(CH) 127, toluene Me]
20 [{Nb(η-C_6H_5Me)(μ-$SMe)_2\}_2$] Dark brown[q] C, 38.6 (38.7); H, 5.0 (5.1)	^1H:[b] 4.64 [tt, 1 H, $J(H^3H^2) = J(H^3H^4)$ 7, $J(H^3H^5) = J(H^3H^1)$ 1, H^3], 4.45 (m, 1 H, H^2), 4.38 (m, 1 H, H^4), 4.30 (m, 1 H, H^5), 4.28 (m, 1 H, H^1), 1.92 (s, 6 H, SMe), 1.39 (s, 3 H, toluene Me) ^{13}C-{^1H}:[e,j] 122.4 (s, quaternary C), 110.7 (s, η-CH), 98.2 (s, η-CH), 97.2 (s, η-CH), 95.5 (s, η-CH), 93.9 (s, η-CH), 22.0 (s, toluene Me), 14.5 (s, SMe)
21 [{Nb(η-C_6H_5Me)(μ-$SBu)_2\}_2$] Black	^1H:[b] 4.78 (m, 1 H, H^3), 4.56 (m, 2 H, H^2 and H^4), 4.47 [d, 1 H, J(HH) 6, H^1 or H^5], 4.36 [d, 1 H, J(HH) 6, H^5 or H^1], 2.50 [t, 4 H, J(HH) 7, SCH_2], 1.51 (s, 3 H, toluene Me), 1.36 (m, 8 H, $CH_2CH_2CH_3$), 0.81 [t, 6 H, J(HH) 7, CH_2Me] ^{13}C:[e,j] 121.5 (s, quaternary C), 110.2 [d, J(CH) 169, η-CH], 99.5 [d, J(CH) 173, η-CH], 98.8 [d, J(CH) 172, η-CH], 93.6 [d, J(CH) 173, η-CH], 91.7 [d, J(CH) 174, η-CH], 36.8 [t, J(CH) 126, SCH_2], 32.1 [t, J(CH) 138, CH_2CH_2], 22.8 [t, J(CH) 127, CH_2CH_2], 22.3 [q, J(CH) 127, toluene Me], 14.2 [q, J(CH) 124, CH_2Me]
22 [{Mo(η-C_6H_5Me)(μ-$SePh)_2\}_2$][PF_6]$_2$ Orange-brown C, 35.2 (35.4); H, 2.8 (2.8)	^1H:[r] 7.40 (m, 6 H, H_p and H_o or H_m of SePh), 7.28 (m, 4 H, H_m or H_o of SePh), 6.78 (m, 2 H, $H_{o,o'}$ of η-toluene), 6.42 (m, 2 H, $H_{m,m'}$ of η-toluene), 6.15 (m, 1 H, H_p of η-toluene), 2.17 (s, 3 H, toluene Me) ^{13}C:[j,s] 136.0 [dt, J(CH) 163, 6, C_o or C_m of SePh], 131.0 [dt, J(CH) 163, 6, C_p of SePh], 130.5 [dd, J(CH) 164, 7, C_m or C_o of SePh], 127.8 [t, J(CH) 9, quaternary C], 122.2 [t, J(CH) 9, quaternary C], 108.6 [d, J(CH) 179, η-CH], 105.1 [d, J(CH) 174, η-CH], 102.8 [d, J(CH) 180, η-CH], 99.9 [d, J(CH) 183, η-CH], 98.9 [d, J(CH) 180, η-CH], 23.0 [q, J(CH) 131, toluene Me]

[a] Analytical data (%) given as found (required). [b] At 300 MHz in [$^2H_6$]benzene. [c] In [$^2H_8$]toluene. [d] At 101.26 MHz in [$^2H_8$]toluene, 200 K. [e] In [$^2H_6$]benzene. [f] Mass spectrum (EI): parent ion at *m/z* 486, (M − PMe_3) at *m/z* 410, (M − 2 PMe_3) at *m/z* 334. [g] Mass spectrum (EI): parent ion at *m/z* 453. [h] Mass spectrum (EI): parent ion at *m/z* 454. [i] At 121.5 MHz. [j] At 75.5 MHz. [k] Infrared spectrum (Nujol mull, cm^{-1}): 1945m, 1852s and 1840s. [l] Infrared spectrum (Nujol mull, cm^{-1}): 1934s, 1865m and 1828m. [m] Br 20.2 (22.4%). [n] I 29.1 (31.4%). [o] S 13.9 (14.9%). Mass spectrum (FAB): parent ion (M − 1) at *m/z* 861, (M − CH_2Ph) at *m/z* 771. [p] In thf. [q] S 21.9 (23.0%). [r] At 300 MHz in [$^2H_3$]acetonitrile. [s] In [$^2H_3$]acetonitrile.

complex [Cr(η-C_5H_5){$P(OMe)_3\}_3H$] remain equivalent down to −110 °C in both the ^1H and ^{31}P NMR spectra and, on this basis only, the trigonal-bipyramidal geometry **B** was proposed.[13]

The structure of the vanadium tricarbonyl anion [V(η-C_5H_5)-$(CO)_3H]^-$ is also uncertain. Bergman and co-workers[14] proposed a square-pyramidal geometry by analogy with the isoelectronic [W(η-C_5H_5)$(CO)_3H$], in which separate *cis* and *trans* ^{13}C–^1H coupling constants may be observed at low temperature.[15] Puttfarcken and Rehder,[16] however, suggested a trigonal-bipyramidal structure (local C_{3v} symmetry of the [ML_3H] fragment), since only two bands were seen in the carbonyl region of the infrared spectrum, and this was coupled with detection of ^{51}V–^1H coupling to the hydride ligand which suggests there is a symmetrical environment around the metal centre.

The tris(phosphine) complexes [$ML(PMe_3)_3H$] (M = Mo, L = C_5H_5;[17] M = W, L = C_5H_5[18] or C_5H_4Et[19]) all exhibit three equivalent phosphine ligands in both the ^1H and ^{31}P NMR spectra at room temperature, and in the case of [W(η-$C_5H_4Et)(PMe_3)_3H$] the equivalence is maintained down to −60 °C in [$^2H_8$]toluene.[19] We conclude that the available data do not distinguish between the structure **A** or **B** for **2**, but that **A** is the more likely on circumstantial grounds.

The infrared spectrum of compound **2** shows no band assignable to ν(Nb–H), a phenomenon previously observed for other transition metal–hydride groups, including that in the complex [Cr(η-C_5H_5){$P(OMe)_3\}_3H$].[20] The origin of the hydride ligand in **2** is presumably abstraction from the trimethylphosphine,[19] possibly *via* the 17-electron tris(phosphine) complex [Nb(η-$C_6H_5Me)(PMe_3)_3$] as a likely intermediate.

The η-benzene analogue of **2** namely the compound [Nb(η-$C_6H_6)(PMe_3)_3H$] **3**, can be prepared similarly, from [Nb(η-$C_6H_6)_2$][2] and trimethylphosphine, as highly sensitive deep red crystals and, owing to the small quantity available, was characterised by NMR spectroscopy only. The ^1H NMR spectrum shows a doublet of quartets centred at δ 3.58, assignable to the η-C_6H_6 ligand coupling to three apparently equivalent ^{31}P nuclei and to a NbH group. At 193 K the NbH resonance occurs as a quartet at δ −0.44 [J(PH) 83 Hz]. The

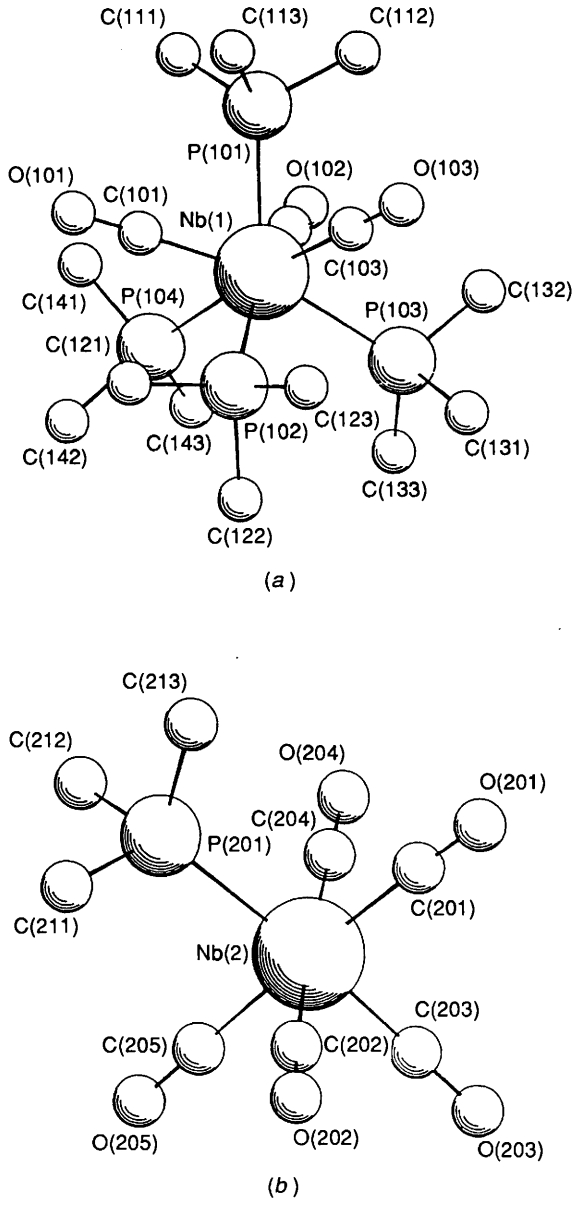


Fig. 1 (*a*) View of the $[Nb(CO)_3(PMe_3)_4]^+$ cation in the salt **5**. (*b*) View of the $[Nb(CO)_5(PMe_3)]^-$ anion in the salt **5**. Hydrogen atoms omitted for clarity

^{31}P NMR spectrum at 193 K showed a single broad resonance at δ −11.5. Again the NMR data do not distinguish between the alternative fluxional square-based pyramidal and static trigonal-bipyramidal isomers.

When a solution of $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ **2** in tetrahydrofuran was passed onto a freshly prepared potassium film it changed rapidly from orange-red to a deep red-brown. Addition of a trace of water restored the initial orange colour and **2** could be recovered. This suggests that **2** undergoes deprotonation by KH to form the anion $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3]^-$. In support of this we found that a solution of the proposed anion reacted with trimethylsilyl chloride to give an orange oil which could not be crystallised from pentane, even at low temperatures. The ^1H and ^{31}P NMR and mass spectra of the oil are given in Table 1 and they clearly indicate the compound to be $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3(SiMe_3)]$ **4**.

The low-temperature (190 K) ^{31}P NMR spectrum of compound **4** in $[^2H_8]$toluene shows only *one* broad symmetrical resonance at δ −11.4 even at 190 K. It may be that **4** has structure **B** rather than **A** due to the bulky nature of the trimethylsilyl group. We note that the magnitude of the barriers to intramolecular exchange for the compounds $[M(\eta\text{-}C_5H_5)(CO)_3X]$ (M = Cr, Mo or W; X = H, alkyl or halide) depend predominantly on the bulk of the X group,[15] and lie in the range 10–13 (X = H), 17–20 (X = Me), and >22 kcal mol^{-1} (X = halide).[15] Also, extended-Hückel molecular-orbital calculations on model complexes $[M(\eta\text{-}C_5R_5)L_4]$ by Hoffmann and co-workers[21] indicated the square-base pyramidal arrangement, **A**, was of lower energy compared to **B**, but the differences were quite small.

Table 2 Selected bond distances (Å) and angles (°) for the complex $[Nb(CO)_3(PMe_3)_4][Nb(CO)_5(PMe_3)]$ **5** with estimated standard deviations (e.s.d.s) in parentheses

Nb(1)–P(101)	2.562(1)	Nb(1)–C(101)	2.090(5)
Nb(1)–P(102)	2.663(1)	Nb(1)–C(102)	2.053(6)
Nb(1)–P(103)	2.675(1)	Nb(1)–C(103)	2.080(5)
Nb(1)–P(104)	2.664(1)		
P(101)–Nb(1)–P(102)	131.25(5)	P(101)–Nb(1)–P(104)	114.80(5)
P(101)–Nb(1)–P(103)	122.26(5)		
Nb(2)–P(201)	2.592(2)	Nb(2)–C(203)	2.031(6)
Nb(2)–C(201)	2.108(7)	Nb(2)–C(204)	2.099(6)
Nb(2)–C(202)	2.085(5)	Nb(2)–C(205)	2.104(7)

Exposure of $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ **2** to an atmosphere of carbon monoxide gave a small quantity of red crystals which a crystal structure determination showed to be the double salt $[Nb(CO)_3(PMe_3)_4][Nb(CO)_5(PMe_3)]$ **5**. Attempts to repeat the synthesis of **5** from **2** were unsuccessful.

The molecular structure of compound **5** is shown in Fig. 1, selected bond distances and angles are given in Table 2, and fractional atomic coordinates are listed in Table 3. The discrete $[Nb(CO)_3(PMe_3)_4]^+$ cations and $[Nb(CO)_5(PMe_3)]^-$ anions exhibit no unusual interionic interactions. The anion has approximately octahedral co-ordination around the metal centre, with the P–Nb–C angle averaging 90.4° for carbon atoms C(201), C(202), C(204) and C(205). The anion exhibits a Nb–C bond length for the axial carbonyl ligand of 2.031(6) Å, significantly shorter than the equatorial Nb–C distances [2.09(1) Å average]. This is presumably a reflection of the greater *trans* influence of the trimethylphosphine ligand. The average Nb–C bond length compares well with that of 2.083(6) Å found in the niobium hexacarbonyl anion in the salt $[N(PPh_3)_2][Nb(CO)_6]$.[22]

The structure of the cation is best described as a face-capped octahedron, with a trimethylphosphine ligand capping a *fac*-$Nb(CO)_3$ face. The Nb–P bond length of the capping phosphine ligand [2.562(1) Å] is significantly shorter than that of the other three phosphine ligands [2.667(7) Å average]. The Nb–C distances in the cation are similar to those of the anion at 2.08(4) Å.

The crystal structure of the tantalum analogue of **5** has been reported[23] and a comparison of the geometries and the M–P and M–C bond lengths reveals no significant differences between the congeners.

We were interested to compare the reactivity of the chelating tripodal phosphine ligand tmps [tmps = tris(dimethylphosphinomethyl)methylsilane, $MeSi(CH_2PMe_2)_3$] with that of a monodentate trialkylphosphine. Thus crystals of $[Nb(\eta\text{-}C_6H_5Me)_2]$ were dissolved in neat tmps to give a deep red solution from which dark red crystals could be isolated. Microanalysis and the electron-impact mass spectrum (P^+ at *m/z* 453) correspond to the zerovalent, paramagnetic, 17-electron compound $[Nb(\eta\text{-}C_6H_5Me)(tmps)]$ **6**. The solution ESR spectrum at room temperature showed a complex signal centred at g = 2.006.

The crystal structure of compound **6** has been determined

Table 3 Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms of $[Nb(CO)_3(PMe_3)_4][Nb(CO)_5(PMe_3)]$ **5** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Nb(1)	6234.2(4)	2537.1(2)	133.3(2)
P(101)	4958(2)	2493(1)	1106.6(6)
P(102)	8291(1)	3444.4(8)	−228.3(6)
P(103)	4892(1)	2793.9(9)	−895.2(6)
P(104)	7577(2)	1238.1(9)	−136.4(7)
C(101)	7719(6)	2375(3)	814(2)
C(102)	4755(6)	1675(3)	95(3)
C(103)	5289(6)	3609(3)	250(2)
C(111)	5089(7)	1589(4)	1518(3)
C(112)	3067(6)	2635(5)	1043(3)
C(113)	5491(8)	3200(5)	1658(3)
C(121)	9927(7)	3462(5)	196(3)
C(122)	8878(7)	3181(4)	−959(3)
C(123)	7966(8)	4478(4)	−297(4)
C(131)	5022(8)	3745(5)	−1241(3)
C(132)	3008(6)	2717(5)	−834(3)
C(133)	5237(8)	2168(5)	−1514(3)
C(141)	7491(9)	536(4)	455(4)
C(142)	9463(8)	1259(4)	−235(3)
C(143)	6956(11)	663(5)	−754(4)
O(101)	8558(5)	2291(3)	1175(2)
O(102)	3943(5)	1178(3)	43(2)
O(103)	4742(6)	4189(3)	311(2)
Nb(2)	1037.9(5)	642.2(3)	2492.4(2)
P(201)	−393(2)	−628(1)	2429.3(7)
C(201)	2956(7)	68(4)	2379(3)
C(202)	926(6)	803(3)	1585(2)
C(203)	2026(6)	1682(3)	2559(2)
C(204)	1324(7)	436(4)	3397(3)
C(205)	−864(7)	1244(4)	2560(3)
C(211)	−1561(14)	−775(8)	1814(6)
C(212)	−1539(19)	−822(10)	2982(8)
C(213)	485(20)	−1539(10)	2328(9)
O(201)	3996(6)	−228(4)	2301(3)
O(202)	934(6)	898(3)	1082(2)
O(203)	2582(5)	2289(2)	2581(2)
O(204)	1513(6)	304(4)	3887(2)
O(205)	−1906(5)	1585(4)	2579(2)

and a view of the molecular structure is shown in Fig. 2. Details of the structure determination, bond lengths and angles, fractional atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The toluene ligand is bonded symmetrically in the expected η^6 fashion with a Nb–$ring_{centroid}$ distance of 1.827(2) Å, *cf.* 1.909 Å in $[Nb(\eta\text{-}C_6H_5Me)_2(PMe_3)][BF_4]$.[24]

Niobium–phosphorus bond lengths to the tmps ligand average 2.528(2) Å, significantly shorter than the Nb–P distance of 2.689(2) Å in $[Nb(\eta\text{-}C_6H_5Me)_2(PMe_3)][BF_4]$, and those of the *fac*-$Nb(PMe_3)_3$ face in $[Nb(CO)_3(PMe_3)_4]^+$ at 2.667(7) Å, but are similar to those of the related zerovalent complex $[Ti(\eta^6\text{-}C_{10}H_8)\{Bu^tSi(CH_2PMe_2)_3\}]$ (average 2.536 Å); the Ti–$ring_{centroid}$ distance of 1.833(1) Å in this complex is also very similar to that found for the niobium complex **6**.[25]

The mono(η-arene) complex **6** represents only the third example of an authentic zerovalent niobium or tantalum compound. Previous examples are $[M(\eta\text{-arene})_2]$ (M = Nb[6] or Ta[7]), and the $[M(dmpe)_3]$ complexes (M = Nb or Ta, dmpe = $Me_2PCH_2PMe_2$).[26]

It has recently been reported that the zerovalent bis(η-arene) complex $[Nb(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$ may be reduced to the 18-electron anion on contact with a potassium film.[24] Therefore, it was decided to attempt to reduce $[Nb(\eta\text{-}C_6H_5Me)(tmps)]$ **6**. It was found that a solution of **6** in tetrahydrofuran reacted rapidly with a freshly prepared potassium film to give a deep red-brown solution. We assume this solution contains the $[Nb(\eta\text{-}C_6H_5Me)(tmps)]^-$ anion since addition of water gave a green solution from which dark green crystals of the hydrido compound $[Nb(\eta\text{-}C_6H_5Me)(tmps)H]$ **7** were isolated.

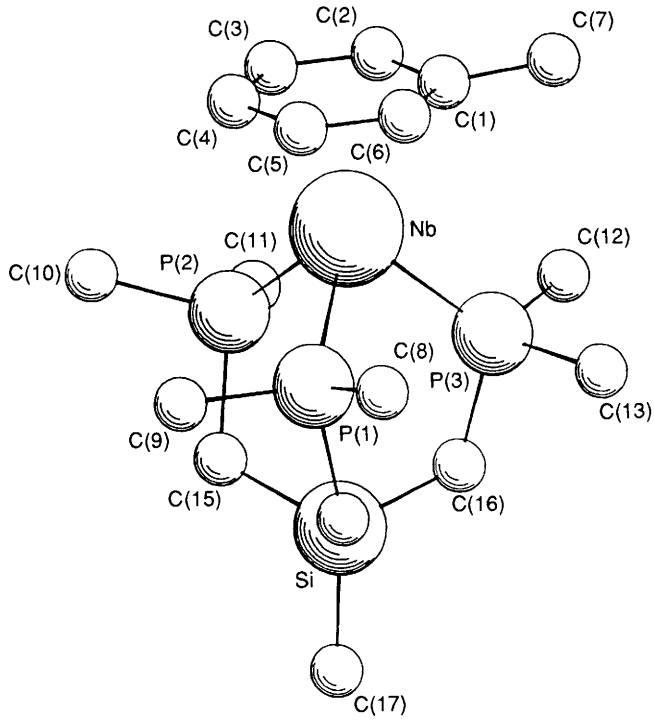


Fig. 2 Molecular structure of $[Nb(\eta\text{-}C_6H_5Me)(tmps)]$ **6**. Hydrogen atoms omitted for clarity

The ^1H NMR spectrum of compound **7** showed resonances assignable to a η-toluene ligand and a symmetrically bound tmps ligand. In addition, the room-temperature spectrum shows a quartet resonance at δ −4.50 [*J*(PH) 53 Hz], characteristic of a metal-bound hydride ligand coupling to three equivalent phosphorus nuclei. On cooling a $[^2H_8]$toluene solution of **7** to 200 K the quartet appearance of the hydride ligand was retained, and there was no evidence for freezing out of any fluxional process. Also, the low-temperature ^{31}P NMR spectrum, at 190 K, shows a slightly broadened (^{93}Nb-coupled) *singlet* resonance. Again these data do not distinguish between a fluxional molecule with structure **A**, or a non-fluxional molecule with structure **B**.

When a solution of compound **2** in toluene was heated to 60 °C with an excess of freshly cracked cyclopentadiene, red-brown crystals of $[Nb(\eta\text{-}C_6H_5Me)(\eta\text{-}C_5H_5)(PMe_3)]$ **8** could be isolated from the reaction products. The monovalent compound **8** represents the first fully characterised example of a $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)L]$ compound (L = two-electron donor) for any of the Group 5 metals. The complexes $[V(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)(CO)]$ and $[Ta(\eta\text{-arene})(\eta\text{-}C_5H_5)(CO)]$ have been reported in the patent literature,[27] but full characterising data have not been published. The only other Group 5 compound containing both η-arene and $\eta\text{-}C_6H_6$ ligands is $[V(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]$.

A toluene solution of compound **2** was heated with freshly distilled indene in a manner analogous to that for cyclopentadiene. Following work-up, red-brown crystals of $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_9H_7)(PMe_3)]$ **9** were isolated. The ^1H NMR spectrum showed two strongly coupled multiplets at δ 7.13 and 6.81, appearing as an AA′BB′ system, which are assigned to protons $H_{d,d'}$ and $H_{c,c'}$ respectively, on the unco-ordinated diene fragment of the η^5-indenyl ligand. Protons $H_{b,b'}$ appear as a doublet of doublets at δ 4.62 [*J*(PH) 7.3, *J*(HH) 3 Hz] due to coupling to both H_a and the phosphine ligand, while H_a is seen at δ 5.35 as a four-line pattern [*J*(HH) ≈ *J*(PH) 3 Hz]. Two further multiplets at δ 4.34 and 2.90 (relative integral 1:4) are assigned to proton H_p, and the overlapping resonances of $H_{m,m'}$

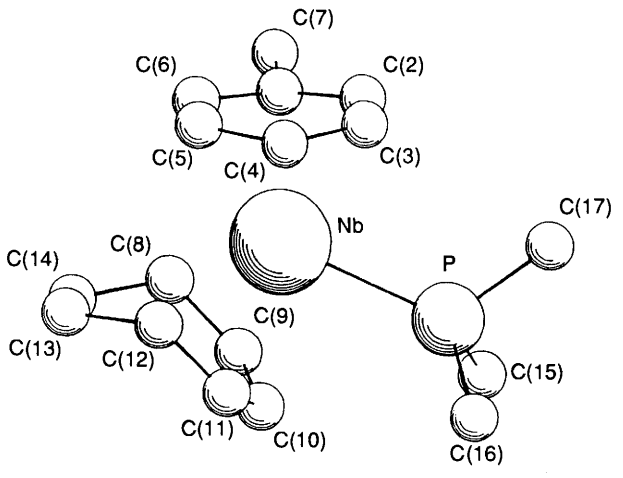


Fig. 3 Molecular structure of $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$ **11**. Hydrogen atoms omitted for clarity

and $H_{o,o'}$, respectively. The methyl group of the toluene ligand occurs as a doublet at δ 2.21 [*J*(PH) 1], while the trimethylphosphine moiety is observed at δ 0.88 [*J*(PH) 6 Hz]. The ^{13}C NMR spectrum supports the proposed formulation, although the quaternary carbon resonance of the η-toluene ligand was not observed at room temperature. The chemical shift of the bridgehead carbon atoms is found to be δ 108.7, which is consistent with the expected η^5 co-ordination and suggests no tendency towards slippage to η^3 co-ordination.[28]

The treatment of a solution of compound **9** in toluene with carbon monoxide (1.5 atm) at room temperature produced a subtle colour change from red to red-brown and red crystals of the tricarbonyl complex $[Nb(\eta^5\text{-}C_9H_7)(CO)_3(PMe_3)]$ **10** could be isolated. The ^{13}C NMR spectrum in $[^2H_6]$benzene reveals all five resonances associated with a symmetrically bound indenyl ligand. The bridgehead carbon atoms are observed at δ 115.1, in the region associated with an undistorted η^5 co-ordination, and there is no evidence for any ring-slipped derivative such as $[Nb(\eta^3\text{-}C_9H_7)(CO)_4(PMe_3)]$.[28] Note that reaction of the related vanadium complex $[V(\eta^5\text{-}C_9H_7)_2(CO)]$ with carbon monoxide *does* lead to a ring-slippage reaction, and the formation of $[V(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_9H_7)(CO)_2]$.[29] The ^{13}C resonances of the carbon monoxide ligands of **10** were not observed, presumably due to significant $^{13}C\text{-}^{93}Nb$ quadrupolar coupling. The infrared spectrum of $[Nb(\eta^5\text{-}C_9H_7)(CO)_3(PMe_3)]$, however, shows three carbonyl stretching modes at 1945, 1852 and 1840 cm^{-1} consistent with a four-legged piano-stool geometry and local C_s symmetry.

When compound **2** was heated in toluene at 60 °C with an excess of freshly distilled cycloheptatriene an orange-brown crystalline product could be isolated. The ^1H NMR spectrum of this solid in $[^2H_6]$benzene showed this to be a mixture of the two compounds $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$ **11** and $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **12** in *ca.* 1:2 ratio. Further recrystallisations from pentane allowed the isolation of pure **11** but **12** could only be obtained as a mixture containing *ca.* 10% of **11** and was characterised by one- and two-dimensional ^1H NMR spectroscopic techniques. The low-temperature (193 K) ^{31}P NMR spectrum of **11** in $[^2H_8]$toluene showed a broad singlet resonance at δ −21.9.

The crystal structure of $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$ **11** has been determined using a crystal grown by slow cooling of a concentrated pentane solution to −80 °C. The molecular structure of **11** is shown in Fig. 3. Details of the structure determination, bond lengths and angles, fractional atomic co-ordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The symmetrically bound η^6-toluene has a $Nb\text{–}ring_{centroid}$ distance of 1.864(2) Å. The η^5-cycloheptadienyl ligand is folded along the C(8)–C(12) vector by 49.4(2)°, and the plane defined by the metal-bound carbon atoms C(8)–C(12) lies 1.823(2) Å from the niobium atom. The metal–carbon distances for the η^5-bound portion of the cycloheptadienyl ligand lie in the range 2.358–2.400 Å, with the longest Nb–C distance being to the carbon atom at the apex of the dienyl fragment. These bond lengths are in close agreement with those found in the bis(dienyl)niobium complex $[Nb(CH_2CMeCHCMeCH_2)_2(PEt_3)]$, which average 2.399(2) Å.[30]

The planes defined by the η^6-toluene ligand and the atoms C(8)–C(12) of the cycloheptadienyl fragment are inclined by 47.1(2)°, giving an angle between the normals to the planes of 132.9°. This comparatively small angle {compare with that of 146.6° in $[Nb(\eta\text{-}C_6H_5Me)_2(PMe_3)]^+$}[24] may be a reflection of the folding of the $\eta^5\text{-}C_7H_9$ moiety reducing steric crowding around the metal centre, allowing the two polyene ligands to bend away from the bulky phosphine group.

The Nb–P distance of 2.664(1) Å is very similar to that of 2.628(2) Å found in the bis(2,4-dimethylpentadienyl) compound described above,[30] and 2.689(2) Å in the cation $[Nb(\eta\text{-}C_6H_5Me)_2(PMe_3)]^+$.[24] These Nb–P distances, however, are significantly longer than those found for chelating phosphine ligands, namely 2.526(3) Å in zerovalent $[Nb(dmpe)_3]$[26] and 2.528(2) Å for $[Nb(\eta\text{-}C_6H_5Me)(tmps)]$.

The compounds **11** and **12** represent two of the rare class of the heavier Group 5 metals (Nb, Ta) bearing a cycloheptatriene or cycloheptadienyl ligand. The only other examples isolated to date are the mixed-ring derivatives $[Nb(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)]$[31,32] and $[Nb(\eta\text{-}C_5H_5)(\eta^4\text{-}C_7H_8)(CO)_2]$.[33]

Treatment of a solution of the η^7-cycloheptatrienyl derivative $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **12** with carbon monoxide results in clean displacement of the η^4-cycloheptatriene ligand and the formation of the dicarbonyl complex $[Nb(\eta\text{-}C_7H_7)(CO)_2(PMe_3)]$ **13**.

Addition of *one* equivalent of allyl bromide or iodide at low temperature to $[Nb(\eta\text{-}C_6H_5Me)_2]$ in light petroleum gave red-brown crystals of $[Nb(\eta\text{-}C_6H_5Me)_2Br]$ **14** or red-purple $[Nb(\eta\text{-}C_6H_5Me)_2I]$ **15**, respectively. Satisfactory microanalytical data proved difficult to obtain. Metal–halogen stretching modes were observed in the infrared spectrum at 295 cm^{-1} for **14** and 290 cm^{-1} for the iodide analogue **15**. The complexes **14** and **15** are isoelectronic with the known bent bis(η-arene) compounds $[W(\eta\text{-arene})_2H]^+$,[34] $[Nb(\eta\text{-}C_6H_5Me)_2(PR_3)]^+$,[24] and $[M(\eta\text{-}C_6H_5Me)_2(PMe_3)]$ (M = Zr or Hf).[35]

Treatment of a solution of $[Nb(\eta\text{-}C_6H_5Me)_2]$ with 1 equivalent of methyl iodide at −80 °C in light petroleum led to a reaction analogous to that observed in the case of allyl iodide, and $[Nb(\eta\text{-}C_6H_5Me)_2I]$ **15** was formed. However, a second minor but more soluble product was also present in the supernatant liquid which the ^1H NMR spectrum showed to be the methyl derivative $[Nb(\eta\text{-}C_6H_5Me)_2Me]$ **16** which is described below.

The abstraction of a halide radical from an alkyl halide reagent is a well known reaction for 17-electron radicals such as $[Mn(CO)_5]^\bullet$ and $[Re(CO)_4L]^\bullet$ (L = CO, phosphine or arsine), which are produced photolytically.[36] However, the reaction of a metal-centred radical with an alkyl halide to produce both alkyl- *and* halide-substituted products is much less common, although it has been observed in the reaction of the 17-electron monomer $[Cr(\eta\text{-}C_5H_5)(CO)_3]$, which is present in low concentrations in solutions of $[\{Cr(\eta\text{-}C_5H_5)(CO)_3\}_2]$, with alkyl halides.[37] A similar type of reaction has also been documented for the radical lanthanide(II) compound $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$.[38]

The reaction of $[Nb(\eta\text{-}C_6H_5Me)_2]$ with 2-bromoethylbenzene ($PhCH_2CH_2Br$) was monitored by ^1H NMR spectroscopy which showed the presence in the reaction products of $[Nb(\eta\text{-}C_6H_5Me)_2Br]$ **14** and also styrene ($PhCH{=}CH_2$) which is presumably formed as the result of a β-elimination reaction from an intermediate $Nb\text{–}CH_2CH_2Ph$ group.

Although the reaction of a bis(η-arene)transition-metal complex with an alkyl halide to produce the corresponding

$[M(\eta\text{-arene})_2X]$ and $[M(\eta\text{-arene})_2R]$ derivatives has not been observed previously, this mode of reactivity *has* been observed for bis(cyclopentadienyl) complexes such as vanadocene, and has recently been the subject of a detailed mechanistic study.[39]

Treatment of a suspension of $[Nb(\eta\text{-}C_6H_5Me)_2Br]$ **14** in diethyl ether with 1 equivalent of methyl- or phenyl-lithium at −80 °C leads to clean metathesis reactions, and the isolation of dark red crystals of the corresponding $[Nb(\eta\text{-}C_6H_5Me)_2R]$ complexes (R = Me, **16**; Ph, **17**) in good yields.

It was found that reaction of $[Nb(\eta\text{-}C_6H_5Me)_2Br]$ **14** with sodium amalgam, or with an excess of isopropylmagnesium bromide, led to a clean reduction to $[Nb(\eta\text{-}C_6H_5Me)_2]$ **1**. Recently, Cloke and co-workers[24] reported that **1** shows a reversible reduction wave at −2.46 V *vs.* saturated calomel electrode in tetrahydrofuran (thf) solution, and that the 18-electron $[Nb(\eta\text{-}C_6H_3Me_3)_2]^-$ anion is accessible in solution *via* potassium metal reduction. It was found that treatment of this anion with carbon monoxide led to the displacement of *both* co-ordinated arene ligands, and the isolation of the hexacarbonylniobate anion $[Nb(CO)_6]^-$.[24]

We have studied the reactions between the bis(η-arene)-niobium anion and alkyl and aryl halides. The addition of a dark red-brown solution of the $[Nb(\eta\text{-}C_6H_5Me)_2]^-$ anion in thf to a solution of methyl iodide in thf at low temperature gave a low yield (*ca.* 20%) of dark red crystals of $[Nb(\eta\text{-}C_6H_5Me)_2Me]$ **16**. Similarly, reaction of a solution of the bis(η-toluene)niobium anion with 1 equivalent of benzyl bromide in thf at low temperature gave the benzyl derivative $[Nb(\eta\text{-}C_6H_5Me)_2(CH_2Ph)]$ **18** in 20% yield. Addition of 1 equivalent of iodobenzene to the $[Nb(\eta\text{-}C_6H_5Me)_2]^-$ anion gave none of the previously described phenyl derivative $[Nb(\eta\text{-}C_6H_5Me)_2Ph]$ **17**.

The compound $[Nb(\eta\text{-}C_6H_5Me)_2]$ **1** in light petroleum was treated with an excess of dibenzyl disulphide giving small black needles of diamagnetic $[\{Nb(\eta\text{-}C_6H_5Me)(\mu\text{-}SCH_2Ph)_2\}_2]$ **19**. A FAB mass spectrum showed the compound was a dimer (P^+ at *m/z* 861). The ^1H and ^{13}C NMR spectra showed the four benzyl groups were equivalent. However, the co-ordinated arene ring had five inequivalent protons indicating that there is no symmetry plane along the Nb–Nb axis. The structure proposed for **19** is essentially similar to that of the isoelectronic molybdenum compound $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}SPh)_2\}_2]$, in which an ABCD pattern was found in the ^1H NMR spectrum for the four cyclopentadienyl protons.[40] The X-ray crystal structure of $[\{Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}SPh)_2\}_2]$ shows a 'propeller' arrangement of bridging thiolate ligands. Also, Silverthorn *et al.*[41] described a similar propeller disposition of the bridging thiolate ligands in the dimers $[\{Mo(\eta\text{-arene})(\mu\text{-}SMe)\}_2]^{2+}$-$[BPh_4^-]_2$.[42]

The reaction between the dialkyl disulphides RSSR (R = Me or Bu) and $[Nb(\eta\text{-}C_6H_5Me)_2]$ gave the binuclear compounds $[\{Nb(\eta\text{-}C_6H_5Me)(\mu\text{-}SR)_2\}_2]$ (R = Me, **20**; or Bu, **21**). In both cases, the ^1H and ^{13}C NMR spectra confirmed the presence of inequivalent ring protons and carbon atoms, and also the equivalence of all four bridging ligands. Thus the complexes are proposed to be isostructural with the benzyl derivative **19**.

Using a modification of the method of Silverthorn *et al.*,[41] treatment of a solution of the salt $[Mo(\eta\text{-}C_6H_5Me)(py)_3][PF_6]$ (py = pyridine) in thf with diphenyl diselenide (PhSeSePh) gave orange-brown crystals of $[\{Mo(\eta\text{-}C_6H_5Me)(\mu\text{-}SePh)_2\}_2]$-$[PF_6]_2$ **22**. The ^{13}C NMR spectrum showed *six* separate carbon resonances in the region associated with co-ordinated arene ligands. We thus propose that **22** is essentially isostructural with $[\{Mo(\eta\text{-}C_6H_5Me)(\mu\text{-}SMe)_2\}_2][PF_6]_2$.

The new reactions and the structures proposed for the new compounds are given in Scheme 1. We have shown that $[Nb(\eta\text{-}C_6H_5Me)_2]$ readily undergoes displacement of one toluene ligand by tertiary phosphine ligands. Indeed this arene-substitution reaction proceeds under milder conditions than for the $[Mo(\eta\text{-arene})_2]$ analogues. The greater reactivity of the 17-electron niobium compound may be associated there being one less metal–ring bonding electron. Also, we have identified several thermally stable compounds $[Nb(\eta\text{-arene})_2R]$ in the rare category of bent sandwich bis(η-arene)metal derivatives.

Experimental

All manipulations of air- and moisture-sensitive materials were performed using standard Schlenk-line techniques under an atmosphere of dinitrogen, which had been purified by passage over BASF catalyst and 4 Å molecular sieves, or in an inert-atmosphere dry-box containing dinitrogen.

Solvents were pre-dried by standing over molecular sieves (4 Å), and then refluxed over, and distilled from, a suitable drying agent under an atmosphere of dinitrogen: sodium (toluene), potassium–benzophenone (tetrahydrofuran) or sodium–potassium alloy (1:3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether, pentane], calcium hydride (acetonitrile). Celite 545 filter aid (Koch-Light) was stored at 60 °C for several hours before use.

Metal-vapour synthesis experiments were performed using the 10 kW positive-hearth machine, details of which have been described previously.[7]

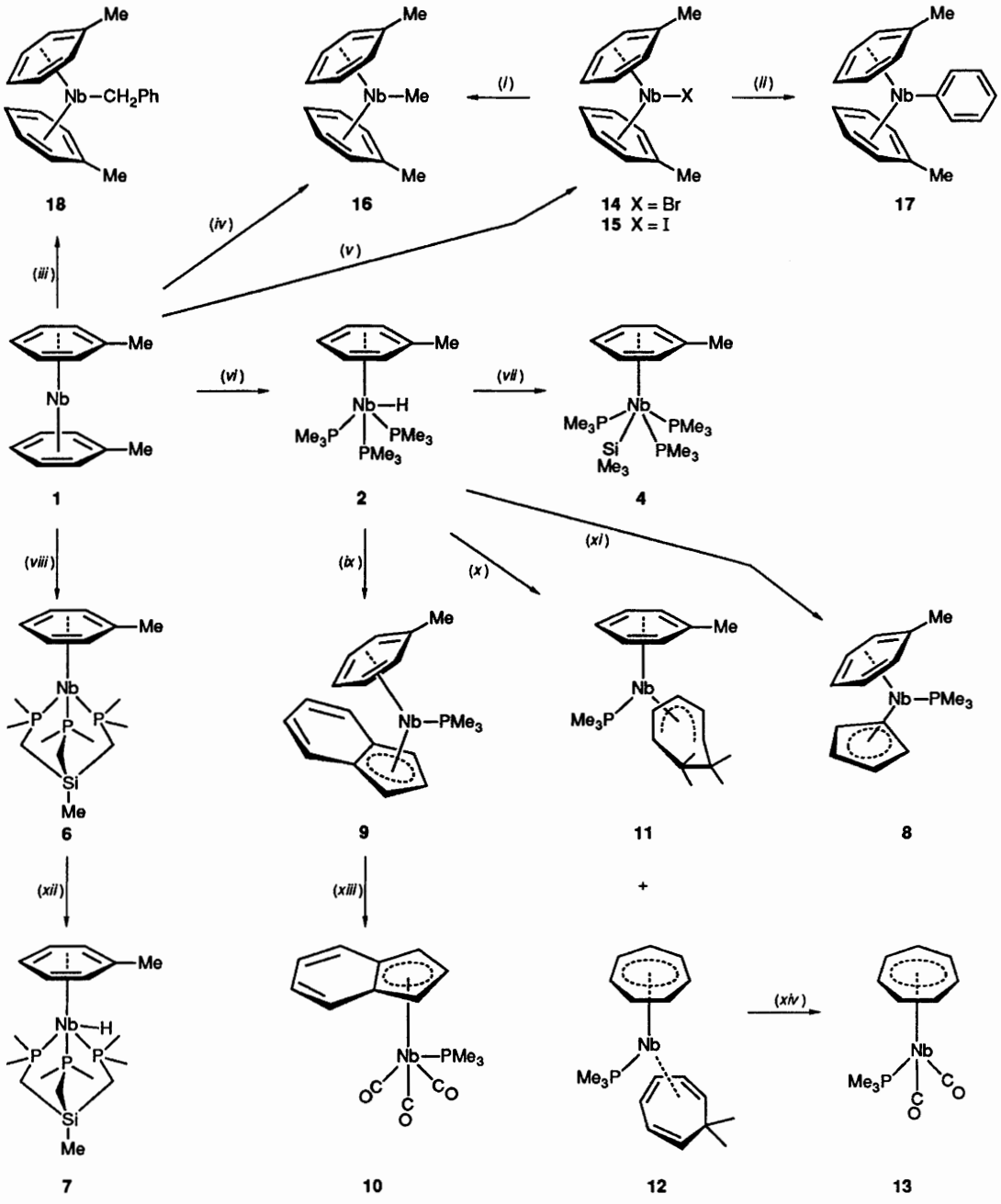
Nuclear magnetic resonance spectra were recorded on the following machines: Brüker AM250 (^1H, 250; ^{31}P, 101.26 MHz), AM300 (^1H, 300; ^{13}C, 75.3; ^{31}P, 121.6 MHz), WH300 (^1H, 300 MHz) and AM500 (^{13}C, 125.6 MHz). Spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ 0), or externally using trimethyl phosphate $[PO(OMe)_3]$ in D_2O (^{31}P). All chemical shifts are quoted in δ and coupling constants are in Hertz. Infrared spectra were recorded on a Perkin-Elmer 1510 FT interferometer or, in the region below 400 cm^{-1}, on a Perkin-Elmer 457 grating spectrometer. Mass spectra were obtained using an AEI MS 302 spectrometer, interfaced with a data-handling system supplied by Mass Spectroscopy Services (electron impact, EI), or by the SERC Mass Spectrometry Centre at the University College of Swansea, under Dr. J. A. Ballantine (FAB). Electron spin resonance measurements were made on a Varian E109 spectrometer.

Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory or, in the case of air-sensitive compounds, by Analytische Laboratorien, Elbach, Germany.

Bis(η-toluene)niobium was prepared using metal-vapour synthesis as previously described.[6] In a typical experiment niobium metal (*ca.* 4 g) was co-condensed with toluene (100 cm^3) at −196 °C over a period of 4 h. Following warm up to room temperature, the reactor vessel was washed out with thf (*ca.* 1000 cm^3) to give a deep red-brown solution. This was filtered through a bed of Celite and the solvent removed under reduced pressure at 40 °C. The dark sticky residue was extracted with light petroleum (500 cm^3) to produce a deep red solution, which was filtered through Celite, reduced in volume to *ca.* 50 cm^3 and cooled to −80 °C overnight to give dark crystals. Typical yield 2.5 g per run (*ca.* 25% based on niobium metal reaching the reaction surface).

Preparations.—$[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ **2**. The compound $[Nb(\eta\text{-}C_6H_5Me)_2]$ (2.00 g, 7.2 mmol) was dissolved in pure trimethylphosphine (20 cm^3) to give a deep red solution. After stirring for 18 h the colour of the solution had changed to orange-red. Excess of trimethylphosphine was removed by trap-to-trap distillation and the dark solid residue was extracted into pentane (50 cm^3). The deep orange-red solution was filtered through a bed of Celite and the volume reduced to *ca.* 10 cm^3 under reduced pressure. Cooling to −80 °C overnight produced dark needles of $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ **2** which were collected by filtration and dried *in vacuo*. Yield 2.22 g (74%).

The deep red compound $[Nb(\eta\text{-}C_6H_6)(PMe_3)_3H]$ **3** was prepared in an analogous manner, starting from $[Nb(\eta\text{-}C_6H_6)_2]$. Yield *ca.* 80 mg (*ca.* 50%).



Scheme 1 (*i*) For X = Br, LiMe in Et_2O, −80 °C with slow warm up, yield 66%; (*ii*) for X = Br, LiPh in Et_2O, −80 °C with slow warm up, 50%; (*iii*) potassium film in thf then benzyl bromide, −80 °C, 20%; (*iv*) MeI in light petroleum, −80 °C; potassium film in thf, then MeI, at −80 °C, 18%; (*v*) allyl bromide or iodide in light petroleum, −80 °C, *ca.* 65%; (*vi*) neat PMe_3, 18 h at r.t., 74%; (*vii*) potassium film in thf at r.t., then $SiMe_3Cl$, 33%; (*viii*) neat tmps, 24 h, r.t., 65%; (*ix*) indene in toluene, 6 h, 60 °C, 41%; (*x*) cycloheptatriene in toluene, 6 h, 60 °C, 38% (1:2 mixture of **11** and **12**); (*xi*) cyclopentadiene in toluene, 8 h, 60 °C, 54%; (*xii*) potassium film in thf at r.t., then water, 45%; (*xiii*) in toluene, CO (1.5 atm) at r.t., 68%; (*xiv*) in toluene, CO (1.5 atm) at r.t., 67%

$[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3(SiMe_3)]$ **4**. The compound $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ (0.20 g, 0.48 mmol) in thf (30 cm^3) was transferred to a Schlenk vessel on the walls of which was deposited a potassium mirror (*ca.* 0.3 g). The solution darkened immediately on contact with the potassium. After stirring for 6 h the deep brown solution was added to a solution of trimethylsilyl chloride (0.25 cm^3) in thf (20 cm^3). When addition was complete, all volatiles were removed under reduced pressure to leave a sticky orange-brown residue. This was extracted with pentane (40 cm^3) and filtered to give a clear orange solution. Removal of the solvent *in vacuo* yielded an orange oil. Yield *ca.* 70 mg (33%).

$[Nb(CO)_3(PMe_3)_4][Nb(CO)_5(PMe_3)]$ **5**. A solution of $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ (0.50 g, 1.21 mmol) in thf (30 cm^3) was treated with carbon monoxide (1.5 atm) at room temperature (r.t.). The colour of the solution changed from orange-red to red-brown over a period of several minutes. After stirring for 1 h the solvent was removed under reduced pressure and the residue extracted into toluene (30 cm^3) to give a deep red-brown solution. This solution was filtered, transferred to a Schlenk vessel, and carefully layered with light petroleum (*ca.* 30 cm^3). The vessel was left undisturbed for 4 d after which time a dark red-brown powder settled out, as well as a few well formed red crystals. Yield *ca.* 20 mg (4%).

$[Nb(\eta\text{-}C_6H_5Me)(tmps)]$ **6**. The compound $[Nb(\eta\text{-}C_6H_5Me)_2]$ (0.25 g, 0.9 mmol) was dissolved in pure tmps[43] (10 cm^3) to give a deep red solution and then left to stir for 24 h. After this time the solution had become orange-red. Excess of tmps was removed by sublimation onto a liquid-nitrogen-cooled probe, and the oily residue dissolved in pentane (30 cm^3).

The solution was filtered and reduced in volume to *ca.* 5 cm^3. On cooling to −80 °C for 12 h, dark red crystals of [Nb(η-C_6H_5Me)(tmps)] **6** were deposited. These were isolated by filtration and dried under reduced pressure. Yield 260 mg (65%).

[Nb(η-C_6H_5Me)(tmps)H] **7**. The compound [Nb(η-C_6H_5Me)(tmps)] (0.15 g, 0.33 mmol) was dissolved in thf (20 cm^3) to give a deep red solution and this was transferred to a Schlenk vessel containing a potassium mirror. After stirring for 6 h the solution had darkened considerably. It was then added slowly to a mixture of thf (30 cm^3) and distilled water (0.2 cm^3), whereupon a colour change occurred from brown-red to green. When addition was complete, volatiles were removed under reduced pressure and the oily green residue extracted with pentane (30 cm^3). The solution was filtered and reduced to *ca.* 5 cm^3. Cooling to −80 °C overnight yielded dark green crystals of [Nb(η-C_6H_5Me)(tmps)H] **7**. Yield 70 mg (45%).

[Nb(η-C_6H_5Me)(η-C_5H_5)(PMe_3)] **8**. To a solution of [Nb(η-C_6H_5Me)(PMe_3)$_3$H] (0.22 g, 0.53 mmol) in toluene (25 cm^3) was added freshly cracked cyclopentadiene (0.5 cm^3), and the solution heated to 60 °C for 8 h. Solvent was removed under reduced pressure and the residue extracted with light petroleum (30 cm^3) to give a red-orange solution. This was filtered, reduced in volume to *ca.* 5 cm^3 and cooled to −80 °C to give red-brown crystals of [Nb(η-C_6H_5Me)(η-C_5H_5)(PMe_3)] **8**. The crystals were filtered off and dried *in vacuo*. Yield 95 mg (54%).

[Nb(η-C_6H_5Me)(η^5-C_9H_7)(PMe_3)] **9**. The compound [Nb(η-C_6H_5Me)(PMe_3)$_3$H] (0.94 g, 2.27 mmol) was dissolved in toluene (40 cm^3) and freshly distilled indene (0.5 cm^3) was added. The mixture was then heated to 60 °C for 6 h, during which time the solution had become green-brown. The solvent was removed under reduced pressure and the residue extracted with pentane (30 cm^3) to give a greenish solution. This was filtered, reduced in volume to *ca.* 10 cm^3 and cooled to −80 °C overnight. Dark crystals appeared in a green supernatant liquid. They were filtered off and dried *in vacuo*. Yield 345 mg (41%).

[Nb(η^5-C_9H_7)(CO)$_3$(PMe_3)] **10**. A solution of [Nb(η-C_6H_5Me)(η^5-C_9H_7)(PMe_3)] **9** (0.045 g, 0.12 mmol) in toluene (10 cm^3) was treated with carbon monoxide (1.5 atm) at room temperature. After stirring for 1 h the solvent was removed under reduced pressure and the residue extracted into light petroleum (20 cm^3) to give an orange solution. This was filtered, reduced in volume to *ca.* 5 cm^3 and cooled to −80 °C overnight to give red-orange crystals of the product. The crystals were filtered off and dried *in vacuo*. Yield *ca.* 30 mg (68%).

[Nb(η-C_6H_5Me)(η^5-C_7H_9)(PMe_3)] **11** *and* [Nb(η-C_7H_7)-(η^4-C_7H_8)(PMe_3)] **12**. The compound [Nb(η-C_6H_5Me)-(PMe_3)$_3$H] (0.260 g, 0.63 mmol) was dissolved in toluene (30 cm^3) and freshly distilled cycloheptatriene (0.5 cm^3) added. The mixture was heated to 60 °C for 6 h, and then all volatiles were removed *in vacuo*. The red-brown residue was extracted with light petroleum (30 cm^3) to give a red solution which was filtered and reduced in volume to *ca.* 10 cm^3. Cooling to −80 °C overnight gave red-brown crystals (85 mg, 38%), which were shown by ^{1}H NMR spectroscopy to be a mixture of compounds **11** and **12**. Two recrystallisations from pentane yielded a pure sample of **11**.

[Nb(η-C_7H_7)(CO)$_2$(PMe_3)] **13**. A red-brown solution of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] (0.05 g, 0.14 mmol) in toluene (20 cm^3) was treated with carbon monoxide (1.5 atm) at room temperature, producing a slight darkening in colour. The solution was then stirred for 1 h, after which all volatiles were removed under reduced pressure and the residue extracted into light petroleum (20 cm^3). This solution was filtered, reduced in volume to *ca.* 5 cm^3 and cooled to −80 °C overnight to give red-brown crystals of [Nb(η-C_7H_7)(CO)$_2$(PMe_3)] **13**. The crystals were filtered off and dried *in vacuo*. Yield *ca.* 30 mg (67%).

[Nb(η-C_6H_5Me)$_2$Br] **14**. A solution of [Nb(η-C_6H_5Me)$_2$] (2.95 g, 10.6 mmol) in light petroleum (60 cm^3) was cooled to −80 °C, and a solution of allyl bromide (1.28 g, 10.6 mmol) in light petroleum (10 cm^3) added dropwise with vigorous stirring. During the course of the addition a brown powder was deposited. The reaction mixture was allowed to warm to room temperature, the pale supernatant liquid decanted off and discarded, and the solid brown residue dried *in vacuo*. Yield 2.47 g (65%). The solid was then extracted into toluene (50 cm^3) to produce a deep red-brown solution. This was filtered through a bed of Celite and reduced in volume to *ca.* 10 cm^3. Cooling to −80 °C overnight yielded dark brown crystals of analytically pure [Nb(η-C_6H_5Me)$_2$Br] **14**.

[Nb(η-C_6H_5Me)$_2$I] **15**. A solution of [Nb(η-C_6H_5Me)$_2$] (0.9 g, 3.25 mmol) in light petroleum (50 cm^3) was cooled to −80 °C. A solution of allyl iodide (0.55 g, 3.27 mmol) in light petroleum (5 cm^3) was added dropwise with vigorous stirring, to produce a red-brown precipitate. The reaction mixture was warmed to room temperature and the supernatant liquid filtered off. The residue was washed with pentane (3 × 10 cm^3) and dried *in vacuo*. Yield 830 mg (63%). This solid may be recrystallised from toluene to give an analytically pure sample of [Nb(η-C_6H_5Me)$_2$I].

[Nb(η-C_6H_5Me)$_2$] *with methyl iodide*. The compound [Nb(η-C_6H_5Me)$_2$] (1.40 g, 5.05 mmol) was treated with methyl iodide (0.72 g, 5.07 mmol) in a manner analogous to that described above for **15**. The supernatant liquid was filtered off and all volatiles removed under reduced pressure. A sample of the sticky dark red residue was dissolved in [$^2H_6$]benzene and shown by ^{1}H NMR spectroscopy to contain resonances assigned to [Nb(η-C_6H_5Me)$_2$Me] **16**.

[Nb(η-C_6H_5Me)$_2$Me] **16**. *Method* 1. To a suspension of [Nb(η-C_6H_5Me)$_2$Br] **14** (0.13 g, 0.36 mmol) in diethyl ether (50 cm^3) at −80 °C was added a 1.4 mol dm^{-3} solution (0.3 cm^3) of methyllithium in ether. On warming to room temperature the brown suspension was slowly consumed and a red solution resulted. Solvent was removed *in vacuo* and the residue extracted into pentane (30 cm^3). This solution was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −80 °C overnight produced dark red needles of [Nb(η-C_6H_5Me)$_2$Me] **16**. Yield 70 mg (66%).

Method 2. The compound [Nb(η-C_6H_5Me)$_2$] (0.23 g, 0.83 mmol) was dissolved in thf (40 cm^3) and run onto a potassium film. After stirring for 4 h the dark solution was slowly added to a solution of methyl iodide (0.12 g) in thf (25 cm^3) at −80 °C. The reaction mixture was allowed to warm to room temperature and the solvent removed under reduced pressure. The residue was extracted with light petroleum (40 cm^3) to give a red solution, which was filtered, reduced in volume to 5 cm^3, and cooled to −80 °C. Overnight, dark red crystals of [Nb(η-C_6H_5Me)$_2$Me] were deposited. Yield 45 mg (18%).

[Nb(η-C_6H_5Me)$_2$Ph] **17**. A suspension of [Nb(η-C_6H_5Me)$_2$-Br] (0.110 g, 0.31 mmol) in diethyl ether (40 cm^3) was cooled to −80 °C and a 1.8 mol dm^{-3} solution (0.2 cm^3) of phenyllithium in cyclohexane–diethyl ether was added. The reaction mixture was stirred for 10 min at −80 °C and then allowed to warm to room temperature to give a deep red solution. All volatiles were removed under reduced pressure and the residue extracted into pentane (50 cm^3), filtered and reduced in volume to *ca.* 10 cm^3. Cooling to −80 °C overnight produced dark red crystals, which were filtered off and dried *in vacuo*. Yield 55 mg (50%).

[Nb(η-C_6H_5Me)$_2$(CH_2Ph)] **18**. Using a method analogous to method 2 described above for [Nb(η-C_6H_5Me)$_2$] the bis-(η-toluene)niobium anion reacted with 1 equivalent of benzyl bromide in thf at −80 °C to give, on work-up from pentane, dark red crystals of [Nb(η-C_6H_5Me)$_2$(CH_2Ph)] **18** in 20% yield.

NMR tube reaction of [Nb(η-C_6H_5Me)$_2$] *with* $PhCH_2$-CH_2Br. The compound [Nb(η-C_6H_5Me)$_2$] (*ca.* 10 mg) was dissolved in [$^2H_6$]benzene (1 cm^3) and 2-bromoethylbenzene (*ca.* 10 mg) added to give a deep red-brown solution. Examination of a ^{1}H NMR spectrum of the solution showed resonances due to [Nb(η-C_6H_5Me)$_2$Br] **14** and styrene.

[{Nb(η-C_6H_5Me)(μ-SCH_2Ph)$_2$}$_2$] **19**. The compound [Nb(η-C_6H_5Me)$_2$] (0.25 g, 0.90 mmol) dissolved in light petroleum (40 cm^3) was added slowly to a solution of dibenzyl

disulphide (0.30 g, 1.22 mmol) in light petroleum (20 cm^3) at room temperature. After several minutes the initially clear red solution had become cloudy and dark brown. Some black needles could be seen on the walls of the Schlenk vessel. The murky brown supernatant liquid was decanted off, the black needles washed several times with pentane (3 × 10 cm^3) and dried *in vacuo*. Yield 80 mg (21%). The product was recrystallised from toluene or tetrahydrofuran.

$[\{Nb(\eta\text{-}C_6H_5Me)(\mu\text{-}SR)_2\}_2]$ (R = Me, **20** *or* Bu, **21**). To a solution of $[Nb(\eta\text{-}C_6H_5Me)_2]$ in light petroleum at −20 °C was added an excess (0.5 cm^3) of the appropriate disulphide as a solution in light petroleum (20 cm^3). On warming to room temperature with stirring the colour of the solution changed from red to a brownish orange over a period of *ca.* 1 h. The solvent was removed under reduced pressure, and the sticky dark red-brown residue left *in vacuo* for several hours to remove unreacted disulphide. The residue was then taken up in pentane (20 cm^3), filtered, reduced in volume to *ca.* 5 cm^3 and cooled to 80 °C overnight to produce dark brown crystals.

$[\{Mo(\eta\text{-}C_6H_5Me)(\mu\text{-}SePh)_2\}_2][PF_6]_2$ **22**. The compound $[Mo(\eta\text{-}C_6H_5Me)(py)_3][PF_6]$ (2.40 g, 4.22 mmol) was dissolved in thf (40 cm^3) and a solution of diphenyl diselenide (1.30 g, 4.22 mmol) in thf added dropwise over a period of *ca.* 0.5 h. An orange-brown powder was deposited. After stirring for 1 h the powder was left to settle, and the supernatant liquid decanted off and discarded. The orange residue was dried *in vacuo* and then dissolved in acetonitrile (50 cm^3). This orange solution was filtered and the volume reduced to *ca.* 10 cm^3. Cooling to −20 °C overnight gave orange crystals of $[\{Mo(\eta\text{-}C_6H_5Me)(\mu\text{-}SePh)_2\}_2][PF_6]_2$. Yield 1.60 g (59%).

X-Ray Crystal Structure Determination of Compound **5**.—A crystal was sealed in a Lindemann glass capillary and transferred to the goniometer head of an Enraf-Nonius CAD4-F diffractometer. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. Data were collected using graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å) and ω–2θ scan mode.

The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[44] based on an azimuthal scan was applied. Equivalent reflections were merged and systematically absent reflections rejected. The niobium atom positions were determined from a Patterson synthesis. Subsequent Fourier difference syntheses revealed the positions of other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by least-squares procedures and hydrogen atoms were placed in estimated positions. A Chebyshev weighting scheme[45] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[46]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[47] on a VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford. Scattering factors were taken from the usual sources.[48]

Crystal data. $C_{28}H_{45}Nb_2O_8P_5$, *M* 790.28, crystal size 0.3 × 0.4 × 0.1 mm, monoclinic, space group $P2_1/c$, a = 9.564(3), b = 17.258(3), c = 22.771(2) Å, β = 91.65(2)°, U = 3757 $Å^3$, Z = 4, D_c = 1.39 g cm^{-3}, μ = 8.28 cm^{-1}, $F(000)$ = 1616; 2θ limits 3–50°, total data collected 5396, no. of observations [$I > 3\sigma(I)$] 3723, no. of parameters 326, weighting scheme coefficients 3.940, 0.0687, 2.677, final residuals R (R') 0.039 (0.044), where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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