Low-valent Niobium Chemistry: Synthesis of Bent Bis-arene Niobium Alkyl and Halide Complexes, Half-sandwich Mono-arene Niobium Tertiary Phosphine Compounds, and Related Studies

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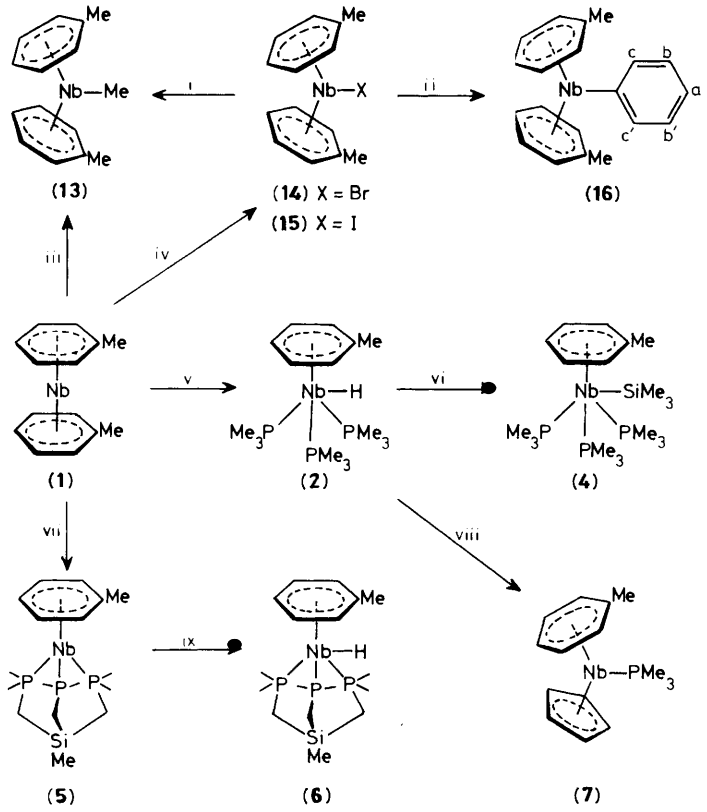
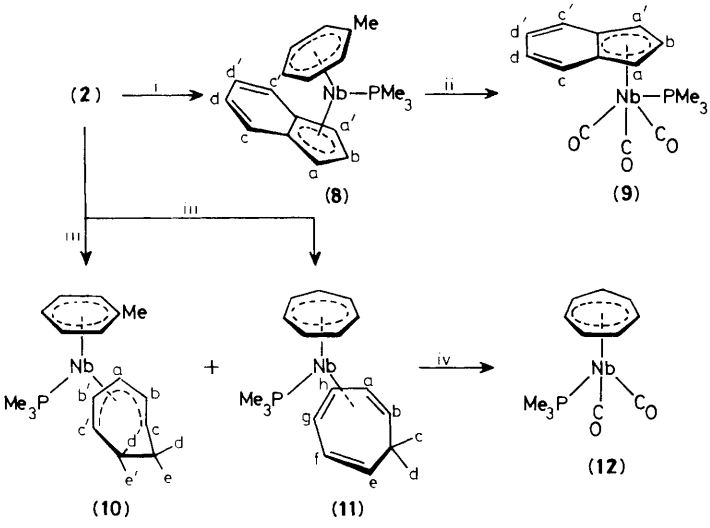
The syntheses of the new compounds $[Nb(\eta\text{-}C_6H_5Me)_2X]$ (X = Me, Ph, Br, I), $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3X$ (X = H, $SiMe_3$), $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$, and $[Nb(\eta\text{-}C_7H_7)(CO)_2(PMe_3)]$ are described.

Organometallic compounds of niobium in which the metal is in a low (≤ 1) oxidation state are uncommon. Previous examples include $[Nb(dmpe)_3]$ [dmpe = 1,2-bis(dimethylphosphino)-ethane],[1] the hexacarbonylniobate anion and substituted derivatives $[Nb(CO)_{6-n}L_n]^-$ (n = 1—3),[2] and the monocyclopentadienyl system $[(\eta\text{-}C_5H_5)NbL_4]$, [L = CO,[3] L_4 = $dmpe(CO)_2$].[4]

Niobium complexes containing an η-arene ring are very rare, being limited to the tetracarbonyl cation $[Nb(\eta\text{-}C_6R_6)(CO)_4][Al_2Br_6Cl]$,[5] zero-valent $[Nb(\eta\text{-arene})_2]$, and the



Scheme 1. *Reagents and conditions:* i, MeLi, THF, −80 °C, 66% (X = Br); ii, PhLi, THF, −80 °C, 50% (X = Br); iii, K film, THF then MeI, THF, −80 °C, 18%; iv, allyl halide (X = Br or I) (1 equiv.), −80 °C, 65% (X = Br), 63% (X = I); v, PMe_3, 12 h, 74%; vi, K film, THF then Me_3SiCl, THF, 33%; vii, tmps, 24 h, 65%; viii, Cp monomer, toluene, 60 °C, 6 h, 54%; ix, K film, THF then H_2O in THF, 45%.



Scheme 2. *Reagents and conditions:* i, indene, toluene, 60 °C, 6 h, 41%; ii, CO, 1.5 atm., toluene, 68%; iii, cycloheptatriene, toluene, 60 °C, 4 h, 38%; iv, CO, 1.5 atm., toluene.

halide-bridged species $[Nb_2(\eta\text{-}C_6Me_6)_2Cl_4]$ and $\{[Nb_3(\eta\text{-}C_6Me_6)_3Cl_6]Cl\}$.[6]

The 17-electron bis-arene derivatives $[Nb(\eta\text{-arene})_2]$ have been prepared using metal vapour synthesis techniques[7] but their chemistry has been only briefly explored.[8] Here we describe a new and extensive chemistry of low-valent niobium compounds derived from $[Nb(\eta\text{-toluene})_2]$ (**1**).

Treatment of (**1**) with pure trimethylphosphine at room temperature for 12 h gives dark red crystalline $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3H]$ (**2**) in 74% yield. The compound (**2**) in tetrahydrofuran (THF) reacts with a potassium film giving a dark red–orange solution which we presume contains the salt $\{K^+[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3]^-\}$ (**3**), since addition of Me_3SiCl to a solution of (**3**) gives the trimethylsilyl derivative $[Nb(\eta\text{-}C_6H_5Me)(PMe_3)_3SiMe_3]$ (**4**) as an orange oil.

The direct reaction between (**1**) and the chelating trisphosphine tmps [tmps = tris(dimethylphosphinomethyl)methylsilane] gives the zero-valent derivative $[Nb(\eta\text{-}C_6H_5Me)(tmps)]$ (**5**), the crystal structure of which has been determined.† Treatment of (**5**) with a potassium film in THF, followed by hydrolysis of the presumed $[Nb(\eta\text{-}C_6H_5Me)(tmps)]^-$ anion, gives the green hydrido compound $[Nb(\eta\text{-}C_6H_5Me)(tmps)H]$ (**6**).

Treatment of a solution of (**2**) with cyclopentadiene or indene at 60 °C results in the formation of the compounds $[Nb(\eta\text{-}C_6H_5Me)(\eta\text{-}C_5H_5)(PMe_3)]$ (**7**) and $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_9H_7)(PMe_3)]$ (**8**), respectively. Reaction of the η^5-indenyl derivative (**8**) with carbon monoxide (*ca.* 1.5 atm.) produces $[Nb(\eta^5\text{-}C_9H_7)(CO)_3(PMe_3)]$ (**9**).

Heating a solution of (**2**) with cycloheptatriene at 60 °C gives a mixture of $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$ (**10**) and $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ (**11**). The crystal structure of (**10**) has been determined.† Treatment of (**11**) with carbon monoxide gives the dicarbonyl $[Nb(\eta\text{-}C_7H_7)(CO)_2(PMe_3)]$ (**12**).

Reduction of the bis-arene compound (**1**) with a potassium film[8] followed by addition of methyl iodide at low temperature gives the methyl derivative $[Nb(\eta\text{-}C_6H_5Me)_2Me]$ (**13**) as dark red crystals. The *X*-ray crystal structure of a reduced bis(η-arene) vanadium complex, $K[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2V]$, has recently been determined.[9]

Addition of one equivalent of allyl bromide or allyl iodide to (**1**) at −78 °C gives the bent-sandwich halide derivatives $[Nb(\eta\text{-}C_6H_5Me)_2X]$, X = Br (**14**) or I (**15**), respectively, in good yield.

Treatment of $[Nb(\eta\text{-}C_6H_5Me)_2Br]$ (**14**) with one equivalent of LiR (R = Me or Ph) in diethyl ether at −80 °C forms the corresponding bis-arene alkyl or aryl derivative $[Nb(\eta\text{-}C_6H_5Me)_2R]$, R = Me (**13**) or Ph (**16**).

The structures proposed for the new compounds (**2**)—(**16**) are shown in Schemes 1 and 2. Compounds (**2**)—(**16**) are

† *Crystal data* for (**5**): $NbP_3SiC_{17}H_{35}$, M = 453.37, monoclinic, space group $P2_1/n$, a = 16.761(3), b = 17.801(5), c = 16.963(5) Å, β = 115.84(2)°, U = 4554.9 Å^3, D_c = 1.32 Mg m^{-3}, Z = 8 (2 molecules in the asymmetric unit), μ = 7.62 cm^{-1}, $F(000)$ = 1896, R = 3.25%, R_w = 3.67%, for 3469 observed reflections $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

For (**10**): $NbPC_{17}H_{26}$, M = 354.27, monoclinic, space group $P2_1/n$, a = 8.049(2), b = 12.700(7), c = 16.066(5) Å, β = 98.33(3)°, U = 1633.79 Å^3, D_c = 1.44 Mg m^{-3}, Z = 4, μ = 7.88 cm^{-1}, $F(000)$ = 736, R = 2.37%, R_w = 2.85%, for 2471 observed reflections $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å.

Data were collected using an Enraf-Nonius CAD4 diffractometer [$2\theta_{max.}$ = 20° for (**5**) and 50° for (**10**)]. The structures were solved by using Patterson and Fourier synthesis and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and allowed to ride on their attached carbons between cycles of refinement. Crystallographic calculations were carried out using the Oxford CRYSTALS package.[10] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

thermally stable at room temperature and are highly sensitive to dioxygen.‡

‡ *N.m.r. data:* ^{1}H n.m.r. at 300 MHz, ^{13}C n.m.r. at 75.5 MHz in [$^2H_6$]benzene unless otherwise stated, ^{31}P n.m.r. at 121.5 MHz in [$^2H_8$]toluene at 200 K unless otherwise stated; chemical shifts (δ) in p.p.m. and coupling constants in Hz.

(**2**): ^{1}H N.m.r. δ 3.65 (br. m, 4H, $H_{o,o'}$ and $H_{m,m'}$), 3.60 (br. s, 1H, H_p), 2.28 (s, 3H, Me), 1.23 [d, 27H, J(P–H) 8, 3PMe$_3$]; (250 MHz, [$^2H_8$]toluene, 200 K) −0.41 [q, 1H, J(P–H) 89, Nb–*H*]; ^{31}P-{^{1}H} n.m.r. (101.2 MHz) δ −6.5 (br. s).

(**4**): ^{1}H N.m.r. (250 MHz) δ 3.75 (m, 1H, H_p), 3.63 (m, 2H, $H_{o,o'}$ or $H_{m,m'}$), 3.50 (m, 2H, $H_{m,m'}$ or $H_{o,o'}$), 2.22 (s, 3H, Me), 1.22 (s, 27H, 3PMe$_3$), 0.35 (s, 9H, SiMe$_3$); ^{31}P-{^{1}H} n.m.r. (101.2 MHz) δ 11.4 (br. s).

(**6**): ^{1}H N.m.r. δ 4.08 (br. m, 4H, $H_{o,o'}$ and $H_{m,m'}$), 3.88 (m, 1H, H_p), 2.01 [d, 3H, J(P–H) 1, tol-*Me*], 1.40 [vt, 18H, J(P–H) 2, 3PMe$_2$], 0.64 (m, 6H, 3CH$_2$), −0.06 [d, 3H, J(P–H) 1, Si-*Me*], −4.50 [q, 1H, J(P–H) 53, Nb–*H*]; ^{31}P-{^{1}H} n.m.r. δ 1.1 (s); ^{13}C-{^{1}H} n.m.r. δ 94.8 (s, C_{quat}), 85.7 (s, η-CH), 79.6 (s, η-CH), 77.7 (s, η-CH), 30.5 (s, –CH$_2$–), 24.9 (s, tol-*Me*), 17.0 (br. s, –PMe$_2$), 1.1 (s, Si*Me*).

(**7**): ^{1}H N.m.r. δ 4.61 [d, 5H, J(P–H) 4, η-Cp], 4.48 (m, 1H, H_p), 3.50 (m, 2H, $H_{o,o'}$), 3.38 (m, 2H, $H_{m,m'}$), 2.13 [d, 3H, J(P–H) 1, Me], 0.76 [d, 9H, J(P–H) 6, PMe$_3$]; ^{31}P-{^{1}H} n.m.r. δ −22.0 (s); ^{13}C-{^{1}H} n.m.r. δ 83.5 (s, η-Cp), 70.3 (s, η-CH), 68.8 (s, η-CH), 64.9 (s, η-CH), 23.6 (s, Me), 21.4 [d, J(P–C) 17, PMe$_3$].

(**8**): ^{1}H N.m.r. δ 7.13 (m, 2H, $H_{d,d'}$), 6.81 (m, 2H, $H_{c,c'}$), 5.35 [q, 1H, $J(H_b–H_a)$ = $J(H_b–P)$ 3, H_b], 4.62 [dd, 2H, J 7,3, $H_{a,a'}$), 4.34 (m, 1H, H_p), 2.90 (m, 4H, $H_{o,o'}$ and $H_{m,m'}$), 2.25 [d, 3H, J(P–H) 1, Me], 0.85 [d, 9H, J(P–H) 6, PMe$_3$]; ^{31}P-{^{1}H} n.m.r. δ −21.3 (s); ^{13}C n.m.r. δ 124.0 [d, J(C–H) 160, C_d], 121.0 [d, J(C–H) 157, C_c], 108.7 (s, C_{quat}), 84.7 [d, J(C–H) 179, η-CH], 80.7 [d, J(C–H) 172, η-CH], 73.7 [d, J(C–H) 164, η-CH], 70.7 [d, J(C–H) 167, η-CH], 68.5 [d, J(C–H) 179, η-CH], 22.2 [q, J(C–H) 120, Me], 21.4 [dq, J(C–H) 129, J(P–C) 17, PMe$_3$].

(**9**): ^{1}H N.m.r. 7.07 (m, 2H, $H_{d,d'}$), 6.63 (m, 2H, $H_{c,c'}$), 5.46 [d, 2H, $J(H_b–H_a)$ 3, $H_{a,a'}$], 5.26 [t, 1H, $J(H_a–H_b)$ 3, H_b], 0.71 [d, 9H, J(P–H) 8, PMe$_3$]; ^{31}P-{^{1}H} n.m.r. δ 8.6 (s); ^{13}C-{^{1}H} n.m.r. δ 124.6 (s, C_d), 123.0 (s, C_c), 115.1 (s, C_{quat}), 82.8 (s, C_a), 58.9 (s, C_b), 17.5 [d, J(P–C) 27, PMe$_3$].

(**10**): ^{1}H N.m.r. δ 5.16 (5 lines, 1H, H_a), 4.95 [q, 2H, $J(H_b–H_a)$ = $J(H_b–H_c)$ 8, $H_{b,b'}$], 4.26 (m, 1H, H_p), 3.90 (m, 2H, $H_{c,c'}$), 3.69 [q, 2H, $J(H_m–H_o)$ = $J(H_m–H_p)$ 7, $H_{m,m'}$], 3.58 (m, 2H, $H_{o,o'}$), 2.16 (s, 3H, Me), 1.99 (m, 2H, $H_{d,d'}$ or $H_{e,e'}$), 1.51 (m, 2H, $H_{e,e'}$ or $H_{d,d'}$); ^{31}P-{^{1}H} n.m.r. δ −21.9 (s); ^{13}C-{^{1}H} n.m.r. δ 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(P–C) 15, PMe$_3$].

(**11**): ^{1}H N.m.r. δ 6.12 (m, 1H, H_f), 4.71 (m, 1H, H_e), 4.41 [d, 7H, J(P–H) 2, η-C$_7$H$_7$], 3.75 (m, 1H, H_g), 3.72 (m, 1H, H_b), ~3.70 (obscured, 2H, H_a and H_h), 2.56 (m, 1H, H_c or H_d), 2.34 (m, 1H, H_d or H_c), 0.51 [d, 9H, J(P–H) 5, PMe$_3$]; ^{13}C-{^{1}H} n.m.r. δ 131.5 (s, C_f), 116.5 (s, C_e), 91.3 (s, C_h or C_a), 84.1 (s, C_g), 83.2 (br. s, η-C$_7$H$_7$), 77.8 (s, C_b), 71.1 (s, C_a or C_h), 34.7 (s, $C_{c,d}$), 16.6 [d, J(P–C) 17, PMe$_3$].

(**12**): ^{1}H N.m.r. 4.55 [d, 7H, J(P–H) 3, η-C$_7$H$_7$], 0.84 [d, 9H, J(P–H) 7, PMe$_3$]; ^{31}P-{^{1}H} n.m.r. δ −12.5 (s); ^{13}C-{^{1}H} n.m.r. δ 87.1 (s, η-C$_7$H$_7$), 20.6 [d, J(P–C) 21, PMe$_3$].

(**13**): ^{1}H N.m.r. 4.50 [tt, 2H, $J(H_p–H_m)$ 7, $J(H_p–H_o)$ 1, H_p], 3.95 (m, 8H, $H_{m,m'}$ and $H_{o,o'}$), 1.93 (s, 6H, tol-*Me*), −0.22 (s, 3H, Nb-*Me*); ^{13}C-{^{1}H} n.m.r. δ 97.0 (s, C_{quat}), 84.5 (s, C_o or C_m), 80.7 (s, C_m or C_o), 78.9 (s, C_p), 21.8 (s, tol-*Me*).

(**14**): ^{1}H N.m.r. δ 4.37 (m, 4 lines, 2H, $H_{m,m'}$), 4.35 [tt, 1H, $J(H_p–H_m)$ 7, $J(H_p–H_o)$ 1, H_p], 4.15 [t, 2H, $J(H_o–H_m)$ 7, $H_{o,o'}$], 2.00 (s, 3H, Me); ^{13}C-{^{1}H} n.m.r. δ 101.7 (s, C_{quat}), 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**): ^{1}H N.m.r. δ 4.69 (m, 1H, H_p), 4.34 (m, 4H, $H_{o,o'}$ and $H_{m,m'}$), 1.95 (s, 3H, Me); ^{13}C n.m.r. δ 98.4 (s, C_{quat}), 86.7 [d, J(C–H) 172, C_o or C_m], 81.5 [d, J(C–H) 172, C_m or C_o], 81.2 [d, J(C–H) 173, C_p], 22.8 [q, J(C–H) 128, Me].

(**16**): ^{1}H N.m.r. δ 8.05 (m, 2H, $H_{b,b'}$ or $H_{c,c'}$), ~7.15 (obscured, 3H, H_a and $H_{c,c'}$ or $H_{b,b'}$), 4.47 [tt, 2H, $J(H_p–H_m)$ 6, $J(H_p–H_o)$ 1, 2H_p], 4.04 [t, 4H, $J(H_o–H_m)$ 6, 4H_o], 3.93 [d, 4H, $J(H_m–H_p)$ 6, 4H_m], 1.77 (s, 6H, 2Me); ^{13}C-{^{1}H} n.m.r. δ 142.1 (s, C_b or C_c), 125.8 (s, C_c or C_b), 123.1 (s, C_a), 98.6 (s, C_{quat}), 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).

The crystal structures of (**5**) and (**10**) are shown in Figures 1 and 2. The η^6-toluene ligands for both (**5**) and (**10**) are bonded symmetrically to the metal with metal to ring$_{centroid}$ distances of 1.827(2) and 1.864(2) Å, respectively. The cycloheptadienyl ligand in (**10**) is bonded *via* C(8)–C(12) with a Nb-plane centre distance of 1.823(2) Å, and is folded along the

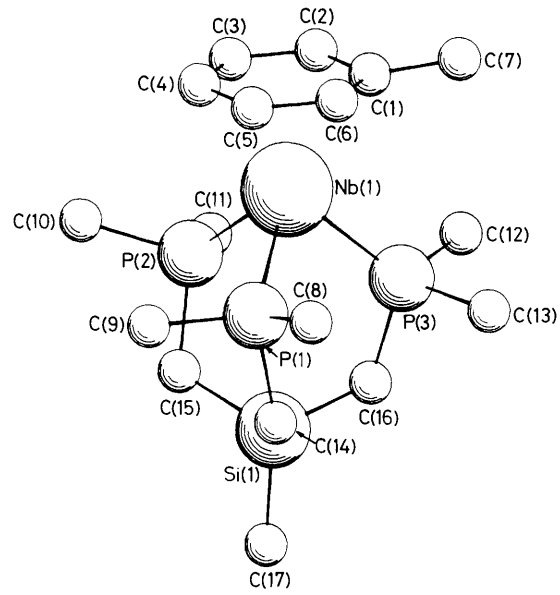


Figure 1. Molecular structure of [Nb(η-C$_6$H$_5$Me)(tmps)] (**5**). Only the important interatomic distances (Å) and angles (°) for one of the unique molecules in the asymmetric unit are given: Nb(1)–P(1) 2.525(2), Nb(1)–P(2) 2.528(2), Nb(1)–P(3) 2.531(2), P(1)–C(8) 1.839(7), P(1)–C(9) 1.836(6), P(1)–C(14) 1.839(6), P(2)–C(10) 1.842(6), P(2)–C(11) 1.840(6), P(2)–C(15) 1.847(6), P(3)–C(12) 1.841(6), P(3)–C(13) 1.835(7), P(3)–C(16) 1.855(7), Si(1)–C(14) 1.876(7), Si(1)–C(15) 1.883(7), Si(1)–C(16) 1.877(7), Si(1)–C(17) 1.869(7), Nb(1)–{C$_6$H$_5$Me plane} 1.827(2); Nb(1)–P(1)–C(14) 117.2(2), Nb(1)–P(2)–C(15) 117.0(2), Nb(1)–P(3)–C(16) 116.4(2).

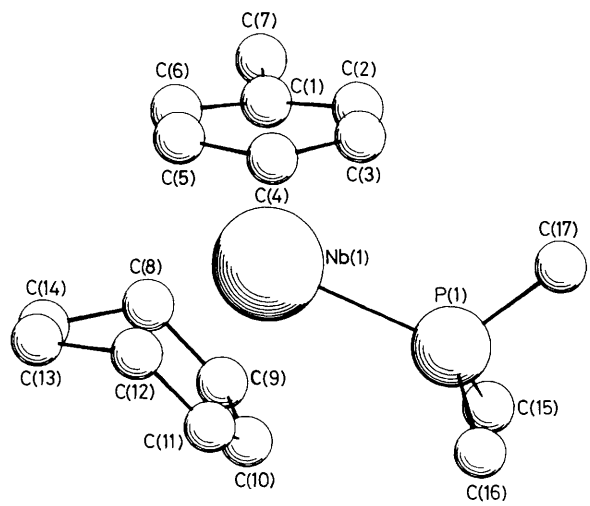


Figure 2. Molecular structure of [Nb(η-C$_6$H$_5$Me)(η^5-C$_7$H$_9$)(PMe$_3$)] (**10**). Important interatomic distances (Å) and angles (°); Nb(1)–P(1) 2.664(1), Nb(1)–C(8) 2.366(2), Nb(1)–C(9) 2.374(2), Nb(1)–C(10) 2.400(2), Nb(1)–C(11) 2.374(2), Nb(1)–C(12) 2.358(2), C(8)–C(9) 1.404(4), C(9)–C(10) 1.399(4), C(10)–C(11) 1.409(4), C(11)–C(12) 1.404(4), C(12)–C(13) 1.511(4), C(13)–C(14) 1.499(4), C(14)–C(8) 1.516(4), Nb(1)–{C(8)–C(12) plane} 1.823(2), Nb(1)–{C(1)–C(6) plane} 1.864(2); C–C–C: (8)–(9)–(10) 122.7(2), (9)–(10)–(11) 126.0(2), (10)–(11)–(12) 124.2(2), (11)–(12)–(13) 124.3(2), (12)–(13)–(14) 115.4(2), (13)–(14)–(8) 115.9(2).

C(8)–C(12) vector by 49.4(2)°. The planes defined by the η^6-toluene ligand and C(8) to C(12) are tilted by 47.1(2)°.

In conclusion, we have shown there to be an extensive new chemistry of η-arene niobium derivatives.

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