Cycloheptatri-ene and -enyl Derivatives of Niobium†

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The new compounds [Nb(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] **1**, [Nb($\eta$-$C_7H_7$)($\eta^4$-$C_7H_8$)($PMe_3$)] **2** and [Nb($\eta$-$C_7H_7$)(CO)$_3$] **4** have been prepared. The 17-electron compound **1** has been crystallographically characterised and contains mutually *trans* tertiary phosphine and chloro ligands. Compound **2** contains the first crystallographically characterised η^4-cycloheptatriene ligand, the structure of which is discussed in relation to its ^{13}C NMR spectrum and the use of inverse-mode (^1H-observed) ^{13}C–^1H shift correlation NMR spectroscopy. Treatment of **1** with magnesium butadiene reagent gives [Nb(η-C_7H_7)(η^4-C_4H_6)(PMe_3)] **3** and photolysis of **4** in the presence of cycloheptatriene gives [Nb(η-C_7H_7)(η^4-C_7H_8)(CO)] **5**. Compound **2** is protonated readily to yield [Nb(η-C_7H_7)(η^5-C_7H_9)(PMe_3)][PF_6] **6**, and reacts with iodomethane to yield paramagnetic [Nb(η-C_7H_7)(PMe_3)$_2$I] **7** which is isomorphous with the analogous 16-electron compound [Zr(η-C_7H_7)(PMe_3)$_2$I], but has an unusually long Nb–I bond. Compound **4** reacts with $Me_2PCH_2CH_2PMe_2$ (dmpe) to give the monomeric [Nb(η-C_7H_7)(dmpe)(CO)] **9**. The analogous compound [Nb(η-C_7H_7)(PMe_3)$_2$(CO)] **10** is prepared by reaction of **4** with PMe_3. The paramagnetic sandwich complexes [Nb(η-C_5H_5)(η-C_7H_7)] **11** and [Nb(η-C_5H_4Me)(η-C_7H_7)] **12** react with 1 equivalent of allyl bromide to yield the diamagnetic bent-sandwich species [Nb(η-C_5H_5)(η-C_7H_7)Br] **13** and [Nb(η-C_5H_4Me)(η-C_7H_7)Br] **14** respectively.

η-Cycloheptatriene and η-cycloheptatrienyl derivatives of the Group 6 metals are well known.[1] More recently a substantial C_7-ring chemistry of the Group 4 metals has been described.[2–5] Here we report the convenient synthesis of new C_7-ring derivatives of niobium. Part of this work has been communicated.[6]

Results and Discussion

A mustard-yellow suspension of [$NbCl_4$(thf)$_2$] in tetrahydrofuran (thf) was treated with 2 equivalents of trimethylphosphine giving a green solution to which an excess of cycloheptatriene was added. The mixture was cooled to −80 °C and 2 equivalents of freshly prepared sodium amalgam were added. From this reaction mixture were isolated green crystals of [Nb(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] **1** in 53% yield. Typically *ca.* 3 g of **1** could be prepared in a one-pot reaction. Characterising data for **1** and for all other new compounds described below are given in Table 1. The ^1H NMR spectrum of **1** in C_6D_6 showed only a signal from residual protio solvent, indicative of paramagnetism. In comfirmation, the ESR spectrum in thf at room temperature showed an isotropic decet [$A(\text{Nb})_{\text{iso}}$ = 145.5 G, g_{iso} = 2.012] due to coupling with the niobium nucleus (spin $I = \frac{9}{2}$). The niobium hyperfine peaks were quite sharp but no other hyperfine structure was detectable.

Single crystals of [Nb(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] **1** were grown from light petroleum by slow cooling to −25 °C and the X-ray crystal structure was determined. A view of the molecular structure is given in Fig. 1, selected bond lengths and angles appear in Table 2, and atomic coordinates for non-hydrogen atoms are given in Table 3. The overall structure is similar to that of the analogous 16-electron zirconium complex [Zr(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$][5] in that six carbons of the cycloheptatriene ring are co-ordinated to the metal centre and that the two phosphine ligands are mutually *trans*. Unfortunately, a more detailed comparison of the various structural parameters of **1** and [Zr(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] is not possible because of considerable disorder in the crystal structure of the latter. The five C–C distances within the essentially planar co-ordinated portion of the C_7 ring do not show the alternating short and long distances which are found in [Mo(η^6-C_7H_8)(CO)$_3$].[7] Lack of alternation is also found for [Zr(η^6-C_7H_8)$_2$][2] and [Zr(*exo*-η^6-$C_7H_7SiMe_3$)(PMe_3)$_2$$I_2$].[4]

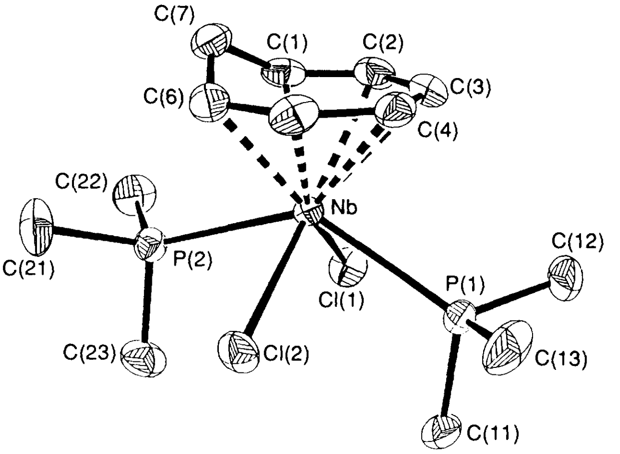

Fig. 1 Molecular structure of [Nb(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] **1** (hydrogen atoms omitted)

Treatment of a thf solution of [Nb(η^6-C_7H_8)(PMe_3)$_2$$Cl_2$] **1** with 2 equivalents of sodium amalgam failed to produce any tractable organometallic products. However, reduction of **1** in thf with sodium amalgam in the presence of a five-fold excess of cycloheptatriene gave, after successive recrystallisations from

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI units employed: G = 10^{-4} T, atm = 101 325 Pa.

Table 1 Analytical and spectroscopic data

Compound	Colour	Analysis[a] (%)			Spectroscopic data[b]
		C	H	Other	
1	Green	37.9 (38.3)	6.2 (6.4)	P 15.0 (15.2) Cl 17.9 (17.4)	ESR (thf, 293 K): decet, $A^{Nb} = 145.5$ G, $g_{iso} = 2.012$ IR: 1509m, 1297m, 1280m, 1270m, 1258m, 1236m, 1181w, 1099 (br), 1018 (br), 956vs (br), 902w, 869w, 851w, 829s, 794s, 736s, 713m, 674m, 508w
2	Lime green	57.7 (58.0)	6.7 (6.9)		^{1}H NMR: 6.21 (t, 1 H, 9, H_h), 4.78 (m, 1 H, H_g), 4.49 [d, 7 H, ^3J(PH) 3, η-C_7H_7], 4.0–3.6 (overlapping m, 4 H, H_{a-d}), 2.60 (d of m, 1 H, H_e or H_f), 2.35 (d of m, 1 H, H_e or H_f), 0.47 [d, 9 H, J(PH) 5, PMe_3] ^{13}C-{^{1}H} NMR: 131.5 (s, C_h), 116.5 (s, C_g), 91.3 (s, C_b or C_c), 84.0 (s, C_b or C_c), 83.1 (br s, η-C_7H_7), 33.4 (s, C_{ef}), 16.5 [d, J(PC) 15, PMe_3] ^{13}C NMR (223 K):[c] 131.4 (d, obscured, C_h), 116.4 (d, 156, C_g), 91.2 (d, 161, C_b or C_c), 83.6 (d, 161, C_b or C_c), 82.8 (br d, 160, η-C_7H_7), 70.7 (br d, 151, C_a or C_d), 67.0 (br d, 150, C_a or C_d), 33.2 (t, 127, C_{ef}), 15.8 [qd, 127, J(PC) 15, PMe_3] ^{31}P NMR (193 K):[c] 4.5 (br s, PMe_3) Mass spectrum (EI): m/z 276 ($M - PMe_3$), 91 (C_7H_7), 76 (PMe_3)
3	Lime green	53.3 (53.5)	6.9 (7.1)		^{1}H NMR: 4.64 (br s, 7 H, η-C_7H_7), 3.88 (m, 2 H, H_c), 2.79 (d, 2 H, 8, H_b), 0.65 (br d, 2 H, 10, H_a), 0.50 [d, 9 H, ^2J(PH) 5, PMe_3] (223 K):[c] 4.60 [d, 7 H, ^3J(PH) 4, η-C_7H_7], 3.82 (m, 2 H, H_c), 2.75 (br d, 2 H, 8, H_b), 0.58 (br d, 2 H, 11, H_a), 0.46 [d, 9 H, J(PH) 5.5, PMe_3] ^{13}C-{^{1}H} NMR: 83.9 (br s), 81.9 (vbr s), 17.8 (br s, PMe_3) ^{13}C NMR (223 K):[c] 83.4 (d, 160, C_c), 81.6 (d, 160, η-C_7H_7), 50.9 (br t, 150 C_{ab}), 17.1 [t of d, J(PC) 16, 121, PMe_3] ^{31}P NMR (193 K):[c] 5.1 (br s, PMe_3)
4	Blue-green	44.7 (44.8)	2.7 (2.6)		^{1}H NMR: 4.35 (s, η-C_7H_7) IR: ν(C≡O) 2003vs, 1934vs Mass spectrum (EI): $m/z = 268$ (M^+), 240 ($M -$ CO), 212 ($M -$ 2CO), 184 ($M -$ 3CO), 91 (C_7H_7), 28 (CO); intense peaks at $m/z = 157, 132, 41$
5	Red	58.9 (59.2)	5.0 (5.0)		^{1}H NMR: 5.83 (t of m, 1 H, 9, H_h), 4.52 (m, 1 H, H_g) [4.3–4.5 (obscured, H_c and H_b) and 4.31 (s, η-C_7H_7), total integral 9 H], 3.58 (m, 1 H, H_a), 3.48 (m, 1 H, H_d), 2.53 (br d, 1 H, ^2J 21, H_e or H_f), 2.18 (d of t, 1 H, ^2J 21, ^1J 4, H_e or H_f) ^{13}C-{^{1}H} NMR: 129.9 (s, C_h), 117.3 (s, C_g), 90.7 (s, C_b or C_c), 87.1 (s, η-C_7H_7), 83.7 (s, C_b or C_c), 70.0[e], 66.9[e], 33.3 (s, C_{ef}) ^{13}C NMR ([$^2H_8$]toluene, 223 K): 129.7 (d, obscured, C_h), 117.1 (d, 155, C_g), 90.3 (d, 161, C_b or C_c), 86.9 (d, 168, η-C_7H_7), 83.3 (d, 159, C_b or C_c), 68.9 (d, 159, C_d), 66.1 (d, 159, C_a), 33.2 (t, 127, C_{ef}) IR: ν(C≡O) 1974 cm^{-1}
6	Yellow	40.6 (41.0)	5.2 (5.1)		^{1}H NMR:[f] 5.96, (br d, 2 H, 10, H_c), 5.17 (m, 1 H, H_e), 5.12 [d, 7 H, J(PH) 5, η-C_7H_7], 5.01 (m, 2 H, H_d), 2.23 (br m, 4 H, H_a and H_b), 1.34 [d, 9 H, J(PH) 7, PMe_3] ^{31}P NMR:[f] −5.5 (s, PMe_3), −146.7 (spt, PF_6^-)
7	Blue	34.0 (33.7)	5.5 (5.4)		IR: 1492m, 1417m, 1300m, 1275m, 1111 (br), 948s (br), 847w, 794m, 780s, 667m ESR:[d] decet, $A^{Nb} = 145.0$ G, $g_{iso} = 1.990$
9	Orange-red	46.2 (46.4)	6.3 (6.4)		^{1}H NMR: 4.72 [t, 7 H, J(PH) 3, η-C_7H_7], 1.01 [d, 6 H, J(PH) 6, H_u or H_d], 0.92 [d, 6 H, J(PH) 6, H_u or H_d] *ca.* 0.87 (m, 4 H, CH_2CH_2) ^{13}C-{^{1}H} NMR: 83.5 (s, η-C_7H_7), 30.0 [t, J(PC) 20, CH_2CH_2], 18.4 (vt, C_u or C_d), 17.6 (vt, C_u or C_d) ^{31}P NMR ([$^2H_8$]toluene, 193 K): 24.7 (br s, dmpe) IR: ν(C≡O) 1785 cm^{-1}
10	Red	45.9 (46.2)	6.7 (6.9)		^{1}H NMR: 4.57 [t, 7 H, J(PH) 3, η-C_7H_7], 0.92 [vt, 18 H, J(PH) 5.5, PMe_3] ^{13}C-{^{1}H} NMR: 84.0 (s, η-C_7H_7), 21.4 [vt, J(PC) 20, PMe_3] ^{31}P NMR (193 K):[d] −15.2 (br s, PMe_3) IR: ν(C≡O) 1779 cm^{-1}
11	Maroon	57.7 (57.9)	4.9 (4.9)		IR: 1420m, 1304w, 1260m, 1232w, 1153w, 1104m, 1011m, 1003m, 949m, 895w, 848m, 800m, 780s Mass spectrum (EI): $m/z = 249$ (M^+) ESR:[d] decet, $A^{Nb} = 33.8$ G, $g_{iso} = 1.988$
12	Maroon	58.8 (59.3)	5.4 (5.4)		IR: 1499w, 1133br, 1038m, 1026m, 949m, 849m, 781s Mass spectrum (EI): $m/z = 263$ (M^+), 91 (C_7H_7) ESR (toluene, 293 K): decet, $A(Nb)_{iso} = 34.0$ G, $g_{iso} = 1.986$
13	Scarlet	43.8 (43.8)	3.5 (3.7)	Br 24.0 (24.3)	^{1}H NMR: 4.91 (s, 5 H, η-C_5H_5), 4.61 (s, 7 H, η-C_7H_7) ^{13}C-{^{1}H} NMR: 98.8 (s, η-C_5H_5), 88.6 (s, η-C_7H_7)

Table 1 (*continued*)

Compound	Colour	*Analysis*[a] (%) C	H	Other	Spectroscopic data[b]
14	Scarlet	46.0 (45.5)	4.1 (4.1)	Br 23.1 (23.3)	^1H NMR: 4.99 (vt, 2 H, 5, η-C_5H_4Me), 4.73 (vt, 2 H, 5, η-C_5H_4Me), 4.70 (s, 7 H, η-C_7H_7), 1.74 (s, 3 H, Me)

[a] Calculated values in parentheses. [b] The NMR spectra were obtained at 25 °C in C_6D_6 unless stated otherwise; data given as chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), relative intensity, coupling constant (Hz), and assignment; for virtual triplets, *J* is the apparent coupling constant; for ^1H and ^{13}C NMR spectra, *J* refers to the ^1H–^1H and ^{13}C–^1H coupling constants respectively. [c] In [$^2H_8$]toluene. [d] In toluene at 293 K. [e] Observed at room temperature using ^{13}C-detected ^{13}C–^1H NMR spectroscopy (see text). [f] In CD_2Cl_2.

Table 2 Selected bond lengths (Å) and angles (°) for [Nb(η^6-C_7H_8)$(PMe_3)_2Cl_2$] **1**

Nb–Cl(1)	2.528(2)	C(1)–C(2)	1.350(8)
Nb–Cl(2)	2.540(1)	C(2)–C(3)	1.405(9)
Nb–P(1)	2.616(1)	C(3)–C(4)	1.421(8)
Nb–P(2)	2.666(2)	C(4)–C(5)	1.397(8)
Nb–C(1)	2.349(5)	C(5)–C(6)	1.398(8)
Nb–C(2)	2.413(5)	C(6)–C(7)	1.489(8)
Nb–C(3)	2.399(5)	C(1)–C(7)	1.542(8)
Nb–C(4)	2.380(6)		
Nb–C(5)	2.406(5)	P(1)–Nb–P(2)	131.9(1)
Nb–C(6)	2.350(5)	Cl(1)–Nb–Cl(2)	108.6(1)

Table 3 Atomic coordinates for [Nb(η^6-C_7H_8)$(PMe_3)_2Cl_2$] **1**

Atom	*x*	*y*	*z*
Nb	0.2168(1)	0.2511(1)	0.7818(1)
Cl(1)	0.3720(1)	0.1852(1)	0.6627(1)
Cl(2)	0.1201(1)	0.4178(1)	0.7047(1)
C(1)	0.3267(5)	0.1779(5)	0.9141(4)
C(2)	0.2686(5)	0.0907(4)	0.8775(4)
C(3)	0.1504(6)	0.0837(4)	0.8560(4)
C(4)	0.0634(5)	0.1642(5)	0.8699(3)
C(5)	0.0704(5)	0.2702(5)	0.9089(3)
C(6)	0.1714(5)	0.3213(5)	0.9418(4)
C(7)	0.2718(5)	0.2623(6)	0.9858(3)
P(1)	0.1002(1)	0.1722(1)	0.6295(1)
C(11)	0.1460(6)	0.2295(6)	0.5100(4)
C(12)	0.1111(7)	0.271(4)	0.6061(4)
C(13)	−0.536(5)	0.1936(6)	0.6296(5)
P(2)	0.3789(1)	0.4052(1)	0.7926(1)
C(21)	0.3536(6)	0.5242(5)	0.8722(5)
C(22)	0.5248(5)	0.3670(6)	0.8283(5)
C(23)	0.4040(6)	0.4682(5)	0.6705(4)

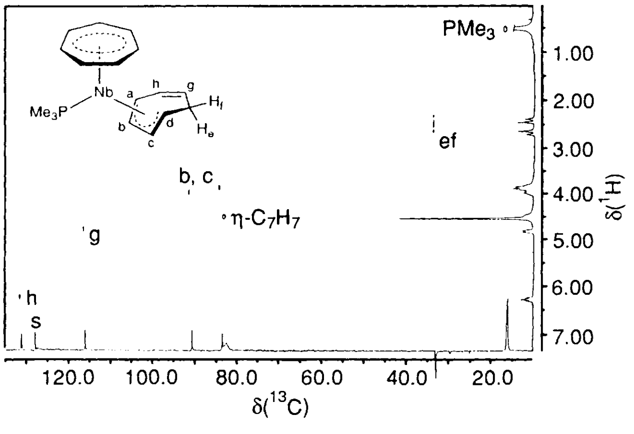


Fig. 2 The ^{13}C–^1H shift correlation NMR spectrum of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2**

light petroleum, lime-green crystals of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2**, in 72% yield. We have recently reported the synthesis of **2** as an inseparable mixture with [Nb(η-C_6H_5Me)(η^5-C_7H_9)(PMe_3)].[8] We set out to develop a more convenient, large-scale synthesis of **2** to facilitate further exploration of the chemistry. It was found that treatment of the green solution formed from [$NbCl_4(thf)_2$] in thf and 2 equivalents of trimethylphosphine with an excess of cycloheptatriene followed by reduction with magnesium turnings at −80 °C gave lime-green crystals of **2** in 45% yield (scale *ca.* 2 g).

The ^{13}C-{^1H} NMR spectrum of compound **2** in C_6D_6 shows resonances at δ 16.5 and 33.4 which may be assigned to the phosphine methyl groups and the methylene group of the η^4-cycloheptatriene ring respectively. There was a rather broad resonance at δ 83.1 assignable to the η-cycloheptatrienyl ring, and further resonances at δ 116.5 and 131.5 in the region expected for unco-ordinated olefinic CH carbons. There were two bands at δ 84.0 and 91.3 assignable to co-ordinated CH groups. However, bands expected for two further ^{13}C resonances from co-ordinated CH groups were not observed. Therefore, it was decided to investigate the ^{13}C NMR spectrum by two-dimensional techniques. The ^{13}C-observed ^{13}C–^1H shift correlation NMR spectrum of a sample of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** in C_6D_6 is shown in Fig. 2. The broad signal at δ 83.1 correlates with the η-C_7H_7 peak in the ^1H dimension. Confirmation of the assignment of the signals at δ 131.5 and 116.5 to the unco-ordinated olefinic groups is straightforward since they show cross-peaks to the signals for H_h and H_g respectively. However no further ^{13}C resonances correlating to the co-ordinated CH region of the ^1H dimension are apparent.

It is well known that ^1H-detected ^{13}C–^1H chemical shift correlation spectroscopy offers a substantial increase in sensitivity over the conventional ^{13}C-detected method.[9] The main disadvantage however has been the dynamic range problem caused by the fact that the majority of protons are bonded to ^{12}C nuclei. Recently, Bax and Subramanian[10] described an elegant solution whereby all the protons bonded to ^{12}C are saturated prior to data acquisition. Using the inverse-mode method, full heteronuclear shift correlation data for high-molecular-weight or sparingly soluble molecules can be obtained in a few hours since ^{13}C satellites in the ^1H NMR spectra have greater signal/noise ratios then the corresponding signals in the directly observed ^{13}C NMR spectrum. A further advantage of the method is described below.

The inverse-mode (^1H-observed) ^{13}C–^1H shift correlation experiment was performed on a sample of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** in [$^2H_8$]toluene. The spectrum is shown in Fig. 3. Comparison with the spectrum in Fig. 2 shows there are two additional cross-peaks which correlate with the shifts of two of the co-ordinated CH protons which have extremely broad signals at δ 67.0 and 70.7 in the ^{13}C dimension. The appropriate portion of the ^{13}C spectrum of the same sample at −80 °C is shown in the inset to Fig. 3, and reveals these two resonances directly. Thus the two ^{13}C resonances for C_a and C_d were broadened into the baseline at room temperature, whilst those for C_b and C_c were sharp. (Consider that the ^1H signals for the protons attached to these carbons are sharp at room temperature, as are the ^{13}C satellites. In the inverse-mode

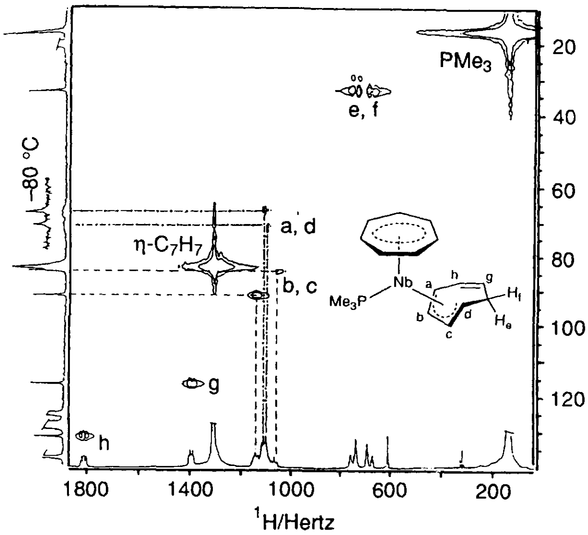


Fig. 3 Inverse mode (^{1}H-observed) ^{13}C–^{1}H shift correlation NMR spectrum of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** in [$^2H_8$]toluene (Inset: ^{13}C-{^{1}H} spectrum of same sample at −80 °C)

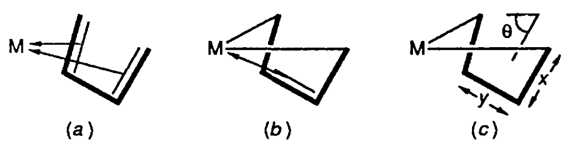
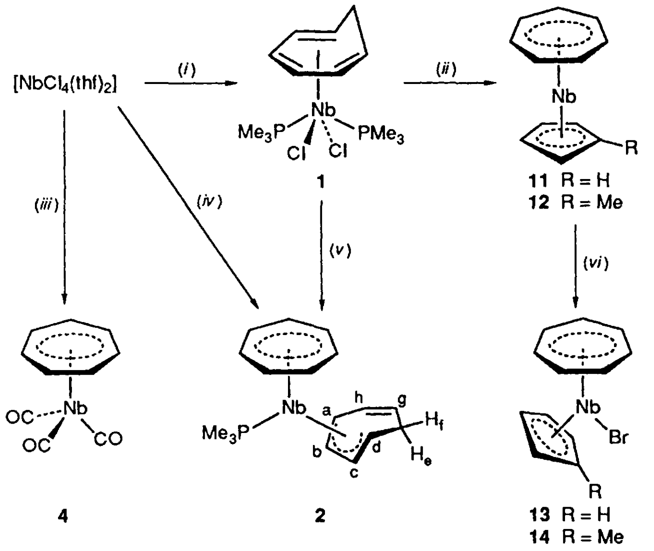


Fig. 4 The structures of co-ordinated butadiene fragments: (*a*) co-ordinated buta-1,3-diene, (*b*) metallacyclopent-3-ene, and (*c*) structural parameters



Scheme 1 *Reagents*: (*i*) $2PMe_3$, C_7H_8 (excess), 2Na/Hg in thf, −80 °C (yield 53%); (*ii*) Na[C_5H_4R] (excess) in thf (80%); (*iii*) C_7H_8 (excess), CO (30 atm), magnesium turnings (excess) in thf, −80 °C (30%); (*iv*) $2PMe_3$, C_7H_8 (excess), magnesium turnings (excess) in thf, −80 °C (45%); (*v*) C_7H_8 (excess), Na/Hg (excess) in thf, −80 °C (72%); (*vi*) allyl bromide (1 equivalent) in toluene, −80 °C (*ca.* 85%)

Table 4 The C–H coupling constants (Hz) for some butadiene complexes of early transition metals

Compound *	$J(C^{1,4}H)$	$J(C^{2,3}H)$
[Ta(η-C_5H_5)(η-dmbd)$_2$][12]	138	—
[Zr(η-C_5H_5)$_2$(η-C_4H_6)][14]	145	165
[Zr(η-C_5H_5)$_2$(η-dmbd)][14]	145	—
[Nb(η-C_5H_5)(η-C_4H_6)Cl_2][11]	145	165
[Nb(η-C_5H_5)(η-dmbd)$_2$][11]	145	—
[Ta(η-C_5H_5)(η-C_4H_6)Cl_2][12]	146	169
[Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2**	150	161
[Nb(η-C_7H_7)(η^4-C_4H_6)(PMe_3)] **3**	150	160
[Nb(η-C_7H_7)(η^4-C_7H_8)(CO)] **5**	159	159

* dmbd = 2,3-Dimethylbuta-1,3-diene.

Table 5 Selected bond lengths (Å) and angles (°) for [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2**

Nb–P	2.6906(6)	C(23)–C(24)	1.397(4)
Nb–C_{ring}	2.34 (mean)	C(24)–C(25)	1.461(4)
$(C–C)_{ring}$	1.40 (mean)	C(25)–C(26)	1.354(5)
C(21)–C(22)	1.405(3)	C(26)–C(27)	1.449(5)
C(22)–C(23)	1.410(4)	C(21)–C(27)	1.499(4)
θ = 86.3		γ = 144.7	

experiment, the ^{13}C signals are observed *via* their coupling to ^{1}H nuclei.) If the broadness of the ^{13}C signals due to C_a and C_d is caused by scalar coupling interaction with the quadrupolar niobium nucleus (spin $I = \frac{9}{2}$), then the C_a–Nb and C_d–Nb bonds must have some σ character. The implication for the structure of **2** is that the η^4-co-ordinated fragment of the cycloheptatriene ligand cannot be described as a regular diene system, as shown in Fig. 4(*a*). Indeed there must be some contribution from a 'metallacyclopentene' structure as shown in Fig. 4(*b*). Thus the method of ^{1}H-detected ^{13}C–^{1}H shift correlation spectroscopy identifies the quadrupolar-broadened ^{13}C signals for C_a and C_d at room temperature. In essence, the appearance of the cross-peaks for these carbons (Fig. 3) may be compared to the observation of ^{31}P coupling to the η-C_7H_7 protons in the one-dimensional ^{1}H NMR spectrum of [Nb(η-C_7H_7)(dmpe)(CO)] (dmpe = $Me_2PCH_2CH_2PMe_2$) (see below) even though the ^{31}P signal itself is not observed at room temperature.

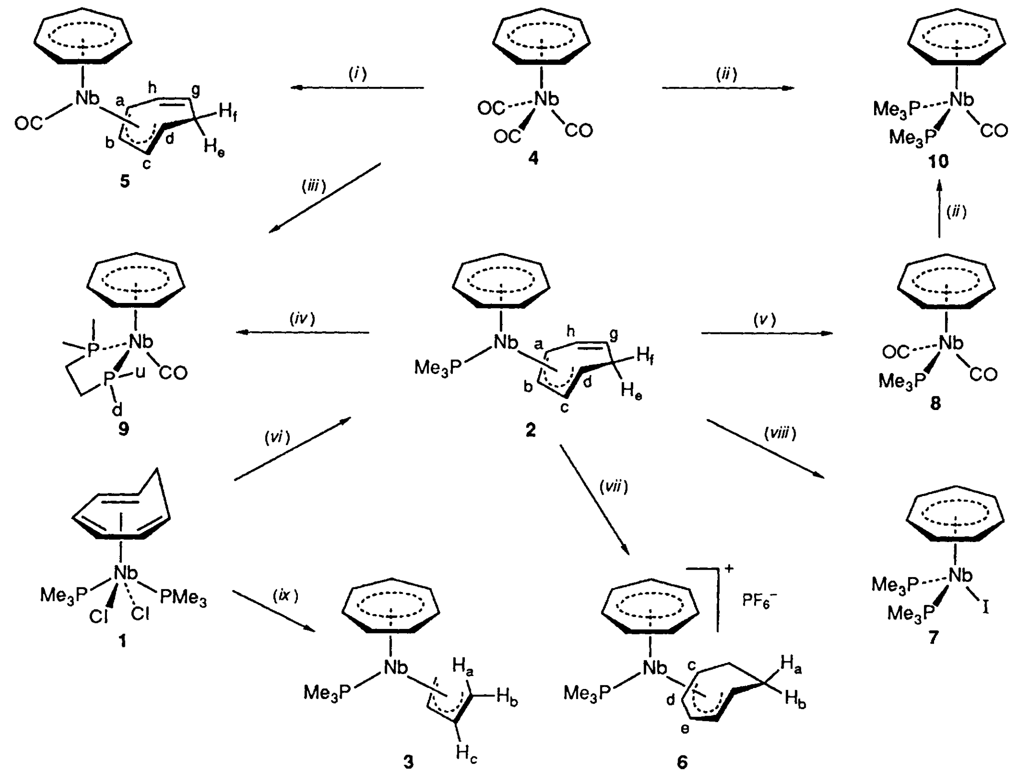
The reactions and the structures proposed for the new compounds are shown in Schemes 1 and 2.

The magnitude of ^1J(CH) for the co-ordinated $C^{1,4}$ carbons of co-ordinated diene ligands is commonly used as an indicator of the bonding in metal–diene systems.[11–13] Table 4 shows the appropriate coupling constants for some representative transition-metal butadiene complexes, with those of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** (obtained at −80 °C) and other new complexes described below. In general, $J(C^{1,4}H) < J(C^{2,3}H)$, although the $J(C^{1,4}H)$ values are much greater than the *ca.* 125 Hz expected for a metallacyclopentene structure or, indeed, for metal alkyl complexes.[15]

The data in Table 4 suggest that the tendency towards a metallacyclopentene structure is less in [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** than in complexes of the type [Nb(η-C_5H_5)(butadiene)Cl_2] and [Nb(η-C_5H_5)(butadiene)$_2$].[11] However, no broadening of the ^{13}C signals due to $C^{1,4}$ was reported in the latter niobium compounds. It seems that the broadening of the lines observed in the ^{13}C NMR spectrum of **2** are not diagnostic of the degree of metallacyclopentene bonding in the (η^4-C_7H_8)Nb fragment.

The X-ray crystal structure of [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** has been determined. A suitable crystal was cleaved from a large single crystal formed on cooling a concentrated [$^2H_8$]toluene solution to −30 °C. Fig. 5 shows two views of the molecular structure, Table 5 lists selected bond lengths and angles, and fractional atomic coordinates are given in Table 6. We believe that **2** represents the first crystallographically characterised compound with a η^4-cycloheptatriene ligand.

Examination of a simple molecular model of free cycloheptatriene suggests that constraining any four carbons of the C_7 ring to be coplanar will induce strain. Nonetheless, the maximum deviations of C(21), C(22), C(23) and C(24) from the least-squares plane defined by these co-ordinated carbons is *ca.* 0.01 Å. The hinge angle γ (Fig. 6) between this plane and that defined by C(24), C(25), C(26), C(27) and C(21)



Scheme 2 *Reagents:* (*i*) C_7H_8 (excess), *hν*, toluene (yield 74%); (*ii*) PMe_3 (excess) in thf (82%); (*iii*) dmpe (1 equivalent) in toluene (*ca.* 100%); (*iv*) CO (1 atm) in toluene then dmpe (1 equivalent) (*ca.* 100%); (*v*) CO (1 atm) in toluene (87%); (*vi*) C_7H_8 (excess), Na/Hg (excess) in thf, −80 °C (72%); (*vii*) NH_4PF_6 in thf (80%); (*viii*) MeI, −80 °C (12%); (*ix*) $[Mg(C_4H_6)(thf)_2]$ in thf (85%)

Table 6 Fractional atomic coordinates for $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2**

Atom	x	y	z
Nb	0.593 49(2)	0.359 686(8)	0.766 46(3)
P	0.330 44(6)	0.370 47(3)	0.612 8(1)
C(1)	0.248 1(3)	0.436 0(1)	0.596 8(7)
C(2)	0.296 1(3)	0.348 3(2)	0.349 3(5)
C(3)	0.203 2(3)	0.331 3(1)	0.726 6(6)
C(11)	0.513 2(3)	0.287 7(1)	0.953 3(4)
C(12)	0.509 2(3)	0.270 3(1)	0.751 5(4)
C(13)	0.606 8(3)	0.273 8(1)	0.618 5(4)
C(14)	0.737 2(3)	0.296 1(1)	0.661 7(5)
C(15)	0.803 4(3)	0.316 3(1)	0.850 6(5)
C(16)	0.749 4(3)	0.324 9(1)	0.031 2(4)
C(17)	0.618 4(3)	0.314 1(1)	0.076 4(4)
C(21)	0.709 4(3)	0.413 6(1)	0.537 6(4)
C(22)	0.592 9(2)	0.440 00(9)	0.584 0(4)
C(23)	0.572 2(3)	0.453 1(1)	0.784 1(4)
C(24)	0.668 8(3)	0.442 9(1)	0.953 5(4)
C(25)	0.815 3(3)	0.450 6(1)	0.972 4(5)
C(26)	0.893 6(3)	0.445 4(1)	0.822 5(6)
C(27)	0.853 1(3)	0.429 0(1)	0.613 4(5)

Table 7 A comparison of structural parameters of co-ordinated butadiene fragments

Compound	x/Å	y/Å	θ/°
$[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2**	1.41	1.41	86.27
$[Zr(\eta\text{-}C_5H_5)_2(\eta\text{-dmbd})]$[14]	1.45	1.39	122.3
$[Nb(\eta\text{-}C_5H_5)(\eta\text{-dmbd})_2]$[11]	1.47	1.37	101.1
$[Ta(\eta\text{-}C_5H_5)(\eta\text{-dmbd})_2]$[12]	1.47	1.35	102.5
$[Ta(\eta\text{-}C_5H_5)(\eta\text{-}C_4H_6)Cl_2]$[12]	1.46	1.38	94.9

(maximum deviation = 0.10 Å) is *ca.* 144.7° (Table 5), compared with 130.6° between the two least-squares planes of the η^5-cycloheptadienyl ligand of $[Nb(\eta\text{-}C_6H_5Me)(\eta^5\text{-}C_7H_9)(PMe_3)]$.[8] Correspondingly the crystallographically located hydrogens H(211) and H(241), which are bonded to the 'hinge' carbons, lie out of the η^4-co-ordinated plane by *ca.* 0.21 and 0.12 Å respectively and towards the niobium atom. The other two hydrogens on the co-ordinated C_4 fragment are also displaced toward the metal, but to a lesser extent (*ca.* 0.09 and 0.11 Å).

Fig. 6 illustrates the distribution of approximate bond lengths around the η^4-C_7H_8 ring. In contrast to the 'short–long–short' bond lengths in the butadiene molecule, the butadiene ligand when co-ordinated to early transition metals often displays a distinct 'long–short–long' alternation of the C–C bond lengths. This implies a contribution from a metallacyclopentene description of the bonding. Erker[14] and Yasuda[11,12] and co-workers have used the angle θ [Fig. 4(*c*) and Table 7] as a measure of metallacyclopentene character in the metal–butadiene bond. Table 7 shows that the angle θ in **2** is rather less than in the other η^4 complexes shown, and also $x \approx y$ [Fig. 4(*c*)]. The above evidence suggests that the contribution of a metallacyclopentene structure in $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** is relatively small.

Wreford and co-workers[16,17] have shown that the magnesium butadiene complex $[Mg(C_4H_6)(thf)_n]$ causes the reductive substitution of metal halides giving η-butadiene complexes. Treatment of the dichloride complex $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ **1** in thf with an excess of the magnesium butadiene complex gave lime-green crystals of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_4H_6)(PMe_3)]$ **3** in 85% yield. The ^1H NMR spectrum in $[^2H_8]$toluene at 223 K gave a doublet at δ 4.60 assignable to a η-C_7H_7 group and a doublet of relative intensity 9 H at δ 0.46 assignable to a trimethylphosphine ligand. The remaining three signals due to the butadiene ligand were assigned with the aid of a series of homonuclear decoupling experiments (Table 1).

A mixture of a suspension of $[NbCl_4(thf)_2]$ in thf and cycloheptatriene was reduced with magnesium metal under 30 atm of carbon monoxide to give a dark solution from which light petroleum-soluble metallic blue platelets of $[Nb(\eta\text{-}C_7H_7)(CO)_3]$ **4** were isolated in 30% yield. Both the crystals and solutions of **4** are highly sensitive to air and water. The

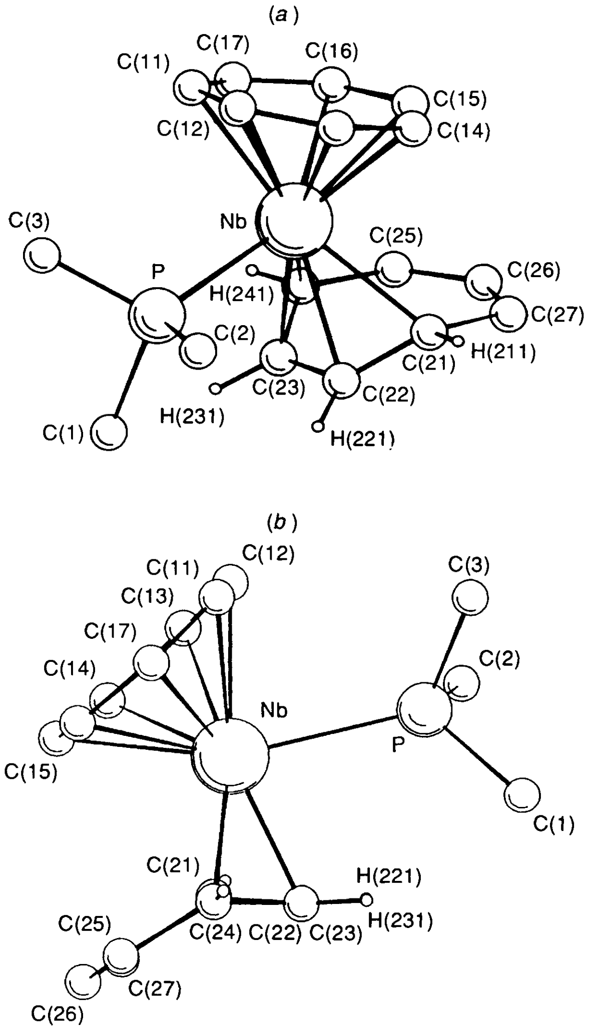


Fig. 5 Molecular structure of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** (most hydrogen atoms omitted)

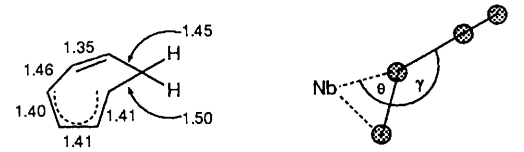


Fig. 6 Structure of the $\eta^4\text{-}C_7H_8$ fragment of compound **2**

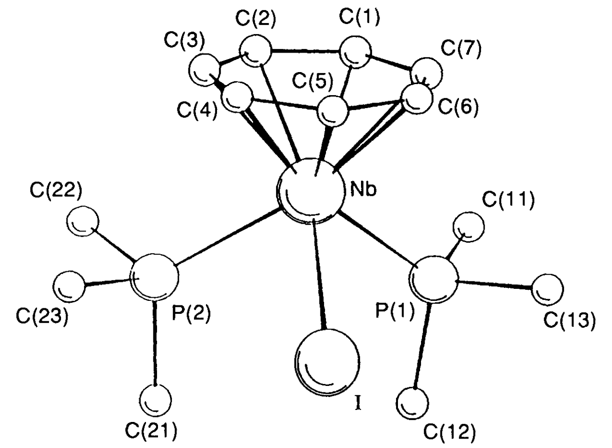


Fig. 7 Molecular structure of $[Nb(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **7** (hydrogen atoms omitted)[6]

Table 8 A comparison of bond lengths (Å) and angles (°) for $[M(\eta\text{-}C_7H_7)(PMe_3)_2I]$; M = Nb **7**[6] or Zr[4]

	Nb	Zr
$(C\text{-}C)_{ring}$(mean)	1.42(2)	1.41(2)
$M\text{-}C_{ring}$(mean)	2.324(1)	2.361(1)
$M\text{-}C_7$(centroid)	1.66	1.71
M-P(1)	2.658(2)	2.811(2)
M-P(2)	2.660(2)	2.807(2)
M-I	2.9130(8)	2.9390(3)
P(1)-M-P(2)	97.46(7)	97.46(3)
P(1)-M-I	81.11(5)	80.81(2)
P(2)-M-I	80.89(5)	80.07(2)

compound sublimes rapidly at 50 °C and 5 × 10^{-2} mbar (5 Pa). The electron impact (EI) mass spectrum shows the parent ion at *m*/*z* = 268, and further intense peaks were observed corresponding to loss of one, two and three carbonyl ligands. The infrared spectrum showed two sharp bands at 2003 and 1934 cm^{-1}, assigned as the a_1 and e ν(C≡O) modes (under the local C_{3v} symmetry).

Previously, King and Hoff[18] reported that $[Nb(\eta\text{-}C_5H_5)(CO)_4]$ reacted with cycloheptatriene under photolysis to give $[Nb(\eta\text{-}C_5H_5)(\eta^4\text{-}C_7H_8)(CO)_2]$. By analogy, a solution of compound **4** in toluene was photolysed in the presence of an excess of cycloheptatriene giving highly sensitive red needles of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(CO)]$ **5**, in 74% yield. The infrared spectrum gave a strong, sharp singlet at 1974 cm^{-1}, consistent with the presence of a single terminal carbonyl ligand. Assignment of the ^1H NMR spectrum was assisted by homonuclear decoupling experiments, and $^{13}C\text{-}^1H$ shift correlation experiments. The $^{13}C\text{-}\{^1H\}$ distortionless enhancement by polarisation transfer (DEPT) NMR spectrum in $[^2H_8]$toluene at room temperature showed resonances attributable to the $\eta\text{-}C_7H_7$ ring and to two unco-ordinated olefinic CH groups. As with **2** however, only two resonances for co-ordinated CH groups of the $\eta^4\text{-}C_7H_8$ ring were observed. However, at 223 K resonances assignable to C_a and C_d appeared. These bands were also observed in the inverse-mode (^1H-observed) $^{13}C\text{-}^1H$ shift correlation spectrum at room temperature from which all the ^{13}C resonances could be assigned unambiguously. The values of ^1J(CH) of 159 Hz for these 1,4-diene carbons (Table 4) indicate a smaller contribution from a metallacyclopentene structure for the co-ordinated 'butadiene' fragment in **5** than in **2** or **3**.

A green solution of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** in thf was treated with 1 equivalent of ammonium hexafluorophosphate giving orange microcrystals of $[Nb(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)(PMe_3)][PF_6]$ **6**. Compound **6** is only sparingly soluble in thf and dichloromethane, and although very soluble in acetonitrile and acetone these solutions rapidly decomposed. Assignment of the ^1H NMR spectrum of a freshly prepared solution in CD_2Cl_2 was made with the aid of a series of homonuclear decoupling experiments. Because of the low solubility and instability in solutions a ^{13}C NMR spectrum could not be obtained.

Treatment of compound **2** with 1 equivalent of iodomethane gave a dark green solution from which large blue paramagnetic crystals of $[Nb(\eta\text{-}C_7H_7)(PMe_3)_2I]$ **7** were isolated in 12% yield. The ESR spectrum in toluene at 293 K showed a decet due to coupling with niobium ($I = \frac{9}{2}$). Single crystals were grown by slow cooling of a toluene solution, and the crystal structure has been determined.[6] The molecular structure is shown in Fig. 7. The analogous 16-electron zirconium compound $[Zr(\eta\text{-}C_7H_7)(PMe_3)_2I]$ is isostructural with **7** (Table 8),[4] and this provides an opportunity to compare the structures of analogous metal complexes in adjacent groups. The unit-cell parameters of the two crystal structures show that they are isomorphous. The two independent Zr–P bond lengths in $[Zr(\eta\text{-}C_7H_7)(PMe_3)_2I]$ are

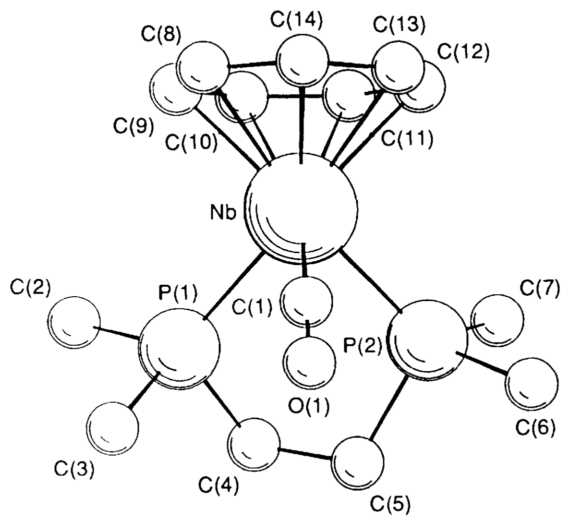


Fig. 8 Molecular structure of [Nb(η-C_7H_7)(dmpe)(CO)] **9** (hydrogen atoms omitted)[6]

ca. 0.15 Å longer than the corresponding Nb–P bonds in **7**. This is as expected since the covalent radius of Zr is 0.11 Å greater than that of Nb.[19] The Zr–I bond length however is only 0.03 Å longer than Nb–I in **7**. Extended-Hückel molecular-orbital calculations on the zirconium compound have shown that the lowest unoccupied molecular orbital (LUMO) is *slightly* antibonding with respect to the Zr–I bond, although in other respects it is essentially a non-bonding d_{z^2} orbital.[20] Presumably, the occupation of a similar orbital in **7** by the extra electron is responsible for the longer Nb–I bond.

The reaction of carbon monoxide with a mixture containing largely [Nb(η-C_7H_7)(η^4-C_7H_8)(PMe_3)] **2** has been reported to give a good yield of the dicarbonyl complex [Nb(η-C_7H_7)(PMe_3)$(CO)_2$] **8**.[8] The reaction was repeated on a sample of pure **2** in C_6D_6 and was complete after 10 mins, giving **8** and cycloheptatriene in the ratio 1:1, as indicated by the ^1H NMR spectrum. No other products or intermediates were observed.

A red solution of [Nb(η-C_7H_7)(PMe_3)$(CO)_2$] **8** in toluene was treated with 1 equivalent of dmpe to give red needles of the monocarbonyl complex [Nb(η-C_7H_7)(dmpe)(CO)] **9**. The tricarbonyl complex **4** also reacted with dmpe to give **9**. The infrared spectrum of a Nujol mull of **9** shows a strong broad peak at 1785 cm^{-1}, which is unusually low for a terminal $\nu(C{\equiv}O)$ stretching mode. The crystal structure of **9** has been determined,[6] and the molecular structure is shown in Fig. 8. The mean Nb–C_{ring} distance of 2.350(1) Å is similar to that in **7** (2.32 Å). The Nb–CO distance [2.061(3) Å] is comparable with that of [Nb(η^5-C_5H_5)$(PMe_3)_2$(CO)Cl(H)] (2.12 Å) and other systems.[21] The bite angle of the dmpe ligand [*i.e.* P(1)–Nb(1)–P(2)] is within the typical range of 75–80°.[22] Hence, [Nb(η-C_7H_7)(dmpe)(CO)] **9** is monomeric in the solid state, and the infrared absorption at 1785 cm^{-1} is due to the terminal C≡O group. Royo and co-workers[23] have reported a series of complexes containing the (η^5-C_5H_5)Nb(CO) fragment, with C≡O stretching vibrations in the range 1675–1930 cm^{-1}. It was noted that the broad absorption at 1675 cm^{-1} in the infrared spectrum of [Nb(η^5-C_5H_5)$(PMe_2Ph)_3$(CO)] suggested the presence of a bridging carbonyl group. However, unusually low $\nu(C{\equiv}O)$ have been reported[24] also for complexes of the type [Nb(η^5-C_5H_5)L_3(CO)] where L represents a neutral two-electron donor ligand, suggesting that [Nb(η^5-C_5H_5)$(PMe_2Ph)_3$(CO)], like **9**, is monomeric.

Treatment of a green solution of [Nb(η-C_7H_7)$(CO)_3$] **4** in thf with an excess of trimethylphosphine gave highly sensitive red crystals of [Nb(η-C_7H_7)$(PMe_3)_2$(CO)] **10**. The infrared spectrum of a Nujol mull of **10** showed a rather broad, intense band at 1779 cm^{-1}. The EI mass spectrum showed no peaks of higher mass than the molecular ion at m/z = 364.

A tetrahydrofuran solution of [Nb(η^6-C_7H_8)$(PMe_3)_2Cl_2$] **1** reacted with excess of sodium cyclopentadienide at room temperature to give a red-brown solution from which maroon crystals of the paramagnetic sandwich complex [Nb(η-C_5H_5)(η-C_7H_7)] **11** were isolated. Groenenboom and co-workers[25] have previously reported an alternative lower-yield synthesis **11**. A similar reaction occurs between [Zr(η^6-C_7H_8)$(PMe_3)_2$-Cl_2] and excess of lithium indenide to give the 16-electron sandwich complex [Zr(η-C_7H_7)(η^5-C_9H_7)].[5] We have also prepared the methylcyclopentadienyl compound [Nb(η-C_5H_4Me)(η-C_7H_7)] **12** in a similar manner as for **11**.

The reaction between [Mo(η-arene)$_2$] and allyl chloride in benzene produces the chloride-bridged dimeric species [{Mo(η-arene)(η^3-allyl)(μ-Cl)}$_2$].[26] This dimer is a precursor to a wide range of complexes containing the (η-arene)Mo fragment.[26–28] Also, it has been shown recently that [Nb(η-C_6H_5Me)$_2$] reacts smoothly with allyl bromide to yield the diamagnetic bent sandwich complex complex [Nb(η-C_6H_5Me)$_2$Br].[8] Indeed the abstraction of halide radicals from alkyl halides by metal-based radical species is well documented.[29] In the hope of making diamagnetic derivatives of **11** and **12**, similar reactions were investigated.

Neither compound **11** nor **12** gives tractable products on treatment with an excess of allyl bromide at room temperature. However, a solution of **11** in toluene at −80 °C containing 1 equivalent of allyl bromide reacted smoothly on warming to room temperature to give scarlet crystals of the bent mixed-ring sandwich compound [Nb(η-C_5H_5)(η-C_7H_7)Br] **13**, in 90% yield. The methylcyclopentadienyl analogue [Nb(η-C_5H_4Me)(η-C_7H_7)Br] **14** was prepared in a similar manner from the allyl bromide and [Nb(η-C_5H_4Me)(η-C_7H_7)] **12**. The scarlet crystals of **13** and **14** are stable in air for a few minutes, but their solutions are air- and water-sensitive. These diamagnetic bent sandwich complexes could be prepared on a scale of *ca.* 1 g.

In conclusion, we have developed convenient routes to the virtually unexplored area of η-cycloheptatriene and η-cycloheptatrienyl derivatives of niobium and shown that the (η-C_7H_7)-Nb fragment can support a variety of auxiliary ligand systems. In a further paper we will describe electrochemical and photoelectron spectroscopic studies of η-cycloheptatrienylniobium complexes.

Experimental

All manipulations and reactions were carried out using standard Schlenk-line techniques under an atmosphere of dinitrogen which was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves. Solvents were pre-dried over activated 5 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium [toluene, light petroleum (b.p. 100–120 °C)] or sodium–potassium alloy [light petroleum (b.p. 40–60 °C), diethyl ether and pentane] under a slow passage of nitrogen. Deuteriated solvents were dried using Na/K alloy (C_6D_6 and [$^2H_8$]toluene) or phosphorus pentaoxide (CD_2Cl_2). Cycloheptatriene (tech., Aldrich) was distilled before use. Celite 545 filtration aid (Koch-Light) was dried at 180 °C overnight before use. Iodomethane was dried over 5 Å molecular sieves then distilled. Ammonium hexafluorophosphate was used as received (Aldrich). The compound [$NbCl_4$(thf)$_2$] was prepared by the method of Manzer.[30] Ultraviolet photolyses were performed using a Hanovia 500 W low-pressure mercury lamp with the sample contained in a quartz ampoule.

Infrared spectra were recorded as Nujol mulls between CsI plates on a Mattson Polaris or on a Perkin-Elmer 1510 FT-IR interferometer, NMR spectra on a Brüker AM-300 [^1H (300), ^{13}C (75.43), ^{31}P (121.44 MHz)] spectrometer, and referenced internally using residual protio solvent resonances (^1H and ^{13}C) relative to tetramethylsilane (δ = 0) or externally using trimethyl phosphate in D_2O (^{31}P). Two-dimensional NMR spectra were acquired using standard Brüker software, and processed using an ASPECT 3000 computer. Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer by Mr. R. Speel of this laboratory, or by the SERC mass spectrometry service, University College, Swansea. Elemental analyses were performed by Analytische Laboratorien, Elbach, Germany. Electron spin resonance spectra were recorded by Dr. A. McCamley at the University of Sussex.

Dichloro(η-cycloheptatriene)bis(trimethylphosphine)niobium **1**.—A suspension of $[NbCl_4(thf)_2]$ (5.0 g, 13 mmol) in thf (250 cm^3) was treated with trimethylphosphine (2.8 cm^3, 27 mmol) to give a green suspension and solution. Cycloheptatriene (20 cm^3, 240 mmol) was added. The mixture was cooled to −80 °C and transferred *via* a wide-bore cannula onto sodium amalgam (0.62 g Na, 27 mmol, 80 g Hg). The mixture was allowed to warm slowly to room temperature with vigorous stirring, which was continued for 8 h. The resultant dark green solution was decanted from the mercury layer and the volatiles were removed under reduced pressure. The resulting brown solid was extracted with toluene (100 + 50 cm^3) and the extracts were evaporated under reduced pressure to give a green-brown solid. This was extracted with light petroleum (b.p. 40–60 °C, 3 × 150 cm^3) and the combined filtered extracts were reduced in volume to 100 cm^3 under reduced pressure, whereupon crystallisation began to occur. The solution was cooled to −80 °C overnight. The green crystals thus formed were filtered off and washed with cold light petroleum (b.p. 40–60 °C, 20 cm^3) and dried *in vacuo* (yield: 2.8 g, 53%).

[(1,2,3,4-η)-η-cycloheptatriene](η-cycloheptatrienyl)(trimethylphosphine)niobium **2**.—*Method A*. A solution of $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ **1** (0.5 g, 1.22 mmol) in thf (50 cm^3) and cycloheptatriene (0.7 cm^3, *ca.* 5 equivalents) was cooled to −80 °C before being transferred onto sodium amalgam (57 mg Na, 2.5 mmol, 10 g Hg). The mixture was allowed to warm to room temperature and was stirred vigorously for 8 h. The resulting dark green solution was decanted away from the mercury layer and the volatiles removed under reduced pressure to give a dark solid. The combined diethyl ether (100 + 50 cm^3) extracts were filtered, and the volatiles were removed under reduced pressure. The resulting green solid was extracted with light petroleum (b.p. 40–60 °C, 2 × 100 cm^3) and the combined extracts filtered, reduced in volume to *ca.* 50 cm^3, filtered again, and placed at −25 °C overnight to give lime-green platelets. These were filtered off and washed with cold light petroleum (b.p. 40–60 °C, 10 cm^3) before drying *in vacuo* (yield 0.31 g, 72%).

Method B. A suspension of $[NbCl_4(thf)_2]$ (5.0 g, 13 mmol) in thf (250 cm^3) and cycloheptatriene (25 cm^3) was treated with trimethylphosphine to give a green solution and suspension. This was cooled to −80 °C and transferred onto magnesium metal (5 g, excess) and stirred vigorously while the mixture warmed to room temperature (r.t.). Stirring was continued for 12 h to give a dark green solution. The supernatant was decanted and the volatiles were removed under reduced pressure to give a dark green solid. This was extracted with diethyl ether (200 + 50 cm^3) and the combined filtered extracts evaporated to dryness. The green solid was extracted with light petroleum (b.p. 40–60 °C, 3 × 100 cm^3) and the combined filtered extracts reduced in volume to 80 cm^3. Cooling to −80 °C overnight afforded green crystals which were washed with cold light petroleum (b.p. 40–60 °C, 20 cm^3). A second crop was obtained in a similar manner (combined yield 2.0 g, 45%).

(η-Butadiene)(η-cycloheptatrienyl)(trimethylphosphine)-niobium **3**.—A solution of $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ **1** (0.50 g, 1.2 mmol) in thf (50 cm^3) was transferred onto an excess of solid 'magnesium butadiene reagent' (0.50 g) and the mixture was stirred for 20 h. The volatiles were removed under reduced pressure and the yellow-brown solid was extracted with diethyl ether (50 + 20 cm^3). The combined filtered extracts were evaporated to dryness. The yellow solid obtained was extracted with light petroleum (b.p. 40–60 °C, 2 × 50 cm^3) and the extracts filtered, reduced in volume to 20 cm^3 and placed at −30 °C to give lime green crystals. These were washed with a small amount of cold light petroleum (b.p. 40–60 °C) and dried *in vacuo* (yield 0.33 g, 85%).

Tricarbonyl(η-cycloheptatrienyl)niobium **4**.—A stainless-steel autoclave (250 cm^3) was charged with $[NbCl_4(thf)_2]$ (4 g, 10.6 mmol) and magnesium (3 g) in a glove-box. A solution of cycloheptatriene (20 cm^3) in thf (130 cm^3) was cooled to −80 °C and added *via* a cannula to the autoclave which was then quickly pressurised to 30 atm with carbon monoxide. After stirring for 24 h the pressure had fallen to 18 atm. The resultant dark red solution was transferred to a Schlenk tube and the volatiles were removed under reduced pressure. The dark solid obtained was extracted with light petroleum (b.p. 40–60 °C, 2 × 100 cm^3) and the combined filtered extracts were reduced in volume under reduced pressure to 20 cm^3, filtered, and cooled to −80 °C. The metallic blue platelets thus formed were washed with a small amount of cold petroleum (b.p. 40–60 °C) and dried *in vacuo* (yield: 0.86 g, 30%).

Carbonyl[(1,2,3,4-η)-cycloheptatriene](η-cycloheptatrienyl)-niobium **5**.—A green solution of $[Nb(\eta\text{-}C_7H_7)(CO)_3]$ **4** (100 mg, 0.37 mmol) in toluene (15 cm^3) and cycloheptatriene (1 cm^3) was placed in a silica glass ampoule. The ampoule was evacuated and the mixture exposed to UV photolysis for 1 h, after which the solution was deep red. The ampoule was re-evacuated and the solution photolysed for 1 h. The red solution was transferred to a Schlenk tube and the volatiles were removed under reduced pressure. Pentane extracts (2 × 30 cm^3) were filtered and combined and the volume was reduced to 10 cm^3. Cooling to −30 °C overnight afforded red needles which were filtered off and washed with a small amount of cold pentane before drying *in vacuo* (yield: 83 mg, 74%).

[(1,2,3,4,5-η)-Cycloheptadienyl](η-cycloheptatrienyl)(trimethylphosphine)niobium Hexafluorophosphate **6**.—A solution of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** (250 mg, 0.71 mmol) in thf (30 cm^3) was treated with solid ammonium hexafluorophosphate (125 mg, 0.77 mmol). An orange microcrystalline precipitate formed over a few minutes which was filtered off, washed with thf (2 × 10 cm^3) and dried *in vacuo* (yield: 0.28 g, 80%).

(η-Cycloheptatrienyl)iodobis(trimethylphosphine)niobium **7**.—A solution of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** (250 mg, 0.71 mmol) in toluene (30 cm^3) was cooled to −80 °C and iodomethane (0.1 cm^3, 1.6 mmol) was added. The mixture was allowed to warm to room temperature with stirring. A flocculent precipitate and dark solution formed over 3 h. The supernatant was filtered and the volatiles were removed under reduced pressure. The dark solid was extracted with toluene (20 cm^3) and the filtered extract reduced in volume to 10 cm^3. Cooling to −25 °C overnight gave dark blue crystals (yield: 39 mg, 12%).

Dicarbonyl(η-cycloheptatrienyl)(trimethylphosphine)niobium **8**.—A solution of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** (1.0 g, 2.8 mmol) in toluene (50 cm^3) was exposed to carbon monoxide (1 atm). A colour change from green to red was observed over 10 min. The mixture was stirred for 1 h and the volatiles were removed under reduced pressure. The red solid was extracted with light petroleum (b.p. 40–60 °C, 2 × 50 cm^3) and the combined filtered extracts were reduced in volume to 30 cm^3. Cooling to −30 °C overnight afforded red crystals which were washed with cold light petroleum (b.p. 40–60 °C) and dried *in vacuo* (yield: 0.77 g, 87%).

Table 9 Crystal data, data collection and processing parameters for $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ **1** and $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2**

	1	**2**
Formula	$C_{13}H_{26}Cl_2NbP_2$	$C_{17}H_{24}NbP$
M	408.1	352.26
Crystal size/mm	0.35 × 0.20 × 0.20	0.20 × 0.40 × 0.40
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a/Å	11.609(3)	9.967(2)
b/Å	12.222(3)	24.824(3)
c/Å	13.271(3)	6.637(4)
β/°		98.03(2)
U	1882.8	1626.1
Z	4	4
D_c/g cm^{-3}	1.44	1.44
μ/cm^{-1}	10.52	7.92
F(000)	836	728
2θ limits/°	3, 60	3, 50
Scan type	2θ–θ	ω–2θ
Total data collected	4176	3817
Total unique data	4011	3633
No. of observations	3118 $[F > 4\sigma(F)]$	2314 $[I > 3\sigma(I)]$
R(merge)	0.0175	0.026
No. of variables	164	192
Obs./variables	19.0	12.1
Weighting scheme	$w^{-1} = \sigma^2(F) + gF^2$	Chebyshev
Weighting coefficients	$g = 0.0006$	4.68, −1.66, 2.53
Maximum, minimum peak in final difference map/e Å^{-3}	0.81, −0.69	0.29, −0.15
R	0.0366 (0.0375)*	0.021
R′	0.0365 (0.0376)*	0.023

* The values in parentheses are for the enantiomorph [*i.e.* with Nb(1) at 0.78, 0.75, 0.22].

[1,2-*Bis(dimethylphosphino)ethane*]*carbonyl*(η-*cycloheptatrienyl*)*niobium* **9**.—A solution of $[Nb(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_8)(PMe_3)]$ **2** (2 g, 5.7 mmol) in toluene (80 cm^3) was exposed to carbon monoxide (1 atm) for 1 h to give a red solution of $[Nb(\eta\text{-}C_7H_7)(PMe_3)(CO)_2]$ **8**. This was treated with dmpe (0.9 g, 6 mmol). An immediate colour change from red to orange accompanied the evolution of a gas. Volatiles were removed under reduced pressure and the residue was dried *in vacuo* at 60 °C to remove the slight excess of dmpe. The orange solid thus formed was found to be pure $[Nb(\eta\text{-}C_7H_7)(dmpe)(CO)]$ **9** by ^{1}H NMR spectroscopy (yield: 2.1 g, 100%), but may be crystallised at −30 °C to give red needles (from light petroleum) or red cubes (from diethyl ether) (yield: 1.9 g, 92%).

Bis(*trimethylphosphine*)(η-*cycloheptatrienyl*)*carbonylniobium* **10**.—A solution of $[Nb(\eta\text{-}C_7H_7)(CO)_3]$ **4** (100 mg, 0.37 mmol) in thf (10 cm^3) was cooled to −196 °C and trimethylphosphine (0.25 g, 3.3 mmol) was condensed in. The mixture was allowed to warm to room temperature under a mercury bubbler and was stirred for 24 h. The colour changed from green to bright red. The volatiles were removed under reduced pressure and the red solid was extracted with pentane (2 × 25 cm^3). The combined filtered extracts were reduced in volume to 10 cm^3 and cooled to −30 °C. Scarlet needles formed overnight which were filtered off and washed with cold pentane (5 cm^3) (yield: 110 mg, 82%).

(η-*Cycloheptatrienyl*)(η-*cyclopentadienyl*)*niobium* **11**.—A solution of $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ **1** (1.0 g, 2.5 mmol) in thf (50 cm^3) was added to solid sodium cyclopentadienide (1.0 g, 11 mmol) and the mixture was stirred for 3 h. The volatiles were removed under reduced pressure and the residue was extracted with toluene (50 cm^3) and filtered. The volume was reduced to 20 cm^3 and light petroleum (b.p. 40–60 °C, 20 cm^3) was added. The solution was filtered again and placed at −80 °C overnight. The red-brown crystals were filtered off and washed with a small amount of cold toluene and dried *in vacuo* (yield: 0.50 g, 80%).

(η-*Cycloheptatrienyl*)(η-*methylcyclopentadienyl*)*niobium* **12**.—A solution of $[Nb(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$ **1** (1.0 g, 2.5 mmol) in thf (50 cm^3) was added to solid sodium methylcyclopentadienide (1.0 g, 10 mmol) and the mixture was stirred for 3 h. The volatiles were removed under reduced pressure and the residue was extracted with light petroleum (b.p. 40–60 °C, 70 cm^3) and filtered. The volume was reduced to 30 cm^3 and the solution was filtered again. Cooling to −25 °C overnight gave maroon crystals which were filtered off and washed with a small amount of cold light petroleum (b.p. 40–60 °C) and dried *in vacuo* (yield: 0.5 g, 80%).

Bromo(η-*cycloheptatrienyl*)(η-*cyclopentadienyl*)*niobium* **13**.—A solution of $[Nb(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ **11** (1.0 g, 4.0 mmol) in toluene (60 cm^3) was cooled to −80 °C and allyl bromide (0.39 cm^3, 4.5 mmol) was added in one portion. The mixture was stirred as it warmed slowly to r.t. After 1 h scarlet needles crystallised from the red solution. These were filtered off and washed with cold toluene (10 cm^3) before drying *in vacuo*. The combined supernatant and washings were reduced in volume to 20 cm^3, filtered and cooled to −30 °C to give a further crop of scarlet needles (combined yield 1.19 g, 90%). The methylcyclopentadienyl analogue $[Nb(\eta\text{-}C_5H_4Me)(\eta\text{-}C_7H_7)Br]$ **14** was prepared in a similar manner from $[Nb(\eta\text{-}C_5H_4Me)(\eta\text{-}C_7H_7)]$ **12** (1.0 g) and allyl bromide (0.35 cm^3) (yield: 85%).

X-Ray Structure Determinations of Compounds **1** *and* **2**.—Crystal data, data collection and processing parameters are given in Table 9. Data were collected at room temperature on a Nicolet R3m/V (for compound **1**) or an Enraf-Nonius CAD4 diffractometer (for **2**) using graphite-monochromated Mo-Kα radiation. Empirical absorptions were applied and the structures solved using Patterson and Fourier difference syntheses and refined using full-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms of **1** were placed in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters. For **2**, all hydrogen atoms were located from Fourier difference syntheses. The positional parameters and isotropic thermal parameters of the hydrogen atoms bonded to C(21), C(22), C(23) and C(24) were refined independently. All other hydrogens were refined 'riding' on their supporting carbon atoms, and an overall isotropic thermal parameter was refined for hydrogen atoms in each of the following ligand groups; (*i*) PMe_3, (*ii*) C_7H_7 and (*iii*) the remainder of the η-C_7H_8 ligand. Crystallographic calculations were carried out using SHELXTL PLUS[31] on a MicroVAX II (for **1**) or using CRYSTALS[32] on a MicroVAX 3800 computer (for **2**).

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

Acknowledgements

We thank the SERC for a quota award (to P. S).

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Received 13*th January* 1992; *Paper* 2/00148I