Halogeno, Hydride, and Alkyl Carbonyl–Monocyclopentadienyl Niobium Derivatives. Crystal and Molecular Structure of $[Nb(\eta\text{-}C_5H_5)Cl(H)(CO)(PMe_3)_2]$†

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The reduction of $[Nb(\eta\text{-}C_5H_5)Cl_2(CO)L_2]$ [L = PMe_3, (**1**); L = PMe_2Ph, (**2**)] with two equivalents of sodium amalgam (10%) yields $[\{Nb(\eta\text{-}C_5H_5)(CO)L_3\}_n]$ [L = PMe_3, (**3**); L = PMe_2Ph, (**4**)]. Complexes (**3**) and (**4**) react with HCl and HBF_4 to give the hydrides $[Nb(\eta\text{-}C_5H_5)Cl(H)(CO)L_2]$ [L = PMe_3, (**5**); L = PMe_2Ph, (**6**)] and $[Nb(\eta\text{-}C_5H_5)H(CO)L_3]BF_4$ [L = PMe_3, (**7**), L = PMe_2Ph, (**8**)], with halogens to give the halides $[Nb(\eta\text{-}C_5H_5)X_2(CO)L_2]$ [X = Cl, L = PMe_3, (**1**); X = Cl, L = PMe_2Ph, (**2**); X = Br; L = PMe_3, (**9**); X = Br, L = PMe_2Ph, (**10**); X = I, L = PMe_3, (**11**); X = I, L = PMe_2Ph, (**12**)], and with MeI to give the alkyls $[Nb(\eta\text{-}C_5H_5)Me(CO)(PMe_3)_3]I$ (**13**) and $[Nb(\eta\text{-}C_5H_5)I(Me)(CO)(PMe_2Ph)_2]$ (**14**). Spectroscopic (i.r. and n.m.r.) data are provided for all these compounds. The *X*-ray crystal and molecular structure of (**5**) has been determined [monoclinic, space group $P2_1/a$, with a = 12.662(6), b = 10.562(3), c = 13.168(6) Å, β = 92.84(1)°, and Z = 4]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods to R = 0.044 for 1 957 observed reflections. The structure was consistent with that expected from spectroscopic observations. The molecule shows a pseudo-octahedral arrangement with CO, Cl, and both PMe_3 ligands occupying equatorial positions. The spectroscopic data infer that the hydride ligand occupies an axial position *trans* to the $\eta\text{-}C_5H_5$ ring.

Reported methods[1] to isolate $[Nb(\eta\text{-}C_5H_4R)Cl_4]$ and $[Nb(\eta\text{-}C_5H_4R)(CO)_4]$ in high yields provide excellent possibilities to develop the chemistry of monocyclopentadienyl niobium derivatives. New monocyclopentadienyl niobium(III) complexes have been previously isolated by Na–Hg reduction of niobium-(IV) and -(V) derivatives.[2] Here we report the isolation and characterization of new halogeno, hydride, and alkyl carbonyl–monocyclopentadienyl niobium-(I) and -(III) derivatives, together with the *X*-ray crystal structure of $[Nb(\eta\text{-}C_5H_5)Cl(H)(CO)(PMe_3)_2]$.

Results and Discussion

The complexes $[Nb(\eta\text{-}C_5H_5)Cl_2(CO)L_2]$ [L = PMe_3, (**1**); L = PMe_2Ph, (**2**)] were prepared as reported.[2] The reduction of (**1**) and (**2**) with two equivalents of Na–Hg (10%) in tetrahydrofuran (thf), in the presence or absence of carbon monoxide (1 atm), gives red-purple solutions which on evaporation rendered $[\{Nb(\eta\text{-}C_5H_5)(CO)L_3\}_n]$ [L = PMe_3, (**3**); L = PMe_2Ph, (**4**)]. Complex (**3**) could not be isolated as a solid but it was spectroscopically characterized in the deep purple oil obtained, whereas complex (**4**) is a deep purple crystalline solid; both are very air-sensitive compounds. The additional phosphine required for these complexes to be formed probably arises from decomposition of the intermediate '$Nb(\eta\text{-}C_5H_5)(CO)L_2$', even when the reduction is carried out in the presence of CO. If stirring of these purple solutions is continued they become orange and by evaporation give orange crystals of (**5**) and (**6**) with yields highly dependent on reaction times and solvent. The formation of these compounds may be explained as the result of the known base character[3,4] of Nb^I which is slowly protonated in the presence of small amounts of water; then, addition of the halide present displaces one phosphine, according to equation (1). The same complexes can also be obtained in higher yields by addition of HCl to the intermediate purple solutions of (**3**) and (**4**). In the same way the corresponding cationic complexes (**7**) and (**8**) were obtained using HBF_4, in this case without displacement of the ligand.

$$[Nb(\eta\text{-}C_5H_5)(CO)L_3] \xrightarrow[-OH^-]{H_2O} [Nb(\eta\text{-}C_5H_5)H(CO)L_3]^+ \xrightarrow[-L]{Cl^-} [Nb(\eta\text{-}C_5H_5)Cl(H)(CO)L_2] \quad (1)$$

L = PMe_3, (**5**); L = PMe_2Ph, (**6**)

The reported hydride derivatives are soluble in thf and dichloromethane and insoluble in diethyl ether and n-hexane. They are air-sensitive solids which can be stored unchanged under nitrogen. Their solutions decompose even under nitrogen to give oily residues which were not investigated.

The treatment of thf solutions of complexes (**3**) and (**4**) with halogens (Cl_2, Br_2, I_2) and MeI in a molar ratio 1:1 yields neutral dihalogeno and iodo–methyl niobium(III) derivatives, according to equation (2), whereas the cationic complex [Nb(η-

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† Carbonyl(chloro)(η-cyclopentadienyl)hydridobis(trimethylphosphine)niobium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Analytical* and physical properties of monocyclopentadienyl niobium complexes

Complex	Analysis (%) C	Analysis (%) H	Colour	Yield (%)
(4) $[Nb(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)_3]$	59.8 (60.0)	6.5 (6.3)	Red-purple	60
(5) $[Nb(\eta\text{-}C_5H_5)Cl(H)(CO)(PMe_3)_2]$	38.7 (38.5)	7.3 (6.4)	Red-orange	40
(6) $[Nb(\eta\text{-}C_5H_5)Cl(H)(CO)(PMe_2Ph)_2]$	52.5 (53.0)	6.1 (5.6)	Red-orange	45
(7) $[Nb(\eta\text{-}C_5H_5)H(CO)(PMe_3)_3]BF_4$	34.6 (35.7)	6.6 (6.5)	Orange	62
(8) $[Nb(\eta\text{-}C_5H_5)H(CO)(PMe_2Ph)_3]BF_4$	51.4 (52.3)	5.7 (5.8)	Orange	58
(9) $[Nb(\eta\text{-}C_5H_5)Br_2(CO)(PMe_3)_2]$	28.2 (28.9)	4.9 (4.6)	Red	55
(10) $[Nb(\eta\text{-}C_5H_5)Br_2(CO)(PMe_2Ph)_2]$	42.1 (42.5)	4.0 (4.3)	Red	50
(11) $[Nb(\eta\text{-}C_5H_5)I_2(CO)(PMe_3)_2]$	24.9 (24.3)	4.1 (3.8)	Red	58
(12) $[Nb(\eta\text{-}C_5H_5)I_2(CO)(PMe_2Ph)_2]$	37.5 (36.9)	4.3 (3.8)	Red	58
(13) $[Nb(\eta\text{-}C_5H_5)Me(CO)(PMe_3)_3]I$	32.4 (32.5)	5.9 (5.4)	Orange	50
(14) $[Nb(\eta\text{-}C_5H_5)I(Me)(CO)(PMe_2Ph)_2]$	44.3 (45.7)	5.1 (4.9)	Orange	35

* Calculated values are given in parentheses.

Table 2. Selected i.r. data (cm^{-1}) for monocyclopentadienyl niobium compounds (Nujol mulls)

Complex	ν(CO)	ν(Nb–H)	ν(Nb–Cl)	BF_4^-
(3)	1 680s,br			
(4)	1 675s,br			
(5)	1 810vs	1 665w	265w	
(6)	1 800vs	1 635w	255m	
(7)	1 885vs	1 665w		1 000—1 100s,br
(8)	1 900vs	1 740w		1 000—1 100s,br
(9)	1 910vs (1 935vs)*			
(10)	1 925vs (1 940vs)*			
(11)	1 880vs (1 920vs)*			
(12)	1 930vs (1 930vs)*			
(13)	1 925vs			
(14)	1 890vs			

* In chloroform solution.

$$[Nb(\eta\text{-}C_5H_5)(CO)L_3] + XY \longrightarrow [Nb(\eta\text{-}C_5H_5)XY(CO)L_2] + L \quad (2)$$

X = Y = Cl, L = PMe_3, **(1)**; X = Y = Cl, L = PMe_2Ph, **(2)**;
X = Y = Br, L = PMe_3, **(9)**; X = Y = Br, L = PMe_2Ph, **(10)**;
X = Y = I, L = PMe_3, **(11)**; X = Y = I, L = PMe_2Ph, **(12)**;
X = Me, Y = I, L = PMe_2Ph, **(14)**

$C_5H_5)Me(CO)(PMe_3)_3]I$ **(13)** was obtained from the reaction of **(3)** with MeI. Analogous oxidative additions of monocyclopentadienyl niobium(I) derivatives have been previously reported.[5]

All these compounds are air-sensitive red or orange crystalline solids, the neutral complexes being soluble in toluene, thf, chloroform, and dichloromethane and insoluble in alkanes, whereas **(13)** is insoluble in most organic solvents and soluble in dichloromethane and acetone. The solutions decompose to give white solids which were not investigated. According to n.m.r. data, complex **(13)** is believed to be in equilibrium with the neutral complex $[Nb(\eta\text{-}C_5H_5)I(Me)(CO)(PMe_3)_2]$ in dichloromethane.

Similar reactions of thf solutions of **(3)** and **(4)** with CH_3COCl, PPh_2Cl, and C_6F_5Br in a molar ratio 1:2 give the dihalogeno complexes $[Nb(\eta\text{-}C_5H_5)X_2(CO)L_2]$ (X = Cl or Br) probably by radical insertion processes.[6] No reaction was observed with neopentyl bromide and chloro(trimethylsilyl)methane even when an excess of these reagents was used. Analytical data for the monocyclopentadienyl niobium compounds are reported in Table 1. All the niobium-(I) and -(III) derivatives are diamagnetic compounds at room temperature.

Infrared Spectroscopy.—The i.r. spectra of the monocyclopentadienyl niobium compounds show the absorptions expected for an $\eta\text{-}C_5H_5$ ligand.[7] The i.r. spectra of complexes **(3)** and **(4)** show the ν(CO) stretching vibration (see Table 2) at *ca.* 1 700 cm^{-1} suggesting the presence of a bridging carbonyl group, although a definitive assignment cannot be made because unusual low frequencies have been reported[4] for monocyclopentadienyl carbonyl niobium(I) derivatives containing terminal CO groups. The hydride derivatives **(5)**—**(8)** show a weak absorption in the region 1 635—1 740 cm^{-1} due to the ν(Nb–H) stretching vibration (see Table 2) according with reported data.[8] The low values for these absorptions are reasonable for these earlier transition metal complexes. The ν(CO) stretching vibration for complexes **(5)**—**(14)** is observed as an intense absorption in the region 1 800—1 940 cm^{-1} (see Table 2) in agreement with reported[2] data for other carbonyl monocyclopentadienyl niobium(III) compounds. The position of this band is related to the different π-acceptor character of the phosphine (PMe_3 or PMe_2Ph) and the electronegativity of the remaining substituents (hydride, bromide, iodide). All the i.r. spectra show absorptions due to the co-ordinated phosphine; complexes **(7)** and **(8)** also show absorptions due to the BF_4^- anion (Table 2).

N.M.R. Spectroscopy.—The ^1H n.m.r. spectra show resonances due to the $\eta\text{-}C_5H_5$ protons (Table 3) as a triplet and a broad unresolved singlet respectively for complexes **(3)** and **(4)**. Two doublets due to the methyl phosphine protons are observed for **(3)** and three doublets and a complex multiplet respectively due to the methyl and phenyl protons are observed for **(4)**. The absence of virtual coupling[2] of the methyl protons in **(3)** and **(4)** suggests that the three phosphines occupy *cis* positions. A pseudo-octahedral arrangement may be considered as the most probable dimeric structure with two carbonyl bridges, although a definitive assignment cannot be made. Phosphorus-31 n.m.r. spectra of both complexes **(3)** and **(4)** exhibit a singlet as a broad signal due to the high ^{93}Nb quadrupolar moment[9] (see Table 3). A triplet for $\eta\text{-}C_5H_5$ protons and a triplet with appreciable broadening due to high ^{93}Nb quadrupolar moment for the hydride ligand both coupled with the phosphorus atoms are observed for **(5)** and **(6)**. The chemical shifts for the hydride ligands are different from those previously reported for other cyclopentadienyl niobium hydride derivatives, *e.g.* $[Nb(\eta\text{-}C_5H_5)H(CO)(Me_2PCH_2CH_2PMe_2)]PF_6$,[6] but similar to that reported by Mayer and Bercaw[10] for $[Ta(\eta\text{-}C_5H_5)Cl(H)(CO)(PMe_3)_2]$. The location of the hydride ligand *trans* to $\eta\text{-}C_5H_5$ in the pseudo-octahedral arrangement, as shown by the *X*-ray crystal structure of **(5)** (below), may explain the displacement downfield. The resonances due to the methyl protons of the

Table 3. Proton and ^{31}P n.m.r. spectra for monocyclopentadienyl niobium compounds

	$^{1}H^{a}$				$^{31}P^{b}$
Complex	δ/p.p.m.		J(P–H)/Hz	Assignment	δ/p.p.m.
(3)^c	4.80	(5,t)	0.8	η-C_5H_5	13 (br)
	4.95	(18,d)	4.5	PMe_3	
	0.83	(9,d)			
(4)^c	1.16	(5,s)		η-C_5H_5	6 (br)
	1.70	(6,d)	5.1	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	
	6.85—7.59	(6,d)	5.5		
	4.78	(6,d)	6.3		
	1.12	(15,cm)		$\mathrm{PMe}_2\mathit{Ph}$	
(5)^c	2.95	(5,t)	1.9	η-C_5H_5	−12 (br)
	4.58	(18,t)	3.0	PMe_3	
	1.58	(1,t)	30.0	Nb–H	
(6)^c	1.62	(5,t)	2.3	η-C_5H_5	2 (br)
	3.51	(6,t)	3.0	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	
	7.38—7.88	(6,t)	3.8		
	4.99	(1,t)	30.0	Nb–H	
	1.50	(10,cm)		$\mathrm{PMe}_2\mathit{Ph}$	
(7)^d	4.95	(5,s)		η-C_5H_5	
	1.22, 1.61	(27,m)		PMe_3	
(8)^d	7.35	(5,s)		η-C_5H_5	20 (br)
		(18,m)		$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	
		(15,cm)		$\mathrm{PMe}_2\mathit{Ph}$	
(9)^c	4.54	(5,t)	2.3	η-C_5H_5	−15 (br)
	1.24	(18,t)	3.7	PMe_3	
(10)^c	4.28	(5,s,br)		η-C_5H_5	−4 (br)
	1.80	(6,t)	3.8	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	
	1.98	(6,t)	4.1		
	6.90—7.63	(10,cm)		$\mathrm{PMe}_2\mathit{Ph}$	
(11)^c	4.57	(5,t)	2.2	η-C_5H_5	−27 (br)
	1.36	(18,t)	3.7	PMe_3	
(12)^c	4.25	(5,t)	2.3	η-C_5H_5	−20 (br)
	2.12	(6,t)	4.1	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	
	1.92	(6,t)	3.8		
	6.85—7.13	(10,cm)		$\mathrm{PMe}_2\mathit{Ph}$	
(13)^d	4.83	(5,t)	2.4	η-C_5H_5	
	1.29	(18,t)	3.5	PMe_3	
	0.27	(3,t)	11.7	Nb–Me	
(14)^d	4.54	(5,t)	2.6	η-C_5H_5	
	1.62	(6,t)	3.4	$\mathrm{P}\mathit{Me}_2\mathrm{Ph}$	
	1.46	(6,t)	3.6		
	6.98—7.30	(10,cm)		$\mathrm{PMe}_2\mathit{Ph}$	
	2.32	(3,t)	1.6	Nb–Me	

[a] Internal standard $SiMe_4$; values given are intensities; s = singlet, d = doublet, t = triplet, m = multiplet, cm = complex multiplet, br = broad. [b] External standard H_3PO_4. [c] In C_6D_6. [d] In CD_2Cl_2.

phosphines appear as a pseudo-triplet and two overlapped pseudo-triplets in complexes (**5**) and (**6**) respectively, suggesting that the phosphines are located in *trans* positions in the equatorial plane of a pseudo-octahedral arrangement. The ^{31}P n.m.r. spectra of these complexes also exhibit a broad singlet (Table 3).

Complexes (**7**) and (**8**) show a singlet due to the η-C_5H_5 protons, however it is not possible to assign the hydride ligand resonance, even when the spectrum is recorded at low temperature, because of broadening of the signal due to coupling with niobium and no equivalent phosphorus atoms. One or two multiplets are observed also for the methyl protons in complexes (**7**) and (**8**) respectively (Table 3). The ^{31}P n.m.r. spectrum of complex (**8**) shows a broad singlet.

The ^1H n.m.r. spectra of complexes (**9**)—(**12**) show the resonance due to the η-C_5H_5 protons as a triplet coupled with the phosphorus atoms. Complexes (**9**) and (**11**) show a pseudo-triplet due to the methyl protons of the PMe_3 ligands[2] and (**10**) and (**12**) show multiplets with patterns depending on the solvent and the resolution of the spectrometer. These multiplets are the result of overlapping the two expected triplets.[2] The experimental and simulated spectra for complex (**12**) agree very well. Complexes (**9**)—(**12**) exhibit a broad singlet in the ^{31}P n.m.r. spectra (Table 3). According with these data a pseudo-octahedral arrangement with the η-C_5H_5 ring and a halogen atom occupying the axial positions and the phosphines in *trans* positions in the equatorial plane may be proposed.

The ^1H spectra of complexes (**13**) and (**14**) show the resonance due to the η-C_5H_5 protons as a triplet coupled with the phosphorus atoms. The presence of a doublet corresponding to free PMe_3 along with a pseudo-triplet for methyl protons (consistent with the presence of two phosphines in *trans* positions) suggests that in solution complex (**13**) replaces two phospines by I^-, according to equation (3). The ^1H n.m.r.

$$[\mathrm{Nb}(\eta\text{-}C_5H_5)\mathrm{Me}(\mathrm{CO})(\mathrm{PMe}_3)_3]^+\mathrm{I}^- \rightleftharpoons [\mathrm{Nb}(\eta\text{-}C_5H_5)\mathrm{I}(\mathrm{Me})(\mathrm{CO})(\mathrm{PMe}_3)_2] + \mathrm{PMe}_3 \quad (3)$$

spectrum of (**13**) also shows a triplet resonance for the methyl group coupled to two equivalent phosphorus atoms. The resonance of the phosphine methyl protons and the methyl group appear as two pseudotriplets and a triplet respectively in complex (**14**). The last one is shifted downfield probably as a consequence of a *trans* situation to the η-C_5H_5 ring in a pseudo-octahedral arrangement. It was not possible to record the ^{31}P n.m.r. spectra for complexes (**13**) and (**14**) as they are unstable for long periods in solution.

Crystal Structure of [Nb(η-C_5H_5)Cl(H)(CO)(PMe_3)$_2$] (**5**).—A view of the molecule with the numbering scheme adopted is shown in the Figure. Atomic co-ordinates for the non-hydrogen atoms are listed in Table 4. Important bond distances and angles are listed in Table 5.

The molecule shows a pseudo-octahedral arrangement fairly common in monocyclopentadienyl niobium(III) 18-electron species,[11] with CO, Cl, and both PMe_3 ligands occupying equatorial positions and the η-C_5H_5 ring and the H(11) atom occupying apical positions. The Nb atom is not situated in the equatorial plane of the pseudo-octahedral arrangement [sum of the four equatorial angles with Nb as apex is 329.6(3)°]. This is also true but less pronounced in [{Nb(η-C_5H_4Me)Cl_3(OH_2)}$_2$(μ-O)],[12] as the more voluminous O atom replaces H in the apical position of the title compound.

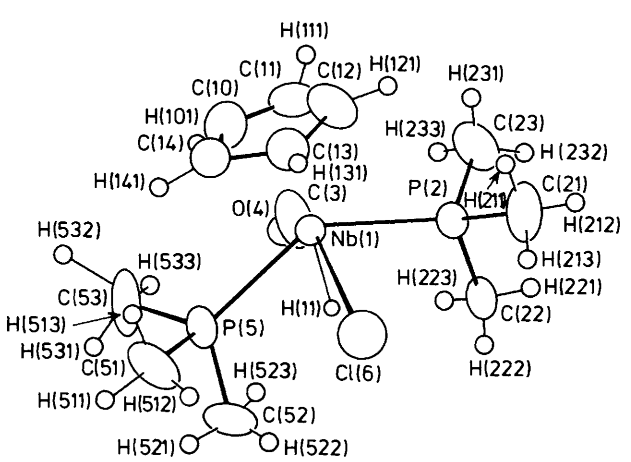

Figure. View of the complex [Nb(η-C_5H_5)Cl(H)(CO)(PMe_3)$_2$]

Table 4. Fractional atomic co-ordinates with e.s.d.s in parentheses for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*
Nb(1)	0.178 2(1)	0.028 6(1)	0.225 3(1)
P(2)	0.172 6(2)	0.208 8(2)	0.356 5(2)
C(21)	0.299 0(8)	0.278 2(11)	0.404 8(8)
C(22)	0.113 8(9)	0.163 5(10)	0.472 5(7)
C(23)	0.093 5(11)	0.348 4(11)	0.323 9(12)
C(3)	0.011 2(8)	0.044 3(8)	0.212 6(8)
O(4)	−0.065 8(7)	0.059 3(7)	0.196 4(7)
P(5)	0.143 0(2)	−0.211 3(2)	0.208 8(2)
C(51)	0.251 8(7)	−0.318 8(10)	0.203 1(9)
C(52)	0.073 5(9)	−0.271 1(8)	0.313 1(8)
C(53)	0.059 3(8)	−0.263 4(11)	0.100 4(9)
Cl(6)	0.305 9(2)	−0.053 6(3)	0.363 6(2)
C(10)	0.168 9(11)	0.054 5(13)	0.048 9(8)
C(11)	0.177 3(11)	0.169 3(11)	0.085 8(10)
C(12)	0.275 0(13)	0.186 3(11)	0.137 6(8)
C(13)	0.328 4(9)	0.066 5(15)	0.124 5(8)
C(14)	0.263 1(11)	−0.008 6(12)	0.068 0(9)

The molecule shows an approximate mirror plane perpendicular to the P–P axis. The cyclopentadienyl ring is aligned accordingly with the C(13) atom over the Nb–Cl bond (Figure). This behaviour has been previously observed in [Ta(η-C_5H_5)Cl_2(CO)(PMe_2Ph)$_2$].[11] This fact could be a consequence of an interaction between the asymmetric component of the cyclopentadienyl e_2 orbital and the d_{xy} orbital of the metal.[13]

The Nb–C,Nb–P, and Nb–Cl distances are similar to those previously described,[12] and the distances and angles involving the Nb–CO system are in good agreement with those found by Herrmann *et al.*[14] The cyclopentadienyl ring is nearly planar [mean torsion angles 2.89(6)°], the average bond length is 1.38(2) Å, and the mean bond angle is 107.7(7)°. The minimum distance between the Nb atom and the C atoms of the cyclopentadienyl ring corresponds to Nb–C(10) [2.336(11) Å], which is the atom with the greatest deviation of the ring plane [0.023(7) Å]. The distance of Nb from the ring plane is 2.076(7) Å, and the minimum angle between the Nb–ring centroid axis and the ring plane is 88.59(5)°.

Experimental

All operations were carried out under vacuum or in an inert atmosphere using Schlenk type glassware. Solvents were dried, distilled under N_2 and degassed before use. $HBF_4 \cdot Et_2O$ and

Table 5. Bond distances (Å), bond angles (°), and torsion angles (°)

Nb(1)–P(2)	2.573(3)	Nb(1)–C(3)	2.119(10)	P(2)–C(22)	1.797(10)	P(2)–C(23)	1.823(13)
Nb(1)–P(5)	2.581(2)	Nb(1)–Cl(6)	2.528(3)	C(3)–O(4)	1.000(13)	P(5)–C(51)	1.790(10)
Nb(1)–C(10)	2.336(11)	Nb(1)–C(11)	2.363(13)	P(5)–C(52)	1.783(11)	P(5)–C(53)	1.821(11)
Nb(1)–C(12)	2.398(13)	Nb(1)–C(13)	2.406(11)	C(10)–C(11)	1.309(18)	C(10)–C(14)	1.377(20)
Nb(1)–C(14)	2.413(13)	P(2)–C(21)	1.845(11)	C(11)–C(12)	1.395(20)	C(12)–C(13)	1.449(20)
				C(13)–C(14)	1.344(18)		

P(5)–Nb(1)–Cl(6)	79.9(1)	C(3)–Nb(1)–Cl(6)	133.2(3)	Nb(1)–P(2)–C(21)	118.2(4)	C(22)–P(2)–C(23)	99.8(6)
C(3)–Nb(1)–P(5)	84.4(2)	P(2)–Nb(1)–Cl(6)	79.0(1)	C(21)–P(2)–C(23)	102.5(5)	C(21)–P(2)–C(22)	101.6(5)
P(2)–Nb(1)–P(5)	140.6(1)	P(2)–Nb(1)–C(3)	86.3(3)	Nb(1)–C(3)–O(4)	170.9(10)	Nb(1)–P(5)–C(53)	117.0(4)
Nb(1)–P(2)–C(23)	118.3(5)	Nb(1)–P(2)–C(22)	113.6(4)	Nb(1)–P(5)–C(52)	111.9(3)	Nb(1)–P(5)–C(51)	119.7(3)
				C(52)–P(5)–C(53)	101.9(5)	C(51)–P(5)–C(53)	101.2(5)
				C(51)–P(5)–C(52)	102.7(5)		

C(3)–Nb(1)–P(5)–C(51)	175.9(5)	Cl(6)–Nb(1)–P(2)–C(23)	176.5(5)	C(3)–Nb(1)–P(2)–C(22)	68.2(5)
C(3)–Nb(1)–P(5)–C(52)	−64.1(4)	Cl(6)–Nb(1)–P(2)–C(21)	51.9(4)	P(5)–Nb(1)–P(2)–C(23)	−124.7(5)
C(3)–Nb(1)–P(5)–C(53)	53.0(5)	Cl(6)–Nb(1)–P(5)–C(52)	71.6(4)	P(5)–Nb(1)–P(2)–C(21)	110.7(4)
C(3)–Nb(1)–P(2)–C(23)	−48.2(6)	P(2)–Nb(1)–P(5)–C(51)	−107.0(4)	Cl(6)–Nb(1)–P(2)–C(22)	−67.1(4)
C(3)–Nb(1)–P(2)–C(21)	−172.8(5)	P(2)–Nb(1)–P(5)–C(52)	13.1(4)	Cl(6)–Nb(1)–P(5)–C(53)	−171.4(4)
P(5)–Nb(1)–P(2)–C(22)	−8.3(4)	P(2)–Nb(1)–P(5)–C(53)	130.1(4)	Cl(6)–Nb(1)–P(5)–C(51)	−48.5(4)

MeI were purchased from Ega-Chemie and Fluka respectively. Other commercial products (phosphines, halogens, *etc.*) were used without further purification. Infrared spectra were recorded as Nujol mulls between CsI plates or in solution in the region 4 000—200 cm^{-1} using a Perkin-Elmer 599 spectrophotometer. Carbon and hydrogen analyses were performed with a Perkin-Elmer 240B microanalyser. Proton and ^{31}P n.m.r. spectra were recorded on Varian FT80A and Bruker WP-60-CW instruments. Measurements of specific conductivities were performed with a WTW Messgërat LF-42 conductimeter using dried acetone as solvent.

Preparation of [{Nb(η-C_5H_5)(CO)L_3}$_n$][L = PMe_3, (**3**); L = PMe_2Ph, (**4**)].—*Method A.* [Nb(η-C_5H_5)Cl_2(CO)L_2] (L = PMe_3, 0.248 g, 0.73 mmol; L = PMe_2Ph, 0.388 g, 0.73 mmol) was added to a vigorously stirred mixture of thf (30 cm^3) and sodium amalgam (10%; 0.035 g, 1.53 mmol Na). After stirring for 5 h, filtration of the reaction mixture gave a purple solution. Removal of thf *in vacuo* gave a purple oil, which was extracted into n-hexane (L = PMe_3) to give a purple oil containing pure (**3**). With L = PMe_2Ph the residue was extracted into toluene, filtered, and the filtrate cooled to −30 °C to give purple crystals of complex (**4**).

Method B. [Nb(η-C_5H_5)Cl_3L_2]^2 (L = PMe_3, 0.333 g, 0.73 mmol; L = PMe_2Ph, 0.395 g, 2.30 mmol) was added to a vigorously stirred mixture of thf (30 cm^3) and sodium amalgam (10%; 0.053 g, 2.30 mmol of Na) under an atmosphere of carbon monoxide (1 atm). After stirring for 5 h, the reaction mixture was worked-up as in method A.

[Nb(η-C_5H_5)Cl(H)(CO)L_2][L = PMe_3, (**5**); L = PMe_2Ph, (**6**)].—*Method A.* When the purple solution of [{Nb(η-C_5H_5)(CO)L_3}$_n$] was stirred for 5 d an orange solution was obtained. Filtration and removal of the solvent gave an orange crystalline solid [(**5**)] and an oily residue [(**6**)] respectively. With L = PMe_2Ph the oily residue was extracted into n-hexane, filtered, and the solution cooled to −30 °C to give orange crystals of complex (**6**).

Method B. To a thf (30 cm^3) solution of [{Nb(η-C_5H_5)(CO)L_3}$_n$] {obtained according to method A: L = PMe_3, 0.298 g, 0.73 mmol; L = PMe_2Ph, 0.388 g, 0.73 mmol; plus related amounts of [Nb(η-C_5H_5)Cl_2(CO)L_2]} was added dropwise a solution of HCl (0.73 mmol) in thf (30 cm^3). After the addition the resulting orange solution was worked-up as in method A.

[Nb(η-C_5H_5)H(CO)L_3]BF_4 [L = PMe_3, (**7**); L = PMe_2Ph, (**8**)].—To a toluene (30 cm^3) solution of [{Nb(η-C_5H_5)(CO)L_3}$_n$] {obtained according to method A: L = PMe_3, 0.298 g, 0.73 mmol; L = PMe_2Ph, 0.388 g, 0.73 mmol; plus related amounts of [Nb(η-C_5H_5)Cl_2(CO)L_2]} was added dropwise a solution of HBF_4·Et_2O (0.120 g, 0.73 mmol) in thf (15 cm^3). After stirring for 1 h the resulting red solution was concentrated under vacuum and then cooled to −30 °C to give pale orange crystals of (**7**) or (**8**). Λ (Ω cm^2 mol^{-1}) in acetone: 87 [L = PMe_3, (**7**)], 90 [L = PMe_2Ph, (**8**)].

[Nb(η-C_5H_5)X_2(CO)L_2] [X = Cl, L = PMe_3, (**1**); X = Cl, L = PMe_2Ph, (**2**); X = Br, L = PMe_3, (**9**); X = Br, L = PMe_2Ph, (**10**); X = I, L = PMe_3, (**11**); X = I, L = PMe_2Ph, (**12**)].—To a thf (30 cm^3) solution of [{Nb(η-C_5H_5)(CO)L_3}$_n$] {obtained according to method A: L = PMe_3, 0.298 g, 0.73 mmol; L = PMe_2Ph, 0.388 g, 0.73 mmol; plus related amounts of [Nb(η-C_5H_5)Cl_2(CO)L_2]} was added dropwise a solution of Br_2 (0.73 mmol) in thf (15 cm^3). After stirring for 1 h filtration of the reaction mixture gave a red solution. Removal of thf *in vacuo* gave a red solid, which was extracted into toluene, filtered, and the filtrate cooled to −30 °C to give red crystals of complex (**9**) or (**10**). Complexes (**1**), (**2**), (**11**), and (**12**) were prepared similarly.

Table 6. Experimental data and structure refinement procedures

Crystal data	
Formula	$C_{12}H_{24}ClNbOP_2$
M	374.628
Crystal size	0.3 mm diameter, almost spheric
Symmetry	Monoclinic, space group $P2_1/a$
Unit-cell determination	Least-squares fit from 25 reflections (θ < 27°)
Unit-cell dimensions: a, b, c/Å, α, β, γ/°	12.662(6), 10.562(3), 13.168(6) 90.0, 92.84(1), 90.0
Packing: U/Å^3	1 759(1) (Z = 4)
D_c/g cm^{-3}	1.415
F(000)	768
μ/cm^{-1}	9.746
Diffractometer	Enraf-Nonius CAD-4 (four-circle)
Monochromator	Graphite orientated
Radiation (λ/Å)	Mo-K_α (0.710 69)
Scan type	ω–2θ
Number of reflections	
Measured	5 369
Independent	2 504
Observed	1 957 [$I > 2\sigma(I)$]
Range of hkl	−16—16, 0—16, 0—14
Max. sinθ/λ	0.7
$R_{int.}$	0.006
Standard reflections	2 every 100 min (no variation)
Solution	Patterson and Fourier methods
Refinement	Least squares on F_o, with 1 block
Parameters:	
Number of variables	181
Degrees of freedom	1 776
Ratio of freedom	10.8
H atoms	Difference Fourier synthesis and geometrical location
Final shift/error	0.08
Weighting scheme	Empirical: to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle\lvert F_o\rvert\rangle$ and $\langle\sin\theta/\lambda\rangle$
Final F peaks	0.26 e Å^{-3}
S, unit weight standard deviation	1.89
Final R, R'	0.044, 0.048

[Nb(η-C_5H_5)Me(CO)(PMe_3)$_3$]I (**13**) *and* [Nb(η-C_5H_5)I(Me)(CO)(PMe_2Ph)$_2$] (**14**).—To a thf (30 cm^3) solution of [{Nb(η-C_5H_5)(CO)(PMe_3)$_3$}$_n$] {obtained according to method A: L = PMe_3, 0.298 g, 0.73 mmol; plus related amounts of [Nb(η-C_5H_5)Cl_2(CO)(PMe_3)$_2$]} was added dropwise a solution of MeI (0.73 mmol) in thf (15 cm^3). After stirring for 1 h, a pale orange precipitate had formed and the supernatant liquor was colourless. The precipitate was collected, washed with n-hexane, and dried *in vacuo* to give complex (**13**). When L = PMe_2Ph, after stirring for 1 h filtration of the reaction mixture gave a red solution. Removal of thf *in vacuo* gave a red solid, which was extracted into n-hexane (four times) and cooled to −30 °C to give orange, solid complex (**14**).

Crystal-structure Determination of Complex (**5**).—Experimental data and parameters are summarized in Table 6 together with the refinement procedures; the crystal used was sealed in a capillary under N_2.

The structure was solved by the heavy-atom method, the Nb atom was found by Patterson and other non-hydrogen atoms by Fourier syntheses. The structure was refined (on *F*) by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. The H(11) atom was shown from a difference Fourier synthesis, after all the other H atoms (found by a previous difference synthesis and geometrical considerations) were included in a mixed refinement with an isotropic thermal parameter. The positions of the H atoms from geometrical locations and also that of H(11) were not refined.

Anomalous dispersion corrections and atomic scattering factors were taken from International Tables.[15] Calculations were performed with the *X*-RAY 76 System,[16] and PARST[17] and PESOS[18] on a VAX-11750 computer. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths, angles, and torsion angles.

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