Mono-η-cyclopentadienylniobium Chemistry: Ternary Phosphine, Carbonyl, 3,4-Dimethylhexa-2,4-diene, Halogeno- and Hydrido-derivatives

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The new compounds $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2]$, $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)X_2]$, X = Cl, Br, or I, $[Nb(\eta\text{-}C_5H_5)(dmpe)_2]$, $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2H][PF_6]$, $[\{Nb(\eta\text{-}C_5H_5)(dmpe)H(\mu\text{-}H)\}_2]$, $[Nb(\eta\text{-}C_5H_5)(dmpe)H(\mu\text{-}H_2BH_2)]$, and $[Nb(\eta\text{-}C_5H_5)(dmpe)Cl][PF_6]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] are described. Sodium amalgam reduction of $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)Cl_2]$ in the presence of but-2-yne followed by addition of hydrogen chloride gives $[Nb(\eta\text{-}C_5H_5)(C_4H_2Me_4)]$ and a further reduction gives $[\{Nb(\eta\text{-}C_5H_5)(\eta\text{-}C_4H_2Me_4)(\mu\text{-}Cl)\}_2]$. The compound $[Ta(\eta\text{-}C_5H_5)(dmpe)(CO)_2]$ is also described.

THE η-cyclopentadienyl ligand when attached to niobium and tantalum can provide derivatives of these metals which are kinetically resistant to hydrolysis and the ligand also stabilises lower valency states of these metals, of which relatively little is known.[1-4] As a continuing development of the chemistry of the heavier members of the Group 4, 5, and 6 transition metals we have explored the compounds $[Nb(\eta\text{-}C_5H_4R)Cl_4]$, which we recently showed could be readily prepared.[5]

RESULTS AND DISCUSSION

Treatment of $[Nb(\eta\text{-}C_5H_5)Cl_4]$ (1) in toluene with 1,2-bis(dimethylphosphino)ethane (dmpe) followed by addition of ethylaluminium dichloride gives violet crystals of the compound $[Nb(\eta\text{-}C_5H_5)(dmpe)Cl_3]$, (2). This compound is paramagnetic and the e.s.r. spectrum in dichloromethane shows a regular decet of triplets, $\langle g \rangle = 1.971 \pm 0.001$ and $a_{\text{iso.}} = 13.5 \pm 0.1$ mT. The decet structure may be assigned to coupling of the d^1 electron with the ^{93}Nb nucleus ($I = \frac{9}{2}$, 100%). The components of the decet show a partially resolved triplet structure due to coupling with the ^{31}P nuclei, $\langle a \rangle_{\text{iso.}}$ 14.3 mT. The mass spectrum of (2) shows a band corresponding to the parent ion at $m/e = 413$. Analytical and spectroscopic data for (2) and for all the other new compounds described below are given in the Table. Only brief comments will be made on these data in the text. The structure for (2) is proposed to be analogous to that shown for the compound $[Nb(\eta\text{-}C_5H_5)(dppe)Cl_3]$ [dppe = 1,2-bis(diphenylphosphino)ethane],[6] and is given in the Scheme.

Reduction, using magnesium amalgam, of tetrahydrofuran (thf) solutions of (2) under 1 atm † of carbon monoxide gives high yields of deep green crystalline $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)Cl_2]$, (3). The ^{1}H n.m.r. spectrum of (3) includes three doublets which may be assigned to hydrogens of a dmpe group which has two non-equivalent pairs of methyl groups and non-equivalent CH_2 groups. The latter are coupling to two inequivalent ^{31}P nuclei. The ^{31}P n.m.r. spectrum of (3) at 33 °C shows two broad bands which become considerably sharper at −60 °C. The proton-decoupled ^{13}C n.m.r. spectrum of (3) supports the above assignment and shows *inter alia* four double doublets assignable to two different CH_2 groups and two different pairs of methyl groups. A resonance due to the CO group is not observed: a phenomena attributed to slow relaxation and possibly to quadrupole broadening by the niobium nucleus. The data for (3) are most consistent with the structure shown in the Scheme. Other isomers have either too high symmetry, such as equivalent CH_2 groups, or too low symmetry, *i.e.* all six carbon atoms of the dmpe ligand would be non-equivalent.

Reduction of (3) with $Na[AlH_2(OCH_2CH_2OMe)_2]$ under 1 atm of carbon monoxide gives deep orange crystals of the compound $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2]$, (4). The ^{1}H n.m.r. spectrum shows a complex series of bands which may be assigned to two pairs of methyl groups, forming separate $X_6AA'X'_6$ systems. The ^{31}P n.m.r. spectrum shows a broad single band and the ^{13}C n.m.r. spectrum shows bands assignable to two equivalent PCH_2 groups and two pairs of methyl groups. The photoelectron spectrum of (4) determined using both He(I) and He(II) shows a lowest ionisation band at 6.15 eV which by virtue of its position and intensity dependence may be assigned to ionisation of a d^4 electron of the molecule. Thus (4) is a very electron-rich (high-energy) molecule. Compound (4) may also be synthesised by reduction of (2) using sodium amalgam, in the presence of 1 atm of carbon monoxide. The dicarbonyl (4) is, as would be expected, a strong metal base and is readily protonated by dilute hydrochloric acid giving the hydride cation, isolated as the hexafluorophosphate salt, $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2H][PF_6]$, (5). The ^{31}P n.m.r. spectrum of (5) shows the two phosphorus nuclei to be equivalent and the ^{1}H and ^{13}C n.m.r. spectra show that PCH_2 groups are equivalent whilst there are two pairs of methyl groups. These data are consistent with addition of the proton to the centre of the basal plane of (4) giving (5).

Treatment of (4) with methyl iodide gives deep green crystals of the compound $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)I_2]$, (6). Similarly (4) reacts rapidly with benzyl bromide giving the dibromo-analogue $[Nb(\eta\text{-}C_5H_5)(dmpe)(CO)Br_2]$, (7). Since the ^{1}H n.m.r. spectra of (6) and (7) do not permit resolution of the resonances due to the dmpe hydrogens we may not assign unambiguous structures to these compounds. It seems probable that these will

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† Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

Analytical and spectroscopic data

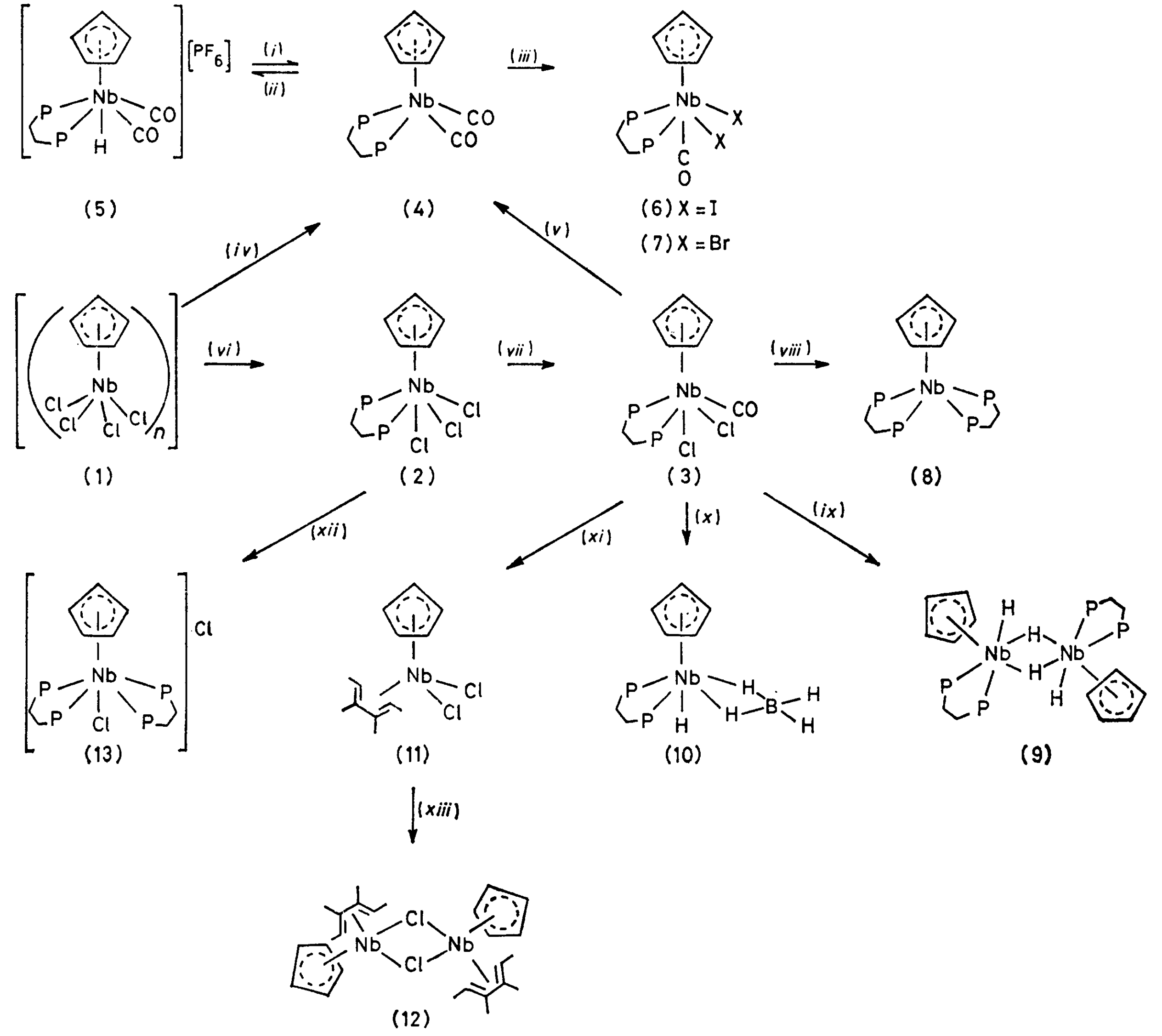
Compound	Colour	Analysis [a] (%)			Selected i.r. data (cm^{-1})	N.m.r.[b] and e.s.r. data
		C	H	Halogen		
(2) [Nb(η-C_5H_5)(dmpe)Cl_3]	Violet	31.7 (31.9)	5.3 (5.1)	25.3 [c] (25.7)		E.s.r. in CH_2Cl_2 at 25 °C, $\langle g \rangle$ 1 971, decet of triplets $\langle a_{iso.} \rangle$ 13.5 mT (^{93}Nb) and 1.4 ± 0.3 mT (^{31}P)
(3) [Nb(η-C_5H_5)(dmpe)(CO)Cl_2]	Dark green	36.1 (35.4)	6.1 (5.2)	17.4 [d] (17.4)	1 879 (sh), 1 860vs	4.83, **5**, *s*, η-C_5H_5; 8.44, **a**, *d* [*J* (P–H) 9.5], 2Me or $2CH_2$; 8.59, **b**, *d* [*J*(P–H) 10.5], 2Me or $2CH_2$; 8.87, **c**, *d* [*J*(P–H) 7.5], 2Me or $2CH_2$ (**a** + **b** + **c** = **16**).[e] ^{31}P in CD_2Cl_2 at −60 °C two singlets at 290 and 70 Hz [f]
(4) [Nb(η-C_5H_5)(dmpe)$(CO)_2$]	Orange-red	42.5 (42.9)	6.0 [g] (5.8)		1 840vs, 1 760vs	4.94, **5**, *s*, η-C_5H_5; 8.86, **6**, *d* [*J*(P–H) 83], 2Me–P; 9.09, **6**, *d* (*J* 6.4) 2Me; 9.12, **4**, *d* [*J*(P–H) 16.5], $(CH_2)_2$.[h] ^{31}P: 53 (h.h.w. = 4 kHz), **5**, 2P.[i] ^{13}C: 92.87, *s*, η-C_5H_5; 30.94, *t* [*J*(P–H) 21.3], $(CH_2)_2$; 21.25, *t* [*J*(P–C) 10.3], 2Me; 19.17, *t* [*J*(P–C) 14.7], 2Me [i]
(5) [Nb(η-C_5H_5)(dmpe)$(CO)_2$H][PF_6]	Yellow	31.3 (30.6)	4.7 (4.35)		2 022vs, 1 958	4.40, **5**, *t* [*J*(P–H) 14.25], η-C_5H_5; 7.94, **4**, *d* [*J*(P–H) 16.3], $2CH_2$; 8.23, **6**, *d* [*J*(P–H) 8.9], 2Me; 8.30, **6**, *d* [*J*(P–H) 9.1], 2Me; 11.04, **1**, *t* [*J*(P–H) 43], NbH.[j] ^{13}C: 92.94, *s*, η-C_5H_5; 29.22, *t* [*J*(P–C) 21.3], $2CH_2$; 19.37, *c* [*J*(P–C) 17.7], 2Me; 16.77, *c* [*J*(P–C) 10.3], 2Me [i, k]
(6) [Nb(η-C_5H_5)(dmpe)(CO)I_2]	Deep green	24.8 (24.4)	3.7 (3.6)	48.4 (43.0)	1 890vs, 1 870vs (sh)	4.79, **5**, *s*, η-C_5H_5; 8.1, **18**, *c*, 4Me + $2CH_2$ [l]
(7) [Nb(η-C_5H_5)(dmpe)(CO)Br_2]	Deep green	28.9 (29.1)	4.4 (4.3)	32.35 (32.2)	1 890vs, 1 871vs	4.95, **5**, *s*, η-C_5H_5; 8.4, *c*, 4Me + $2CH_2$ [e]
(8) [Nb(η-C_5H_5)$(dmpe)_2$]	Yellow		*m*	*n*		5.51, **5**, *q* [*J*(P–H) 1.8], η-C_5H_5; 8.6, **32**, *c*, $(dmpe)_2$ [l]
(9) [{Nb(η-C_5H_5)(dmpe)H(μ-H)}$_2$]	Emerald green	40.7 (42.6)	6.7 [o] (7.5)			5.09, **5**, *s*, η-C_5H_5; 8.61, **6**, *d* [*J*(P–H) 7.3], 2Me; 9.1, **4**, *c*, $2CH_2$; 9.41, **6**, *d* [*J*(P–H) 5.2], 2Me; 12.13, **1**, *t* [*J*(P–H) 4.44], NbH; 21.47, **1**, *vbr*, μ-NbH [h]
(10) [Nb(η-C_5H_5)(dmpe)H(BH_4)]	Blue-black	40.7 (40.8)	7.9, (8.1)	18.6 [p] (19.1)		5.13, **5**, *t* [*J*(P–H) 2.7], η-C_5H_5; 8.61, **6**, *d* [*J*(P–H) 7.8, 2Me; 9.1, **4**, *c*, $2CH_2$; 9.53, **6**, *d* [*J*(P–H) 6.3], 2Me; 17.5, **3—6**, *vbr*, BH_4/H [h]
(11) [Nb(η-C_5H_5)(η^4-MeCHCMeCMe-CHMe)Cl_2]	Orange-brown	45.5 (46.05)	5.8 (5.6)	20.8 [q] (30.9)		4.09, **5**, *s*, η-C_5H_5; 7.73, **6**, *s*, 2Me; 8.70, **6**, *d* [*J*(H–H) 6.3], 2Me; 9.1, **2**, *br*, 2CH [h]
(12) [{Nb(η-C_5H_5)(MeCHCMeCMe-CHMe)(μ-Cl)}$_2$]	Purple-black	*r*				
(13) [Nb(η-C_5H_5)$(dmpe)_2$Cl]Cl	Golden yellow	38.2 (38.6)	7.1 (7.0)	13.2 (13.4)		5.46, **5**, *q* [*J*(P–H) 2.6], η-C_5H_5; *ca.* 8.6, **32 ± 2**, *c*, 8Me + $4CH_2$ [i]
(14) [Ta(η-C_5H_5)(dmpe)$(CO)_2$]	Orange-red	34.2 (34.5)	5.0 [s] (4.9)			4.85, **5**, *s*, η-C_5H_5; 8.39, **6**, *d* [*J*(P–H) 7.0], 2Me; 8.91, **6**, *d* [*J*(P–H) 5.6], 2Me; 8.87, **4**, *d* [*J*(P–H) 15.5], $2CH_2$ [h]

[a] Calculated values are given in parentheses. [b] Given as chemical shift, **relative intensity**, *multiplicity* (*J* in Hz), assignment, *etc.* *c* = Complex multiplet, *q* = quintet, h.h.w. = half height width. [c] Mass spectrum shows a highest band, parent ion (P^+) at *m/e* = 413. [d] Mass spectrum shows P^+ − CO + Cl at *m/e* = 413. [e] In $CDCl_3$. [f] ^{13}C n.m.r. in CD_2Cl_2 with broad-band decoupling (p.p.m.): 99.4, *s*, η-C_5H_5; 26.41, *dd* [*J*(P–C) 26.5 and 13.2 Hz]; 22.51, *dd* [*J*(P–C) 23 and 10 Hz], CH_2; 12.40, *dd* [*J*(P–C) 20.6 and 23.5 Hz], 2Me; 10.09, *dd* [*J*(P–C) 17.6 and 10.2 Hz], 2Me. See text. [g] Mass spectrum, P^+ at *m/e* = 364. [h] In C_6D_6. [i] In CD_3CN. [j] In $(CD_3)_2CO$. [k] ^{31}P n.m.r. in $(CD_3)_2CO$ relative to $PO(OMe)_3$: 31 (h.h.w. 1.3 kHz), 2P; −147, *septet* [*J*(P–F) 710 Hz], PF_6^-. [l] In CD_2Cl_2. [m] Mass spectrum, P^+ at *m/e* = 458. [n] Poor analytical data, possibly due to solvent impurity. [o] Extreme sensitivity causes partial oxidation during manipulation. [p] % P. Mass spectrum, P^+ − H_2 at *m/e* 322; for i.r. data see text. [q] Mass spectrum, P^+ at *m/e* = 338. [r] Sufficient quantity for i.r. and *X*-ray data only, see Experimental section. [s] P^+, *m/e* = 452.

be the same as for the dichloro-compound (3). Treatment of (4) with chlorinated hydrocarbons such as chloroform yields only (2).

Reduction of (3) with sodium amalgam in the presence of butadiene results in the formation of low yields of yellow pyrophoric crystals. The ^{1}H n.m.r. spectrum shows a quintet assignable to the η-C_5H_5 group coupled to four equivalent ^{31}P nuclei. This, together with the data in the Table, suggests the compound to be [Nb(η-C_5H_5)$(dmpe)_2$], (8). The yield of (8) is, surprisingly, not improved when (3) is reduced in the presence of an excess of dmpe.

Treatment of (3) with Na[$AlH_2(OCH_2CH_2OMe)_2$] gives deep green crystals of (9). The i.r. spectrum shows broad bands at 1 640 and 1 170 cm^{-1} which may be assigned to terminal ν(Nb–H) and bridging ν(Nb–H–Nb) systems. The ^{1}H n.m.r. spectrum shows a triplet at τ 12.12 assignable to terminal Nb–H coupled to two equivalent ^{31}P nuclei. Furthermore, there is a broad band at τ 21.5, the contours of which suggest there to be partially resolved coupling with four equivalent ^{31}P nuclei (J = 22 Hz). No mass spectrum could be obtained for (9). Treatment of (9) with dilute hydrochloric acid gives (2) in good yield which shows that (9) contains the system [Nb(η-C_5H_5)(dmpe)]. A binuclear structure is proposed for (9) (Scheme).



SCHEME (*i*) Na[OH] (aq), >95%; (*ii*) HCl (aq) in acetone, then $[NH_4][PF_6]$, 76%; (*iii*) X = I: MeI in toluene at 70 °C for 12 h, 46%; X = Br: benzyl bromide in toluene at 70 °C for 2 h, 73%; (*iv*) sodium amalgam, dmpe, and CO in toluene, then thf at r.t., 63%; (*v*) $Na[AlH_2(OCH_2CH_2OMe)_2]$ and CO (1 atm) in benzene for 6 h, 94%; (*vi*) $(AlEtCl_2)_2$ and dmpe in toluene at r.t. for 2 h, 73%; (*vii*) CO at 1 atm and magnesium amalgam in thf at r.t. for 2—7 h, 87%; (*viii*) sodium amalgam and butadiene in thf, *ca.* 13 h, 12.6%; (*ix*) $Na[AlH_2(OCH_2CH_2OMe)_2]$ in benzene for 12 h, then H_2O, 11%; (*x*) $Na[BH_4]$ in thf at 70 °C for 4 h, 35%; (*xi*) sodium amalgam in but-2-yne in thf at r.t. for 12 h, 34%; (*xii*) magnesium amalgam and but-2-yne in thf for 30 min at r.t., 21%; (*xiii*) sodium amalgam in toluene at r.t. for 20 h, 34% yield

Reduction of (3) with sodium tetrahydroborate in thf gave dark black-blue fern-like crystals of (10), from a deep red solution. The i.r. spectrum showed bands at 2 414, 2 378, 1 753, 1 425, and 1 150 cm^{-1} assignable to a [Nb(μ-H_2BH_2)] unit and a band at 1 600 cm^{-1} assignable to a terminal Nb–H group. The ^1H n.m.r. spectrum shows a 1 : 2 : 1 triplet assignable to a η-C_5H_5 group and two doublets assignable to two pairs of methyl groups. Also there is a broad band centred at τ 17.5 which may be assigned to Nb–H and Nb–BH_4 hydrogens. The mass spectrum of (10) showed a highest peak at *m/e* corresponding to loss of H_2 from the proposed parent ion, namely, [Nb(η-C_5H_5)(dmpe)H(BH_4)]$^+$.

Treatment of (3) in thf with sodium amalgam in the presence of an excess of but-2-yne, followed by treatment of the reaction mixture with aqueous hydrochloric acid, gives orange-brown crystals of the compound [Nb(η-C_5H_5)(η-MeCHCMeCMeCHMe)Cl_2], (11). The crystal structure of (11) has been determined [7] and this together with the data in the Table characterise compound (11) with the structure shown in the Scheme. Reduction of (11) with sodium amalgam gives green-black crystals of the compound [$\{Nb(\eta\text{-}C_5H_5)(C_4H_2Me_4)(\mu\text{-}Cl)\}_2$], (12), whose structure[8] is represented in the Scheme. The four atoms of the $(NbCl)_2$ group of (12) lie in a plane as is found for the compounds $(NbCl_5)_2$ and $(NbCl_4)_n$. Further studies on compound (12) are in progress.

When (2) is treated with magnesium amalgam in the presence of but-2-yne then (11) is not formed but rather a small yield of the compound [$Nb(\eta\text{-}C_5H_5)(dmpe)_2Cl$]Cl, (13). The crystal structure of (13) has been determined[8] and is shown in the Scheme. Finally, the compound [$Ta(\eta\text{-}C_5H_5)dmpe(CO)_2$], (14), may be prepared from [$Ta(\eta\text{-}C_5H_5)Cl_4$] using similar conditions to those employed for the synthesis of the niobium analogue.

All the reactions and structures of the new compounds (2)—(14) are represented in the Scheme. Clearly compound (1) is a useful precursor of a fruitful chemistry of monocyclopentadienylniobium compounds in a variety of formal oxidation states. Some of the reactions are commonplace whilst others are quite unexpected. The loss of the dmpe ligand implicit in the formation of (11) from (3) was not to be predicted. Also, there must be several intermediate steps in the formation of (11) *via* the reductive dimerisation of but-2-yne.

EXPERIMENTAL

All reactions and manipulations were carried out under an inert atmosphere or *in vacuo*. Glassware was dried by flaming under vacuum immediately before use. Solvents were dried and distilled immediately before use. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 or 580 instrument and were calibrated using polystyrene film. Hydrogen-1 n.m.r. spectra were recorded at 60 MHz on a JEOL C60HL and a Perkin-Elmer R12 and at 90 MHz on a Perkin-Elmer R14 spectrometer. Pulse-Fourier ^1H, ^{13}C, and ^{31}P n.m.r. spectra were recorded using a Bruker WH90 spectrometer. Electron spin resonance spectra were recorded on a Varian E-line spectrometer calibrated using 1,1-diphenyl-2-picrylhydrazyl. Quoted values were obtained by iterative correction of the hyperfine spacings employing the Breit–Rabi equation. Mass spectra were obtained on A.E.I. MS9 and V.G. Micromass 16F instruments. Photoelectron spectra were determined by Dr. J. C. Green using a Perkin-Elmer PS 16/18 spectrometer. Spectra were calibrated using helium, xenon, and dinitrogen.

[1,2-*Bis(dimethylphosphino)ethane*]*trichloro*(η-*cyclopentadienyl*)*niobium*, (2).—A suspension of the compound [$Nb(\eta\text{-}C_5H_5)Cl_4$] (9.42 g, 31 mmol) in toluene (250 cm^3) was treated with dmpe (5.0 g, 33 mmol) with vigorous stirring. After 1.5 h the mixture was cooled to *ca.* -20 °C and $(AlEtCl_2)_2$ (17.7 g, 139 mmol) in toluene (75 cm^3) was added. The mixture separated into a dark viscous oil and a pale yellow toluene phase. The mixture was stirred at room temperature (r.t.) for 2 h and the supernatant liquor was then decanted from the dark oil. This was washed with toluene and then cooled to *ca.* -50 °C and treated with cold ethanol (150 cm^3 at -100 °C). The mixture was shaken until the oil had solidified and this finally dissolved. Violet crystals began to appear and the solution was cooled to -30 °C for 12 h. The resulting violet crystals were filtered off, washed with cold ethanol, and dried *in vacuo*, yield 10.6 g, 82%. Recrystallisation could be carried out from dichloromethane–ethanol (1 : 1) giving large, deep violet crystals, yield *ca.* 9.48 g, 73%.

[1,2-*Bis(dimethylphosphino)ethane*]*carbonyldichloro*(η-*cyclopentadienyl*)*niobium*, (3).—The compound [$Nb(\eta\text{-}C_5H_5)(dmpe)Cl_3$] (8.08 g, 19.52 mmol) in thf (300 cm^3) under carbon monoxide (1 atm) was treated with magnesium turnings (4 g, 165 mmol) and several drops of mercury. The mixture was stirred for 2 h. It was then filtered and the filtrate was stirred under a carbon monoxide atmosphere at 40 °C for 2 h giving a bright green solution. The solvent was then removed under reduced pressure giving a dark green solid which was dried under vacuum for 8 h. The solid was extracted with dichloromethane and addition of light petroleum and cooling to -30 °C gave dark green crystals. These were collected and dried *in vacuo* giving the pure product, yield 6.9 g, 87%.

In a study of this synthesis it was found that the time required for the reduction with magnesium amalgam varied, up to 7 h on one occasion. At no time did the reduction go as to form the dicarbonyl [$Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2$]. The reduction step was monitored by close attention to colour changes to ensure that there was no unreacted material. The colour changes were subtle passing from an initial ' heavy ' green through to a yellow green which, after warming under carbon monoxide, became a bright green if the reduction step was essentially complete.

[1,2-*Bis(dimethylphosphino)ethane*]*dicarbonyl*(η-*cyclopentadienyl*)*niobium*, (4).—*Method* (*i*). The salt $Na[AlH_2(OCH_2CH_2OMe)_2]$ (1 cm^3 of a 70% solution in benzene, 3.8 mmol) was added to a stirred suspension of (3) (0.455 g, 1.1 mmol) in benzene (120 cm^3) under CO (1 atm). After stirring for several hours the deep orange solution was cooled and water (50 cm^3) was added. The resulting emulsion was passed through Celite and the resulting organic phase was separated. The solvent was removed under reduced pressure and the resulting red solid was extracted with warm diethyl ether (2 × 30 cm^3). The extract was filtered and light petroleum (60 cm^3) was added to the filtrate. Cooling to -30 °C for 12 h gave deep orange-red crystals. These were washed with light petroleum (b.p. 30—40 °C) and dried *in vacuo*, yield 0.38 g, 94%.

Method (*ii*). The compound dmpe (2.7 g, 18.0 mmol) was added to a suspension of [$Nb(\eta\text{-}C_5H_5)Cl_4$] (5.28 g, 17.8 mmol) in toluene (500 cm^3) followed by sodium amalgam (170 g of 1.1% Na–Hg w/w, 80 mmol). The mixture was stirred for 15 h under carbon monoxide (1 atm). Tetrahydrofuran (120 cm^3) was then added and the stirring was continued for 48 h by which time the colour of the solution had become a deep orange. The amalgam was allowed to settle and the solution was filtered. The solvent was removed from the filtrate under reduced pressure and the orange residue was recrystallised from diethyl ether–light petroleum (b.p. 30—40 °C) at -30 °C giving deep orange-red crystals, yield 4.0 g, 63%.

[1,2-*Bis(dimethylphosphino)ethane*]*dicarbonyl*(η-*cyclopentadienyl*)*hydridoniobium Hexafluorophosphate*, (5).—The compound [$Nb(\eta\text{-}C_5H_5)(dmpe)(CO)_2$] (0.8 g, 2.2 mmol) in acetone (30 cm^3) was treated with an excess of concentrated aqueous hydrochloric acid (0.1 mol dm^{-3}, 80 cm^3). Ammonium hexafluorophosphate (0.5 g, 3.1 mmol) was then added and the mixture was concentrated under reduced pressure to remove the acetone. A thick yellow precipitate formed which was filtered off, washed with water (3 × 40

cm^3), and dried *in vacuo*. The compound was recrystallised from acetone–ethanol at −30 °C giving long yellow needle crystals of the pure product. These were collected and dried *in vacuo*, yield 0.85 g, 76%.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*carbonyl*(η-*cyclopentadienyl*)*di-iodoniobium*, (6).—The compound [Nb(η-C_5H_5)(dmpe)$(CO)_2$], (4) (0.08 g, 0.22 mmol), in toluene (40 cm^3) was treated with methyl iodide (0.2 cm^3, 1.6 mmol) and the mixture heated at 70 °C for 12 h. The resulting lime coloured solution was filtered and the solvent was removed from the filtrate under reduced pressure giving green crystals. These were recrystallised from dichloromethane–light petroleum (b.p. 30—40 °C) and dried *in vacuo*, yield 0.06 g, 46%.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*dibromocarbonyl*(η-*cyclopentadienyl*)*niobium*, (7).—The reaction was carried out as described above for compound (6) using benzyl bromide (1 cm^3, 8.4 mmol) instead of the methyl iodide, yield 0.08 g, 73%.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](η-*cyclopentadienyl*)*niobium*, (8).—The compound [Nb(η-C_5H_5)(dmpe)(CO)Cl_2] (0.353 g, 0.86 mmol) in thf (80 cm^3) was treated with sodium amalgam (46 g of 1% Na–Hg w/w). The mixture was stirred under butadiene (1 atm) for 30 s, after which time the system was closed to further butadiene. The mixture, containing *ca.* 50 cm^3 of butadiene vapour, was stirred for 30 min. Dinitrogen was then added to permit the pressure to reach 1 atm. The mixture was stirred for 13 h, allowed to settle, and the red-orange solution was filtered from the sodium amalgam. The filtrate was concentrated under reduced pressure until crystals appeared and was then cooled to −30 °C for 12 h. The orange supernatant liquor was filtered from the resulting pale yellow needles. These were then washed with diethyl ether and dried *in vacuo*. Yield *ca.* 0.05 g, 12.6%.

Reaction between [Nb(η-C_5H_5)(dmpe)(CO)Cl_2] *and* Na[AlH_2(OCH_2CH_2OMe)$_2$] *in the Presence of But*-2-*yne*. *Synthesis of* [{Nb(η-C_5H_5)(dmpe)H(μ-H)}$_2$], (9).—*Method* (*i*). The compound [Nb(η-C_5H_5)(dmpe)(CO)Cl_2] (0.159 g, 0.39 mmol) in benzene (25 cm^3) was treated with but-2-yne (0.2 cm^3, 3 mmol) and then Na[AlH_2(OCH_2CH_2OMe)$_2$] (0.5 cm^3 of a 70% solution in benzene). The initially green solution turned orange-brown. The mixture was stirred for 3 days during which time both this solution and supernatant vapours were monitored by gas–liquid chromatography. Butane, *trans*-but-2-ene, and *cis*-but-2-ene were detected in the volatile products. The mixture was then cooled (*ca.* −10 °C) and treated with water (25 cm^3). The resulting emulsion was passed through a short Celite column and then the original layer was separated from the filtrate. The solvent was removed under reduced pressure leaving a green-brown oily solid which was further dried under vacuum at 40 °C for 1 h. The solid residue was extracted with diethyl ether (2 × 15 cm^3) giving a brown-green dichroic solution. This was concentrated under reduced pressure and cooled to −30 °C overnight. Deep emerald green crystals separated which were collected and washed in cold light petroleum (b.p. 30—40 °C) and dried *in vacuo*. The compound was identified as [{Nb(η-C_5H_5)(dmpe)H(μ-H)}$_2$] from the i.r. spectrum. The yield was 0.015 g, *ca.* 12.5%.

Method (*ii*). The compound Na[AlH_2(OCH_2CH_2OMe)$_2$] (1.5 cm^3 of a 70% solution in benzene, 5 mmol) was added to a stirred suspension of (3) (0.6 g, 1.47 mmol) in toluene (90 cm^3). After 12 h the mixture was cooled to −10 °C and water (20 cm^3) was added. The resulting emulsion was passed through a Celite column and the product was isolated as described in method (*i*), yield 0.05 g, 11%.

[1,2-*Bis*(*dimethylphosphino*)*ethane*](η-*cyclopentadienyl*)*hydridotetrahydroboratoniobium*, (10).—Excess of dried Na[BH_4] (1.11 g, 29 mmol) was added to [Nb(η-C_5H_5)(dmpe)(CO)Cl_2] (0.18 g, 0.44 mmol) in thf (60 cm^3) and the mixture was stirred at 70 °C for 4 h. The resulting deep red solution was filtered and solvent was removed from the filtrate under reduced pressure. The dark solid was extracted at 6.0 °C with light petroleum (20 + 10 cm^3) giving a deep burgundy extract. After filtration the filtrate was concentrated under reduced pressure giving dark blue-black crystals which were washed with light petroleum and dried *in vacuo*, yield 0.05 g, 35%. The i.r. spectrum (Nujol) showed bands at 3 110w, 3 080w, 2 415s, 2 376s, 2 280m, 1 755br, 1 600s br, 1 425s, 1 295m, 1 280m, 1 150s, 1 125w, 1 103w, 1 071w (sh), 1 062w, 1 012w (sh), 998m, 935s, 910w (sh), 895m (sh), 830m, 815m, 790m, 720m, 690m, and 636m cm^{-1}.

Dichloro(η-*cyclopentadienyl*)(3,4-*dimethylhexa*-2,4-*diene*)*niobium*, (11).—Excess of sodium amalgam (46.35 g of 1.1% Na–Hg by weight) and then but-2-yne (2 g, 37 mmol) were added to [Nb(η-C_5H_5)(dmpe)(CO)Cl_2] (1.16 g, 3.91 mmol) in dry thf (200 cm^3). The mixture was stirred for 12 h during which time the initially green solution became plum red. The mixture was allowed to settle for 30 min and then was decanted from the amalgam. The residual amalgam was washed with thf (5 cm^3) and the washing was combined with the bulk reaction solution. The solvent was removed under reduced pressure and the red-orange oil residue was dried under vacuum at *ca.* 50 °C for 30 min. The resulting solid was extracted with dry diethyl ether (3 × 50 cm^3) and the combined extracts were filtered. Hydrochloric acid was then added (150 cm^3 of a 5 mol dm^{-3} solution). The mixture was shaken and then the ethereal layer was separated and concentrated under reduced pressure. Orange-brown crystals separated which were recrystallised from diethyl ether–light petroleum. The yield was 0.45 g, 34%.

Single crystals of the compound, suitable for *X*-ray crystal-structure determination, were obtained by cooling a saturated solution in benzene (at 40 °C) to 6 °C for 1.5 days.

Attempts to obtain suitable crystals from dichloromethane, diethyl ether–light petroleum, toluene–light petroleum, or toluene gave either irregular crystals or polycrystalline samples.

Di-μ-*chloro-bis*[(η-*cyclopentadienyl*)(3,4-*dimethylhexa*-2,4-*diene*)*niobium*], (12).—The compound [Nb(η-C_5H_5)(η-C_4H_2-Me_4)Cl_2] (65 mg, 0.19 mmol) in toluene (50 cm^3) was stirred with sodium amalgam (34 g of 1% Na–Hg w/w) for 20 h. The initially golden yellow solution became deep red. After filtration the solvent was removed from the filtrate under reduced pressure giving a purple-brown solid. This was recrystallised from diethyl ether as deep green-black crystals, yield 0.02 g, 34%. Infrared bands (cm^{-1}) at 3 095w, 3 078w, 2 710w, 1 730w br, 1 431m, 1 290w—m, 1 263w, 1 235vw, 1 140w—m, 1 120m, 1 078vw, 1 065w, 1 040w (sh), 1 025m, 1 010s, 958m, 918w, 888w—m, 845w (sh), 838m (sh), 828s, 785vs, 720vw, 704w, 590m, and 543w.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(η-*cyclopentadienyl*)*niobium Chloride*, (13).—The compound [Nb(η-C_5H_5)(dmpe)Cl_3] (0.35 g, 0.845 mmol) in thf (50 cm^3) was treated with but-2-yne (0.25 g, 4.5 mmol). Magnesium turnings (1.5 g, 62 mmol) and a few drops of mercury were added to the mixture which was then stirred for 30 min. The solution became yellow and was then filtered. The golden yellow filtrate was concentrated under reduced pressure (to *ca.* 35 cm^3) until crystallisation commenced. The solution was warmed to redissolve the solid and then cooled to −30 °C for 12 h. The resulting shimmering golden crystals were separated from the red mother-liquor and were washed with cold toluene and dried *in vacuo.*

The compound was found to be very soluble in acetonitrile or dichloromethane, moderately soluble in thf, and almost insoluble in toluene. It was recrystallised from dichloromethane–toluene giving golden yellow needles, yield 0.95 g, 21%.

[1,2-Bis(dimethylphosphino)ethane]dicarbonyl(η-cyclopentadienyl)tantalum.—The compound [$Ta(\eta$-$C_5H_5)Cl_4$] (4.47 g, 11.5 mmol) suspended in toluene (400 cm^3) was treated with dmpe (1.73 g, 11.5 mmol) and sodium amalgam (131 g of 1% Na–Hg w/w, 57 mmol). The mixture was placed under carbon monoxide (1 atm) and stirred at room temperature for 12 h. Tetrahydrofuran (150 cm^3) was added and the mixture was stirred at room temperature for 3 days giving an orange solution. This was filtered and the solvent was removed from the filtrate under reduced pressure. The orange-red residue was extracted with diethyl ether (4 × 25 cm^3) and then toluene–diethyl ether, (1 : 10, 6 × 25 cm^3). The combined extracts were cooled to −30 °C giving pale yellow crystals which were identified as [$Ta(dmpe)_2(CO)_2Cl$] from the i.r. and ^1H n.m.r. spectra (0.75 g, 11%). Concentration of the mother-liquor and cooling to −30 °C gave deep orange-red crystals of the title compound, yield 1.3 g, 25%.

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