

New Alkyne Complexes of Niobium(I)[†]

Fausto Calderazzo,^a Christian Felten,^b Guido Pampaloni^a and Dieter Rehder^{*,b}

^a *Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*

^b *Universität Hamburg, Institut für Anorganische und Angewandte Chemie, Martin Luther King Platz, 6, W-2000 Hamburg 13, Germany*

The reaction between the seven-co-ordinated niobium(I) complexes $[\text{NbX}(\text{CO})_4(\text{dppe})]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{X} = \text{Br}$ or I) or $[\text{NbX}(\text{CO})_3(\text{PEt}_3)_3]$ ($\text{X} = \text{Cl}$, Br or I) and alkynes leads to the d^4 niobium alkyne complexes $[\text{NbX}(\text{CO})_2(\eta^2\text{-RCCR})(\text{dppe})]$ ($\text{R} = \text{Ph}$) and $[\text{NbX}(\text{CO})_2(\eta^2\text{-RCCR})(\text{PEt}_3)_2]$ ($\text{R} = \text{H}$, Me , Et or Ph). These complexes have been characterized by ^1H , ^{13}C , ^{31}P and ^{93}Nb NMR and IR spectroscopies. Low-field acetylenic proton and carbon resonances confirm the description of the alkyne as a four-electron donor. The ^{93}Nb NMR resonances exhibit the expected dependence of shielding on the nature of the halide ligand, *i.e.* $\text{Cl} < \text{Br} < \text{I}$. The crystal and molecular structures of $[\text{NbI}(\text{CO})_2(\text{MeCCMe})(\text{PEt}_3)_2]$ have been determined: triclinic, space group $P\bar{1}$, $a = 9.000(1)$, $b = 16.906(2)$, $c = 17.952(3)$ Å, $\alpha = 80.07(1)$, $\beta = 78.59(1)$, $\gamma = 75.50(1)^\circ$. The molecule has a slightly distorted octahedral geometry with the carbonyl and the phosphine ligands in *trans* positions. Average distances are: $\text{Nb}-\text{CO}$ 2.11(5), $\text{Nb}-\text{C}(\text{alkyne})$ 2.09(9) and $\text{Nb}-\text{I}$ 2.91(2) Å.

While, for π -bonded alkyne complexes of molybdenum and tungsten, a rich chemistry has been established,¹ the alkyne chemistry of Group 5 metals (V, Nb, Ta) is much less developed especially in their low oxidation states. Most of the reported alkyne complexes contain one or more cyclopentadienyl molecules (cp) as ligands.^{2a-i,3a-k} Alkyne complexes of niobium(I) without cp are rare^{4a-d} and only a few niobium(III) derivatives (without cp) have been reported.^{5a-c} This situation is due in part to the lack of readily available starting materials. For the preparation of $[\text{Nb}(\text{CO})_6]^-$ by reductive carbonylation only relatively inefficient high-pressure routes had been known prior to 1983. Since the advent of convenient low-pressure syntheses,^{6,7} a number of seven-co-ordinated d^4 carbonyl niobium(I) complexes such as $\text{NbX}(\text{CO})_6\text{L}_n$ have been reported, prepared by oxidation of the $[\text{Nb}(\text{CO})_6]^-$ anion with halogens^{8,9} or pyridinium halides^{9,10} in the presence of a oligodentate phosphine L_n . We have now exploited the reported synthetic potential of these compounds by replacing part of the weakly bonded CO ligands in a number of substitution reactions.

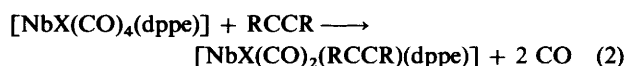
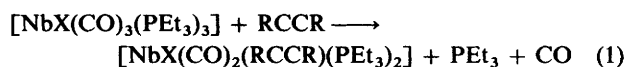
Here, we describe the synthesis of a series of *trans*- $[\text{NbX}(\text{CO})_2(\text{RCCR})\text{L}_2]$ complexes [$\text{X} = \text{Cl}$, Br or I ; $\text{L}_2 = 2 \text{PEt}_3$ or $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe); $\text{R} = \text{Ph}$, Et , Me or H)] and their characterization by IR, multinuclear NMR spectroscopy and X-ray diffraction methods.

Results and Discussion

The seven-co-ordinated tricarbonyl complexes $[\text{NbX}(\text{CO})_3(\text{PEt}_3)_3]$ ($\text{X} = \text{Cl}$ 1, Br 2 or I 3) and $[\text{NbX}(\text{CO})_4(\text{dppe})]$ ($\text{X} = \text{Br}$ 4 or I 5) react with alkynes RCCR ($\text{R} = \text{Ph}$, Et , Me or H) under mild conditions to form red-violet, six-co-ordinate, alkyne adducts of niobium(I), *viz.* $[\text{NbX}(\text{CO})_2(\text{RCCR})(\text{PEt}_3)_2]$ ($\text{X} = \text{Cl}$, $\text{R} = \text{Ph}$ 1a or Et 1b; $\text{X} = \text{Br}$, $\text{R} = \text{Ph}$ 2a or Et 2b; $\text{X} = \text{I}$, $\text{R} = \text{Ph}$ 3a, Et 3b, Me 3c or H 3d) and $[\text{NbX}(\text{CO})_2(\text{PhCCPh})(\text{dppe})]$ ($\text{X} = \text{Br}$ 4a or I , 5a), see equations (1) and (2), respectively. These red-violet crystalline compounds are



Fig. 1 Proposed structures of compounds $[\text{NbX}(\text{CO})_2(\text{RCCR})(\text{PEt}_3)_2]$ 1a–3d, I and $[\text{NbX}(\text{CO})_2(\text{PhCCPh})(\text{dppe})]$ 4a and 5a, II, based on IR and NMR data



slightly air sensitive; they can be stored under N_2 over long periods, except for the very sensitive complex 3d. They are soluble in toluene, tetrahydrofuran, dichloromethane, and slightly soluble in alkanes. Yields differ from poor (27%, 3d) to good (85%, 2b). Reaction times vary from 2 h (3d) to nearly 3 d (3a).

If the starting complexes contain the monodentate phosphine PEt_3 , one phosphine and one CO are replaced by the alkyne, whereas in the case of the tetracarbonyl species with the chelating dppe as a ligand, dicarbonyl complexes without loss of the tertiary phosphine are formed. While in the compounds 1a–3d the phosphines and the carbonyl groups occupy *trans* positions, the phosphorus atoms in 4a and 5a are forced into *cis* positions, see Fig. 1.

IR Spectroscopy.—No alkyne ν_{CC} stretching vibrations for the complexes 1a–5a were observed, which is frequently the case for co-ordinated symmetrical alkynes. The spectra of the alkyne derivatives 1a–3d with the monodentate tertiary phosphines show the typical carbonyl pattern expected for the *trans* geometry (idealized C_{2v} symmetry) of the two CO groups, *i.e.* a weak and a strong band, see Table 1. These results correspond to those reported for similar tantalum(I) complexes.^{4b} There are two carbonyl stretching absorptions

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

Table 1 Infrared data (cm^{-1} , 0.1 mm CaF_2 ; thf) for the complexes $[\text{NbX}(\text{CO})_2(\text{RCCR})\text{L}_2]$ ($\text{L}_2 = 2 \text{ PEt}_2$ or dppe) in the carbonyl stretching region

1a	$[\text{NbCl}(\text{CO})_2(\text{PhCCPh})(\text{PEt}_3)_2]$	1992m, 1910vs
1b	$[\text{NbCl}(\text{CO})_2(\text{EtCCEt})(\text{PEt}_3)_2]$	1990m, 1890vs
2a	$[\text{NbBr}(\text{CO})_2(\text{PhCCPh})(\text{PEt}_3)_2]$	1990m, 1925vs*
2b	$[\text{NbBr}(\text{CO})_2(\text{EtCCEt})(\text{PEt}_3)_2]$	1960w, 1890vs
3a	$[\text{NbI}(\text{CO})_2(\text{PhCCPh})(\text{PEt}_3)_2]$	1988m, 1917vs
3b	$[\text{NbI}(\text{CO})_2(\text{EtCCEt})(\text{PEt}_3)_2]$	1973w, 1904vs
3c	$[\text{NbI}(\text{CO})_2(\text{MeCCMe})(\text{PEt}_3)_2]$	1980w, 1900vs
3d	$[\text{NbI}(\text{CO})_2(\text{HCCH})(\text{PEt}_3)_2]$	1997w, 1920vs
4a	$[\text{NbBr}(\text{CO})_2(\text{PhCCPh})(\text{dppe})]$	2065m, 2020vs
5a	$[\text{NbI}(\text{CO})_2(\text{PhCCPh})(\text{dppe})]$	2060m, 2015vs

* In KBr, Nujol.

Table 2 Proton and ^{31}P NMR data for the complexes $[\text{NbX}(\text{CO})_2(\text{RCR})\text{L}_2]$ ($\text{L}_2 = 2 \text{ PEt}_3$ or dppe)

Compound	$\delta(^1\text{H})^a$	$\delta(^{31}\text{P})^b$
1a	0.94 (m, 18 H, PCH_2CH_3), 1.32 (m, 12 H, PCH_2), 7.32 (m, 10 H, Ph)	14.8
1b	0.95 (m, 18 H, PCH_2CH_3), 1.15 (t, $J_{\text{HH}} = 7.7$, 6 H, CCH_2CH_3), 1.34 (m, 12 H, PCH_2), 3.28 (q, 4 H, $J_{\text{HH}} = 7.7$, CCH_2)	15.8
2a	1.05 (m, 18 H, PCH_2CH_3), 1.41 (m, 12 H, PCH_2), 7.21 (m, 10 H, Ph)	11.6
2b	0.96 (m, 18 H, PCH_2CH_3), 1.21 (t, 6 H, $J_{\text{HH}} = 7.7$, CCH_2CH_3), 1.37 (m, 12 H, PCH_2), 3.32 (q, 4 H, $J_{\text{HH}} = 7.7$, CCH_2)	12.7
3a	0.97 (m, 18 H, PCH_2CH_3), 1.32 (m, 12 H, PCH_2), 7.33 (m, 10 H, Ph)	6.4
3b	0.99 (m, 18 H, PCH_2CH_3), 1.24 (t, 6 H, $J_{\text{HH}} = 7.5$, CCH_2CH_3), 1.39 (m, 12 H, PCH_2), 3.32 (q, 4 H, $J_{\text{HH}} = 7.5$, CCH_2)	7.9
3c	0.96 (m, 18 H, PCH_2CH_3), 1.54 (m, 12 H, PCH_2), 2.72 (s, 6 H, CCH_3)	8.2
3d	0.96 (m, 18 H, PCH_2CH_3), 1.33 (m, 12 H, PCH_2), 11.3 (s, 2 H, CCH)	7.4
4a		37.4 (br), 41.2 (br)
5a		32.2 (br), 36.9 (br)

^a In $[\text{H}_8]\text{thf}$, SiMe_4 , given as δ (multiplicity, relative intensity, J/Hz , assignment); s = singlet, t = triplet, q = quartet, m = multiplet. ^b In $[\text{H}_8]\text{thf}$, H_3PO_4 as external standard, 210 K, values given as δ , br = broad.**Table 3** Carbon-13 NMR data for the complexes $[\text{NbX}(\text{CO})_2(\text{EtCCEt})(\text{PEt}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I)^a

Compound	$\delta(^{13}\text{C})$			
	PEt_3	Et	$\text{C}\equiv\text{C}$	CO
1b	7.9, ^b 19.0 ^{c,d}	14.8 (d), 29.6 ^d	209.0	226.9
2b	8.1, ^b 19.5 ^{c,d}	14.9 (d), 29.8 ^d	209.0	227.1
3b	8.2, ^b 19.5 ^{d,e}	14.9 (d), 29.8 ^d	207.7	226.5

^a Internal standard SiMe_4 in $[\text{H}_8]\text{thf}$. ^b Terminal C. ^c Triplet, $J_{\text{PC}} = 9 \text{ Hz}$. ^d Methylene C. ^e Triplet, $J_{\text{PC}} = 8 \text{ Hz}$.

above 2000 cm^{-1} (medium and very strong, respectively) for the dppe derivatives **4a** and **5a**, consistent with a *cis* structure of C_2 symmetry.

In the iodide complexes **3a–3d**, phenyl substituents on the alkyne increase ν_{CO} relative to the values for the alkylated

Table 4 Niobium-93 NMR data for the complexes $[\text{NbX}(\text{CO})_2(\text{RCCR})(\text{PEt}_3)_2]$

Compound	$\delta(^{93}\text{Nb})^* w_1/\text{kHz}$
1b	−799, 44
2a	−795, 45
2b	−834, 33
3b	−931, 35
3c	−967, 49

* In $[\text{H}_8]\text{thf}$, external standard $[\text{NEt}_4][\text{NbCl}_6]$.

alkyne ligands. Complex **3d**, with the parent acetylene, shows the highest wavenumber in this series. There is no significant dependence upon the nature of X in $[\text{NbX}(\text{CO})_2(\text{RCCR})\text{L}_2]$. A crude calculation of the OC–Nb–CO angle based on the intensity ratio of the two CO absorptions¹¹ yields approximately 170° , which has been confirmed by the X-ray data for **3c**. Phenyl substituents appear to decrease this angle to about 160° in compounds **1a**, **2a** and **3a**. The π acidity of the diphenylacetylene ligand can qualitatively be estimated by comparison of ν_{CO} for the starting tetracarbonyl complexes **4** and **5** with those of the alkyne complexes **4a** and **5a**. In view of the fact that the ν_{CO} of **4a** and **5a** are larger than those of **4** and **5**, it can be concluded that diphenylacetylene removes more d_π electron density than two carbon monoxide groups. The π -acid strengths of co-ordinated carbon monoxide and co-ordinated alkyne have also been compared for some d^4 molybdenum(II) compounds.¹²

^{31}P NMR Spectroscopy.—The ^{31}P NMR spectra at room temperature are broadened into the baseline due to interaction with the ^{93}Nb nucleus (^{93}Nb , 100%, $I = \frac{9}{2}$). However, at 210 K the niobium nuclei become partially decoupled and resonances with a linewidth at half-height of 50(10) Hz can be observed. As shown in Table 2, the spectra of **1a–3d** exhibit one singlet for the triethylphosphine ligands, indicating that the phosphorus atoms are equivalent and should therefore occupy *trans* positions, as is confirmed for the solid-state structure of **3c**. The ^{31}P resonances exhibit a significant deshielding effect in the order $\text{Cl} > \text{Br} > \text{I}$, as has been observed for similar complexes containing halide and tertiary phosphines.^{8,9} In contrast, the dppe-containing alkyne complexes **4a** and **5a** show two (broad) signals each, suggesting two non-equivalent co-ordinated phosphorus atoms. This is consistent with the *cis* position of the phosphorus atoms, the mutual *cis* positions of the halide and the alkyne, and the *trans* orientations of the carbonyl groups already assumed on the basis of the IR data.

^{13}C and ^1H NMR Spectroscopy.—The ^{13}C NMR spectra (Table 3) of the complexes show acetylenic and carbonyl resonances in the range δ 205–230 comparable to those reported for similar four-electron donor alkyne complexes.^{4b} No significant dependence of the ^{13}C NMR shifts on X has been observed. The complex $[\text{NbI}(\text{CO})_2(\text{HCCH})(\text{PEt}_3)_2]$ has a unique ^1H NMR singlet at δ 11.3 (Table 2). This very low-field chemical shift is considered to be in agreement with a four-electron donation from the alkyne to the metal centre.

Niobium NMR Properties.—The ^{93}Nb nucleus [natural abundance 100%, relative receptivity ($^1\text{H} = 1$) 0.48, spin $\frac{9}{2}$] belongs to the medium category of quadrupoles [the quadrupole moment is 0.28 barn ($2.8 \times 10^{-29} \text{ m}^2$)].¹³ Relaxation times are normally in the μs or ms range (w_1 range from several hundred Hz up to several kHz).¹³ The $\delta(^{93}\text{Nb})$ range is about 3000 ppm, corresponding to a high intrinsic sensitivity of the ^{93}Nb nucleus to modifications in its environment, and that is why ^{93}Nb NMR spectra can indeed be used to monitor electronic effects in co-ordination compounds of this element. The ^{93}Nb nucleus in $[\text{NbX}(\text{CO})_2(\text{RCCR})(\text{PEt}_3)_2]$ (Table 4) is significantly less shielded than in the closely related complexes

Table 5 Selected bond lengths (Å) and angles (°) for complex **3c**

I(1)–Nb(1)	2.913(1)	Nb(1)–P(11)	2.643(2)	I(2)–Nb(2)	2.919(2)	Nb(2)–P(21)	2.650(2)
Nb(1)–P(12)	2.639(2)	Nb(1)–C(11)	2.12(1)	Nb(2)–P(22)	2.660(3)	Nb(2)–C(21)	2.112(9)
Nb(1)–C(12)	2.11(1)	Nb(1)–C(13)	2.100(8)	Nb(2)–C(22)	2.108(9)	Nb(2)–C(23)	2.089(9)
Nb(1)–C(14)	2.095(9)	O(11)–C(11)	1.16(1)	Nb(2)–C(24)	2.091(9)	O(21)–C(21)	1.15(1)
O(12)–C(12)	1.15(1)	C(13)–C(14)	1.30(1)	O(22)–C(22)	1.15(1)	C(23)–C(24)	1.31(1)
C(13)–C(16)	1.49(1)	C(14)–C(15)	1.51(1)	C(23)–C(26)	1.52(1)	C(24)–C(25)	1.51(1)
I(1)–Nb(1)–P(12)	86.24(6)	P(11)–Nb(1)–C(14)	94.1(2)	I(2)–Nb(2)–P(22)	88.21(7)	P(21)–Nb(2)–C(24)	91.8(2)
I(1)–Nb(1)–C(12)	93.4(3)	P(12)–Nb(1)–C(12)	88.6(3)	I(2)–Nb(2)–C(22)	90.7(3)	P(22)–Nb(2)–C(22)	93.1(2)
I(1)–Nb(1)–C(14)	158.4(2)	P(12)–Nb(1)–C(14)	94.4(2)	I(2)–Nb(2)–C(24)	163.3(2)	P(22)–Nb(2)–C(24)	92.4(2)
P(11)–Nb(1)–C(11)	90.6(3)	C(11)–Nb(1)–C(13)	111.5(4)	P(21)–Nb(2)–C(21)	89.4(3)	C(21)–Nb(2)–C(23)	74.3(3)
P(11)–Nb(1)–C(13)	93.4(2)	C(12)–Nb(1)–C(13)	72.2(4)	P(21)–Nb(2)–C(23)	92.8(2)	C(22)–Nb(2)–C(23)	109.0(3)
P(12)–Nb(1)–C(11)	89.7(3)	C(13)–Nb(1)–C(14)	36.1(3)	P(22)–Nb(2)–C(21)	89.8(3)	C(23)–Nb(2)–C(24)	36.5(3)
P(12)–Nb(1)–C(13)	94.7(2)	Nb(1)–C(11)–O(11)	174.0(1)	P(22)–Nb(2)–C(23)	91.0(2)	Nb(2)–C(22)–O(22)	175.7(9)
C(11)–Nb(1)–C(12)	176.1(4)	Nb(1)–C(13)–C(14)	71.8(5)	C(21)–Nb(2)–C(22)	175.5(3)	Nb(2)–C(23)–C(26)	151.0(7)
C(11)–Nb(1)–C(14)	75.4(4)	C(14)–C(13)–C(16)	136.3(9)	C(21)–Nb(2)–C(24)	110.8(4)	Nb(2)–C(24)–C(25)	71.7(5)
C(12)–Nb(1)–C(14)	108.2(4)	Nb(1)–C(14)–C(15)	150.0(7)	C(22)–Nb(2)–C(24)	72.6(3)	C(23)–C(24)–C(25)	136.0(9)
I(1)–Nb(1)–P(11)	85.10(6)	Nb(1)–C(12)–O(12)	172.8(9)	I(2)–Nb(2)–P(21)	87.56(6)	Nb(2)–C(21)–O(21)	175.3(9)
I(1)–Nb(1)–C(11)	83.0(3)	Nb(1)–C(13)–C(16)	151.9(7)	I(2)–Nb(2)–C(21)	85.9(3)	Nb(2)–C(23)–C(24)	71.9(6)
I(1)–Nb(1)–C(13)	165.5(3)	Nb(1)–C(14)–C(13)	72.2(5)	I(2)–Nb(2)–C(23)	160.2(2)	C(24)–C(23)–C(26)	137.2(9)
P(11)–Nb(1)–P(12)	171.24(8)	C(13)–C(14)–C(15)	137.8(8)	P(21)–Nb(2)–P(22)	175.75(9)	Nb(2)–C(24)–C(25)	152.3(7)
P(11)–Nb(1)–C(12)	90.6(3)			P(21)–Nb(2)–C(22)	87.5(2)		

Table 6 Fractional atomic coordinates for complex **3c**

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
I(1)	0.547 2(1)	0.160 37(5)	0.697 17(5)	I(2)	0.071 66(7)	0.698 29(4)	0.765 39(4)
Nb(1)	0.273 74(8)	0.267 37(4)	0.773 21(4)	Nb(2)	0.347 27(8)	0.767 71(4)	0.732 84(4)
P(11)	0.291 8(3)	0.367 2(1)	0.642 8(1)	P(21)	0.471 5(3)	0.645 7(1)	0.831 7(1)
P(12)	0.297 3(3)	0.154 5(1)	0.894 4(1)	P(22)	0.205 0(3)	0.884 8(1)	0.634 9(1)
O(11)	0.077(1)	0.163 3(6)	0.707 4(5)	O(21)	0.483(1)	0.649 7(5)	0.597 6(4)
O(12)	0.465 0(9)	0.367 2(5)	0.845 9(4)	O(22)	0.222(1)	0.874 8(5)	0.876 1(4)
C(11)	0.154(1)	0.198 2(6)	0.728 3(6)	C(21)	0.428(1)	0.690 5(6)	0.645 7(5)
C(12)	0.407(1)	0.329 6(6)	0.817 4(5)	C(22)	0.260(1)	0.837 0(5)	0.825 4(5)
C(13)	0.119(1)	0.358 6(5)	0.833 9(4)	C(23)	0.563 6(9)	0.790 9(5)	0.680 2(5)
C(14)	0.037 9(9)	0.318 3(5)	0.808 6(5)	C(24)	0.510(1)	0.835 3(5)	0.736 7(5)
C(15)	–0.132(1)	0.319 8(6)	0.810 9(6)	C(25)	0.565(1)	0.897 3(7)	0.769 6(7)
C(16)	0.085(1)	0.429 9(5)	0.877 8(6)	C(26)	0.708(1)	0.776 2(8)	0.619 7(6)
C(17)	0.214(1)	0.343 0(8)	0.563 9(5)	C(27)	–0.003(1)	0.931 2(9)	0.658 7(8)
C(18)	0.037(1)	0.350 2(9)	0.580 8(7)	C(28)	–0.047(1)	0.970 0(8)	0.734 0(8)
C(19)	0.185(1)	0.472 2(5)	0.657 0(5)	C(29)	0.295(1)	0.973 8(7)	0.614 9(8)
C(110)	0.172(1)	0.538 5(7)	0.586 5(6)	C(210)	0.248(2)	1.045 9(9)	0.556 6(9)
C(111)	0.484(1)	0.381 0(6)	0.589 6(5)	C(211)	0.219(2)	0.860 6(9)	0.535 7(8)
C(112)	0.584(1)	0.407(1)	0.636 0(7)	C(212)	0.142(1)	0.800 0(9)	0.527 6(8)
C(113)	0.213(1)	0.065 9(5)	0.899 0(6)	C(213)	0.614(1)	0.677 3(5)	0.875 2(5)
C(114)	0.035(1)	0.086 2(7)	0.908 6(7)	C(214)	0.701(1)	0.612 4(7)	0.932 8(7)
C(115)	0.201(1)	0.199 6(6)	0.982 6(5)	C(215)	0.344(1)	0.603 0(7)	0.913 1(6)
C(116)	0.202(1)	0.142 0(8)	1.058 2(6)	C(216)	0.251(1)	0.664 8(9)	0.967 7(6)
C(117)	0.493(1)	0.099 7(7)	0.915 0(7)	C(217)	0.582(1)	0.550 7(5)	0.793 3(6)
C(118)	0.592(1)	0.157(1)	0.928 9(9)	C(218)	0.730(1)	0.559 3(7)	0.735 1(7)

[NbX(CO)₃(PMe₂Ph)₃] (δ – 1290 to – 1410).⁹ This deshielding effect on substituting CO for an alkene or an alkyne is a general trend also observed with other transition metals¹⁴ and may be interpreted in terms of lower strength in a magnetochemical series of ligand strengths.¹³ In contrast to [NbX(CO)₃(PMe₂Ph)₃], but in accord with other findings for low-valent (closed-shell) transition-metal complexes, the alkyne complexes exhibit a *normal* dependence of metal shielding on the nature of X, i.e. an increase in shielding in the series Cl < Br < I, paralleling an increase in the polarizability of X. Spin–spin relaxation times T_2 for compounds **1b–3c** are between 6×10^{-6} and 9×10^{-6} s, and hence are one order of magnitude less than for the carbonyl precursors (ca. 5×10^{-5} s).

Crystal Structure of [NbI(CO)₂(MeCCMe)(PEt₃)₂] **3c.**—There are two independent molecules in the asymmetric unit. The compound crystallizes in the space group $P\bar{1}$. Selected bond distances and angles are collected in Tables 5 and 6; Fig. 2 is a SCHAKAL drawing¹⁵ of **3c**. The co-ordination sphere of

niobium can be described as octahedral, with the alkyne occupying one co-ordination site. The alkyne C–C axis is parallel to OC–Nb–CO, as expected for optimum π -back bonding from the Nb 3d_{xy}/d_{yz} orbitals into π^* orbitals of the ligand. The niobium–alkyne carbon distances in both molecules do not differ significantly and are similar to those in [TaCl(Me₃SiOCCOSiPr₃)(dmpe)₂],^{4a} [TaI(CO)₂(PhCCPh)(PMe₃)₂],^{4b} and [MCl(Me₃SiOCCOSiMe₃)(dmpe)₂] (M = Nb or Ta, dmpe = Me₂PCH₂CH₂PMe₂).^{4c,d} They are relatively short in comparison to some cyclopentadienyl–niobium and –tantalum alkyne complexes,^{2g,3a} but relatively long when compared to some alkyne complexes of d⁴ Mo^{II}.¹² As expected, the alkyne C–C distance (1.31 Å) in **3c** is longer than in the unco-ordinated molecule, consistent with the reduction of bond order on complexation. The carbon monoxide and phosphine ligands are nearly uniformly bent away from the alkyne (molecule 1, OC–Nb–CO 176°, P–Nb–P 171°; molecule 2, OC–Nb–CO 175°, P–Nb–P 175°). Similar values for OC–Nb–CO have been obtained from IR intensity data (see above).

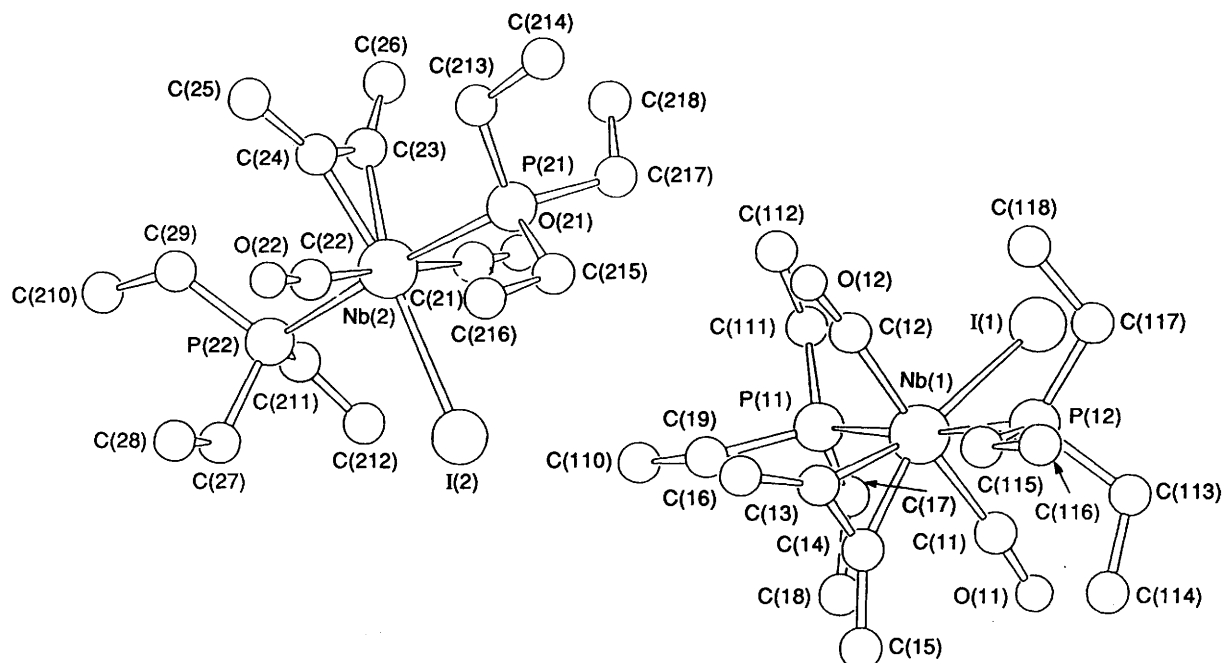


Fig. 2 A SCHAKAL drawing of the molecular structure of *trans*-[NbI(CO)₂(MeCCMe)(PEt₃)₂]

Experimental

Materials and Procedures.—All operations were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried over appropriate desiccants (Na/K alloy for hexane, lithium aluminium hydride for tetrahydrofuran and sodium for toluene) and distilled under N₂ prior to use. Niobium pentachloride (Fluka) was purified by vacuum sublimation, PEt₃ and alkynes were purchased and used without further purification. 1,2-Bis(diphenylphosphino)ethane was prepared according to a procedure of Hewertson and Watson.¹⁶ Pyridinium bromide was prepared directly from pyridine and concentrated HBr in aqueous solution and recrystallized from ethanol–toluene. The hexacarbonylniobate anion was synthesised by a published procedure,⁶ and precipitated as the tetraethylammonium salt in Et₂O solution by adding an aqueous solution of [NEt₄]Br. The complexes [NbX(CO)₄(dppe)] (X = Br or I) were prepared by published methods;¹⁰ [NbX(CO)₃(PEt₃)₃] were prepared as described below by modifications of procedures previously reported by Sattelberger⁸ and Rehder⁹ and their co-workers.

Physical Measurements.—Infrared spectra were recorded in tetrahydrofuran (thf) (0.1 mm CaF₂ cuvette) or in Nujol suspension between KBr plates on a Perkin-Elmer 577 spectrophotometer calibrated with a polystyrene film, NMR spectra on a Bruker AM 360 (360 MHz, ¹H; 90.56 MHz, ¹³C; 145.8 MHz, ³¹P) spectrometer at ambient temperatures (¹H, ¹³C) or at 210 K (³¹P) and ⁹³Nb NMR spectra on a modified Varian SWL 3-100 wide-line spectrometer at 16 MHz (*B*₀ = 1.546 T), sweep width 15 mT, number of scans 150, scan time 2 min, 14 mm tubes, with a saturated solution of [NEt₄][NbCl₆] in MeCN as standard.

Synthesis of the Starting Materials.—[NbCl(CO)₃(PEt₃)₃] **1**. Pyridinium chloride (0.474 g, 4.10 mmol) was suspended at room temperature in a thf solution (25 cm³) of [NEt₄][Nb(CO)₆] (0.782 g, 2.00 mmol) and PEt₃ (0.82 cm³, 6.20 mmol). The reaction started after ca. 1 h of stirring with the evolution of gas. After 16 h of stirring at room temperature the red solution was filtered (removal of [NEt₄]Cl), and the solvents and excess of PEt₃ were removed *in vacuo* at room temperature. The residue of **1** [*v*(CO) 1935s, 1854s and 1832s cm^{−1} (thf)] was

redissolved in thf (20 cm³), filtered, and used as reagent solution for the preparation of complexes **1a** and **1b**. A very similar procedure was employed to prepare the bromide derivative [NbBr(CO)₃(PEt₃)₃] **2**: pyridinium bromide (0.648 g, 2.00 mmol), [NEt₄][Nb(CO)₆] (0.782 g, 2.00 mmol), PEt₃ (0.83 cm³, 6.28 mmol), 24 h of stirring, *v*(CO) 1930s, 1845s and 1820s cm^{−1} (thf).

[NbI(CO)₃(PEt₃)₃] **3**. A thf solution (25 cm³) of [NEt₄][Nb(CO)₆] (0.782 g, 2.00 mmol) was treated, under stirring and at room temperature, with PEt₃ (0.82 cm³, 6.20 mmol). The solution was cooled to about −78 °C, and iodine (0.501 g, 1.97 mmol) added. Immediate reaction with gas evolution took place, and the solution darkened. After 2 h of reaction the solution was warmed to room temperature and stirred for 5 h. A greyish precipitate of [NEt₄]I was filtered off, and the dark red solution of complex **3** [*v*(CO) 1925s, 1840s and 1815s cm^{−1} (thf)] was used directly for the preparations of **3a–3d**.

Alkyne Complexes.—[NbCl(CO)₂(PhCCPh)(PEt₃)₂] **1a**. Diphenylacetylene (0.349 g, 1.96 mmol) was added with stirring to a thf solution (25 cm³) of complex **1**, prepared as described above. Infrared spectroscopy was used to monitor the reaction. Small amounts of an unidentified, colourless precipitate were filtered off after 67 h of stirring, and the solvent was removed *in vacuo*. The dark oily residue was dissolved in toluene (20 cm³), filtered again, and evaporated to dryness. The residue was washed with three portions of cold (0 °C) hexane (3.5 cm³), dried *in vacuo*, then redissolved in warm (45 °C) hexane (10 cm³) and filtered immediately. Recrystallization at about −20 °C yielded dark pink crystals of [NbCl(CO)₂(PhCCPh)(PEt₃)₂] **1a** {0.970 g, 81% with respect to [NEt₄][Nb(CO)₆]} (Found: C, 56.0; H, 6.8; Cl, 6.0; Nb, 15.3; P, 10.5. C₂₈H₄₀ClNbO₂P₂ requires C, 56.1; H, 6.7; Cl, 5.9; Nb, 15.5; P, 10.3%). Complex **1b** was obtained in the same way, the reaction requiring only 8 h. Recrystallization yielded crystalline **1b** {0.734 g, 73% with respect to [NEt₄][Nb(CO)₆]} (Found: C, 43.9; H, 7.3; Br, 14.6; Nb, 16.8; P, 11.3. C₂₀H₄₀BrNbO₂P₂ requires C, 43.9; H, 7.4; Br, 14.6; Nb, 17.0; P, 11.3%). **3a**, 86; **3b**, 79 (Found: C, 40.1; H, 6.7; I, 21.4; Nb, 15.4;

P, 10.1. $C_{20}H_{40}INbO_2P_2$ **3b** requires C, 40.4; H, 6.8; I, 21.3; Nb, 15.6; P, 10.4%; **3c**, 65%.

$[NbI(CO)_2(HCCH)(PEt_3)_2]$ **3d**. A thf solution (25 cm³) of complex **3**, prepared as described above, was cooled to about -15°C and stirred gently under an atmosphere of acetylene prepurified by passage through concentrated sulfuric acid and molecular sieves. Gas evolution was observed, and the colour darkened. After 2 h the solvent was removed *in vacuo* at about -15°C (warming to room temperature led to polymerization of excessive alkyne and decomposition of the complex). The residue was evacuated for 30 min and then dissolved in thf (10 cm³). Addition of hexane (10 cm³) at -30°C caused precipitation of red, crystalline compound **3d**, which was filtered off and dried *in vacuo* {0.290 g, 27% with respect to $[NEt_4][Nb(CO)_6]$ }.

$[NbBr(CO)_2(PhCCPh)(dppe)]$ **4a**. Diphenylacetylene (0.089 g, 0.50 mmol) was added to a red solution of complex **4** (0.370 g, 0.54 mmol) in thf (25 cm³). After 30 min a moderate evolution of CO was observed. The reaction was monitored by IR spectroscopy. After 8 h of stirring any carbonyl absorptions of the starting complex had disappeared. A small amount of colourless, unidentified precipitate was filtered off, and the solvent was removed *in vacuo*. The residue was dissolved in thf (10 cm³) and cooled to about -10°C . Addition of cold (0°C) hexane (20 cm³) caused precipitation of red crystalline complex **4a**, which was filtered off and dried *in vacuo* (0.27 g, 63%). Following the same procedure, and using a solution of the starting complex **5**, $[NbI(CO)_2(PhCCPh)(dppe)]$ **5a** was obtained (0.266 g, 58%).

Crystal Structure Determination for Complex 3c.—The crystals for the diffraction experiments were obtained from hexane solutions at about -26°C and sealed in a Lindemann capillary.

Crystal data. $C_{18}H_{36}INbO_2P_2$, $M = 566.2$, triclinic, space group $P\bar{1}$, $a = 9.000(1)$, $b = 16.906(2)$, $c = 17.952(3)$ Å, $\alpha = 80.07(1)$, $\beta = 78.59(1)$, $\gamma = 75.50(1)^\circ$, $U = 2570(7)$ Å³, $Z = 4$, $D_c = 1.37$ g cm⁻³, $F(000)$ 992, dark pink slightly air-sensitive plates, approximate crystal dimensions $0.96 \times 0.47 \times 0.20$ mm, $\mu(\text{Mo-K}\alpha) = 17.6$ cm⁻¹.

Data collection and processing. Syntex P2₁ diffractometer, Mo-K α radiation, range $4.5 < 2\theta < 55.0^\circ$; total number of reflections 10 832, 6787 of which with $I > 2\sigma(I)$ were retained, number of parameters 435. Data were recorded using the θ - 2θ scan technique, $h = 0$ –12, $k = -22$ to 22, $l = -24$ to 24. Two standard reflections were measured every 100 and no significant change in intensities was detected. Intensities were corrected for Lorentz and polarization effects in the usual manner. Neither absorption nor extinction corrections were made.

Structure analysis and refinement. The atom positions were located *via* direct methods which used the complete set of data. Atomic coordinates, see Table 6, were refined by full-matrix least-squares techniques, first assuming isotropic parameters for all non-hydrogen atoms and then with anisotropic thermal parameters. In the later stages of refinement the hydrogen atoms were included for geometric calculations with fixed positions and thermal parameters. Final values of R and R' are 0.061 and 0.075 with a weighting scheme $w = 2.2185/(\sigma^2 F_o + 0.0005 F_o)$ giving satisfactory agreement analyses. Anomalous dispersion corrections and atomic scattering factors were taken from ref. 17. Calculations were performed with the SHELXS 86 and SHELX 76 programs^{18,19} on a VAX computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

The authors gratefully acknowledge financial support from the Deutscher Akademischer Austausch Dienst (DAAD) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologia (MURST).

References

- 1 J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1.
- 2 (a) Daekeun Kwon, J. Real, M. D. Curtis, A. Rheingold and B. S. Haggerty, *Organometallics*, 1991, **10**, 143; (b) M. D. Curtis, J. Real and Daekeun Kwon, *Organometallics*, 1989, **8**, 1644; (c) M. D. Curtis and J. Real, *Organometallics*, 1985, **4**, 940; (d) A. N. Nesmeyanov, N. E. Kobolova, A. B. Antonova, K. N. Anisimov and O. M. Khitrova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 859; (e) N. I. Kirillova, N. E. Kolobova, A. I. Gusev, A. B. Antonova, Yu. T. Struchkov, K. N. Anisimov and O. M. Khitrova, *Zh. Strukt. Khim.*, 1974, **15**, 651; (f) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kobolova and A. A. Pasynskii, *Dokl. Akad. Nauk SSSR*, 1968, **181**, 1142; (g) A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kobolova and Yu. T. Struchkov, *Chem. Commun.*, 1969, 277; (h) A. I. Gusev and Yu. T. Struchkov, *Z. Strukt. Khim.*, 1969, **10**, 294; (i) A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kobolova and Yu. T. Struchkov, *Chem. Commun.*, 1969, 739; (j) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1969, **10**, 515; (k) A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kobolova and Yu. T. Struchkov, *Chem. Commun.*, 1968, 1365; (l) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kobolova and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 774.
- 3 (a) A. Antiñolo, P. Gómez-Sal, J. Martínez de Ilarduya, A. Otero, P. Royo, S. Martínez Carrera and S. García Blanco, *J. Chem. Soc., Dalton Trans.*, 1987, 975; (b) R. S. Threlkel and J. E. Bercaw, *J. Am. Chem. Soc.*, 1981, **103**, 2650; (c) J. Sala-Pala, J. Amaudrut, J. E. Guerschais, R. Mercier, J. Douglade and J. G. Theobald, *J. Organomet. Chem.*, 1981, **204**, 347; (d) M. L. H. Green and B. Jousseau, *J. Organomet. Chem.*, 1980, **193**, 339; (e) A. A. Pasynskii, Yu. V. Skripkin, V. T. Kalinnikov, M. A. Porai-Koshits, A. S. Antsyshkina, G. G. Sadikov and V. N. Ostrikova, *J. Organomet. Chem.*, 1980, **201**, 269; (f) J. L. LeQuere, F. Y. Pettillon, J. E. Guerschais and J. Sala-Pala, *Inorg. Chim. Acta*, 1980, **43**, 5; (g) A. A. Pasynskii, Yu. V. Skripkin, I. L. Eremenko, V. T. Kalinnikov, G. G. Alexandrov and Yu. T. Struchkov, *J. Organomet. Chem.*, 1979, **165**, 39; (h) J. Sala-Pala, J. Amaudrut, J. E. Guerschais, R. Mercier and M. Cerutti, *J. Fluorine Chem.*, 1979, **14**, 269; (i) S. Fredericks and J. L. Thomas, *J. Am. Chem. Soc.*, 1978, **100**, 350; (j) J. A. Labinger and J. Schwartz, *J. Am. Chem. Soc.*, 1975, **97**, 1596; (k) J. A. Labinger, J. Schwartz and J. M. Townsend, *J. Am. Chem. Soc.*, 1974, **96**, 4009.
- 4 (a) R. N. Vrtis, Shuncheng Liu, Ch. Pulla Rao, S. G. Bott and S. J. Lippard, *Organometallics*, 1991, **10**, 275; (b) M. J. McGeary, A. S. Gamble and J. L. Templeton, *Organometallics*, 1988, **7**, 271; (c) P. A. Bianconi, I. D. Williams, M. P. Engeler and S. J. Lippard, *J. Am. Chem. Soc.*, 1986, **108**, 311; (d) P. A. Bianconi, R. N. Vrtis, Ch. Pulla Rao, I. D. Williams and M. P. Engeler, *Organometallics*, 1987, **6**, 1968.
- 5 (a) J. B. Hartung, jun. and S. F. Pedersen, *Organometallics*, 1990, **9**, 1414; (b) F. A. Cotton and M. Shang, *Inorg. Chem.*, 1990, **29**, 508; (c) F. A. Cotton and W. T. Hall, *Inorg. Chem.*, 1980, **19**, 2352.
- 6 F. Calderazzo, U. Englert, G. Pampaloni, G. Pelizzi and R. Zamboni, *Inorg. Chem.*, 1983, **22**, 1865.
- 7 C. G. Dewey, J. E. Ellis, K. L. Fjare, K. M. Pfahl and G. F. P. Warnock, *Organometallics*, 1983, **2**, 388.
- 8 M. C. Luetgens, jun., D. J. Santure, J. C. Huffmann and A. P. Sattelberger, *J. Chem. Soc., Chem. Commun.*, 1985, 522.
- 9 C. Felten, J. Richter, W. Pribsch and D. Rehder, *Chem. Ber.*, 1989, **122**, 1617.
- 10 F. Calderazzo, G. Pampaloni, G. Pelizzi and F. Vitali, *Organometallics*, 1988, **7**, 1083.
- 11 W. Beck, A. Melnikow and R. Stahl, *Chem. Ber.*, 1966, **99**, 3721.
- 12 P. B. Winston, S. J. N. Burgmayer, T. L. Tonker and J. L. Templeton, *Organometallics*, 1986, **5**, 1707.
- 13 D. Rehder, in *Transition Metal Nuclear Magnetic Resonance*, ed. P. S. Pregosin, Elsevier, Amsterdam, 1991.
- 14 D. Rehder, *Coord. Chem. Rev.*, 1991, **110**, 161; K. Ihmels and D. Rehder, *Organometallics*, 1985, **4**, 1340.
- 15 E. Keller, SCHAKAL, Plot Program for Molecular Models, University of Freiburg, 1980.
- 16 W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.
- 17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
- 18 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingen, 1986.
- 19 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

Received 16th January 1992; Paper 2/00249C