New Alkyne Complexes of Niobium(I)†

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The reaction between the seven-co-ordinated niobium(I) complexes [$NbX(CO)_4$(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$, X = Br or I) or [$NbX(CO)_3(PEt_3)_3$] (X = Cl, Br or I) and alkynes leads to the d^4 niobium alkyne complexes [$NbX(CO)_2(\eta^2$-RCCR)(dppe)] (R = Ph) and [$NbX(CO)_2(\eta^2$-RCCR)$(PEt_3)_2$] (R = 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.* Cl < Br < I. The crystal and molecular structures of [$NbI(CO)_2$(MeCCMe)$(PEt_3)_2$] have been determined: triclinic, space group $P\bar{1}$, a = 9.000(1), b = 16.906(2), c =17.952(3) Å, α = 80.07(1), β = 78.59(1), γ = 75.50(1)°. The molecule has a slightly distorted octahedral geometry with the carbonyl and the phosphine ligands in *trans* positions. Average distances are: Nb–CO 2.11(5), Nb–C(alkyne) 2.09(9) and Nb–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–l,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 $[Nb(CO)_6]^-$ 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 $NbX(CO)_{6-n}L_n$ have been reported, prepared by oxidation of the $[Nb(CO)_6]^-$ 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*-[$NbX(CO)_2$(RCCR)L_2] complexes [X = Cl, Br or I; L_2 = 2 PEt_3 or $Ph_2PCH_2CH_2PPh_2$ (dppe); R = 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 [$NbX(CO)_3(PEt_3)_3$] (X = Cl **1**, Br **2** or I **3**) and [$NbX(CO)_4$(dppe)] (X = Br **4** or I **5**) react with alkynes RCCR (R = Ph, Et, Me or H) under mild conditions to form red-violet, six-co-ordinate, alkyne adducts of niobium(I), *viz.* [$NbX(CO)_2$(RCCR)$(PEt_3)_2$] (X = Cl, R = Ph **1a** or Et **1b**; X = Br, R = Ph **2a** or Et **2b**; X = I, R = Ph **3a**, Et **3b**, Me **3c** or H **3d**) and [$NbX(CO)_2$(PhCCPh)(dppe)] (X = Br **4a** or I, **5a**), see equations (1) and (2), respectively. These red-violet crystalline compounds are

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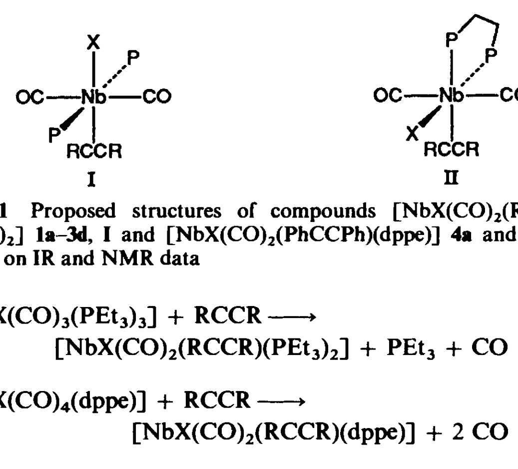

Fig. 1 Proposed structures of compounds [$NbX(CO)_2$(RCCR)$(PEt_3)_2$] **1a**–**3d**, **I** and [$NbX(CO)_2$(PhCCPh)(dppe)] **4a** and **5a**, **II**, based on IR and NMR data

$$[NbX(CO)_3(PEt_3)_3] + RCCR \longrightarrow [NbX(CO)_2(RCCR)(PEt_3)_2] + PEt_3 + CO \quad (1)$$

$$[NbX(CO)_4(dppe)] + RCCR \longrightarrow [NbX(CO)_2(RCCR)(dppe)] + 2\,CO \quad (2)$$

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

Table 1 Infrared data (cm^{-1}, 0.1 mm CaF_2; thf) for the complexes $[NbX(CO)_2(RCCR)L_2]$ (L_2 = 2 PEt_2 or dppe) in the carbonyl stretching region

1a $[NbCl(CO)_2(PhCCPh)(PEt_3)_2]$	1992m, 1910vs
1b $[NbCl(CO)_2(EtCCEt)(PEt_3)_2]$	1990m, 1890vs
2a $[NbBr(CO)_2(PhCCPh)(PEt_3)_2]$	1990m, 1925vs*
2b $[NbBr(CO)_2(EtCCEt)(PEt_3)_2]$	1960w, 1890vs
3a $[NbI(CO)_2(PhCCPh)(PEt_3)_2]$	1988m, 1917vs
3b $[NbI(CO)_2(EtCCEt)(PEt_3)_2]$	1973w, 1904vs
3c $[NbI(CO)_2(MeCCMe)(PEt_3)_2]$	1980w, 1900vs
3d $[NbI(CO)_2(HCCH)(PEt_3)_2]$	1997w, 1920vs
4a $[NbBr(CO)_2(PhCCPh)(dppe)]$	2065m, 2020vs
5a $[NbI(CO)_2(PhCCPh)(dppe)]$	2060m, 2015vs

* In KBr, Nujol.

Table 2 Proton and ^{31}P NMR data for the complexes $[NbX(CO)_2(RCCR)L_2]$ (L_2 = 2 PEt_3 or dppe)

Compound	$\delta(^1H)^a$	$\delta(^{31}P)^b$
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_{HH} = 7.7, 6 H, CCH_2CH_3), 1.34 (m, 12 H, PCH_2), 3.28 (q, 4 H, J_{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_{HH} = 7.7, CCH_2CH_3), 1.37 (m, 12 H, PCH_2), 3.32 (q, 4 H, J_{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_{HH} = 7.5, CCH_2CH_3), 1.39 (m, 12 H, PCH_2), 3.32 (q, 4 H, J_{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 $[^2H_8]$thf, $SiMe_4$, given as δ (multiplicity, relative intensity, J/Hz, assignment); s = singlet, t = triplet, q = quartet, m = multiplet. ^{b} In $[^2H_8]$thf, H_3PO_4 as external standard, 210 K, values given as δ, br = broad.

Table 3 Carbon-13 NMR data for the complexes $[NbX(CO)_2(EtCCEt)(PEt_3)_2]$ (X = Cl, Br or I)^a

	$\delta(^{13}C)$			
Compound	PEt_3	Et	C≡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 $[^2H_8]$thf. ^{b} Terminal C. ^{c} Triplet, J_{PC} = 9 Hz. ^{d} Methylene C. ^{e} Triplet, J_{PC} = 8 Hz.

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

In the iodide complexes **3a**–**3d**, phenyl substituents on the alkyne increase ν_{CO} relative to the values for the alkylated 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 $[NbX(CO)_2(RCCR)L_2]$. A crude calculation of the OC–Nb–CO angle based on the intensity ratio of the two CO absorptions [11] 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]

Table 4 Niobium-93 NMR data for the complexes $[NbX(CO)_2(RCCR)(PEt_3)_2]$

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

* In $[^2H_8]$thf, external standard $[NEt_4][NbCl_6]$.

^{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 Cl > Br > 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 $[NbI(CO)_2(HCCH)(PEt_3)_2]$ has an 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 (^1H = 1) 0.48, spin $\frac{9}{2}$] belongs to the medium category of quadrupoles [the quadrupole moment is 0.28 barn (2.8×10^{-29} m^2)].[13] Relaxation times are normally in the μs or ms range ($w_{\frac{1}{2}}$ range from several hundred Hz up to several kHz).[13] The $\delta(^{93}Nb)$ 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 $[NbX(CO)_2(RCCR)(PEt_3)_2]$ (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(23)	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)

[$NbX(CO)_3(PMe_2Ph)_3$] (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 metals[14] and may be interpreted in terms of lower strength in a magnetochemical series of ligand strengths.[13] In contrast to [$NbX(CO)_3(PMe_2Ph)_3$], 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 [$NbI(CO)_2(MeCCMe)(PEt_3)_2$] **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 drawing[15] 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 $3d_{xz}/d_{yz}$ 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 [$TaCl(Me_3SiOCCOSiPr^i_3)(dmpe)_2$],[4a] [$TaI(CO)_2(PhCCPh)(PMe_3)_2$],[4b] and [$MCl(Me_3SiOCCOSiMe_3)(dmpe)_2$] (M = Nb or Ta, dmpe = $Me_2PCH_2CH_2PMe_2$).[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 d^4 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).

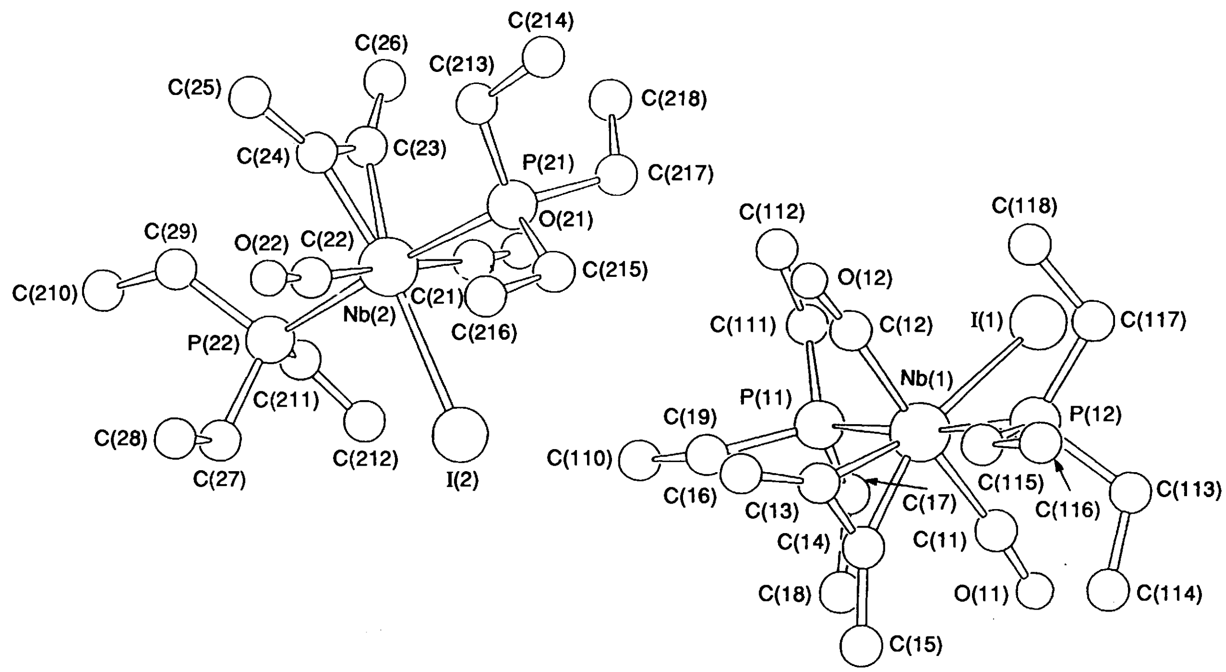

Fig. 2 A SCHAKAL drawing of the molecular structure of *trans*-[NbI(CO)$_2$(MeCCMe)(PEt$_3$)$_2$]

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 N_2 prior to use. Niobium pentachloride (Fluka) was purified by vacuum sublimation, PEt$_3$ 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 Et$_2$O solution by adding an aqueous solution of [NEt$_4$]Br. The complexes [NbX(CO)$_4$(dppe)] (X = Br or I) were prepared by published methods;[10] [NbX(CO)$_3$(PEt$_3$)$_3$] were prepared as described below by modifications of procedures previously reported by Sattelberger[8] and Rehder[9] and their co-workers.

Physical Measurements.—Infrared spectra were recorded in tetrahydrofuran(thf) (0.1 mm CaF$_2$ 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, ^{1}H; 90.56 MHz, ^{13}C; 145.8 MHz, ^{31}P) spectrometer at ambient temperatures (^{1}H, ^{13}C) or at 210 K (^{31}P) and ^{93}Nb NMR spectra on a modified Varian SWL 3-100 wideline 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 [NEt$_4$][NbCl$_6$] in MeCN as standard.

Synthesis of the Starting Materials.—[NbCl(CO)$_3$(PEt$_3$)$_3$] **1**. Pyridinium chloride (0.474 g, 4.10 mmol) was suspended at room temperature in a thf solution (25 cm^3) of [NEt$_4$][Nb(CO)$_6$] (0.782 g, 2.00 mmol) and PEt$_3$ (0.82 cm^3, 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 [NEt$_4$]Cl), and the solvents and excess of PEt$_3$ were removed *in vacuo* at room temperature. The residue of **1** [ν(CO) 1935s, 1854s and 1832s cm^{-1} (thf)] was redissolved in thf (20 cm^3), 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)$_3$(PEt$_3$)$_3$] **2**: pyridinium bromide (0.648 g, 2.00 mmol), [NEt$_4$][Nb(CO)$_6$] (0.782 g, 2.00 mmol), PEt$_3$ (0.83 cm^3, 6.28 mmol), 24 h of stirring, ν(CO) 1930s, 1845s and 1820s cm^{-1} (thf).

[NbI(CO)$_3$(PEt$_3$)$_3$] **3**. A thf solution (25 cm^3) of [NEt$_4$][Nb(CO)$_6$] (0.782 g, 2.00 mmol) was treated, under stirring and at room temperature, with PEt$_3$ (0.82 cm^3, 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 [NEt$_4$]I was filtered off, and the dark red solution of complex **3** [ν(CO) 1925s, 1840s and 1815s cm^{-1} (thf)] was used directly for the preparations of **3a**–**3d**.

Alkyne Complexes.—[NbCl(CO)$_2$(PhCCPh)(PEt$_3$)$_2$] **1a**. Diphenylacetylene (0.349 g, 1.96 mmol) was added with stirring to a thf solution (25 cm^3) 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 cm^3), filtered again, and evaporated to dryness. The residue was washed with three portions of cold (0 °C) hexane (3.5 cm^3), dried *in vacuo*, then redissolved in warm (45 °C) hexane (10 cm^3) and filtered immediately. Recrystallization at about −20 °C yielded dark pink *crystals* of [NbCl(CO)$_2$(PhCCPh)(PEt$_3$)$_2$] **1a** {0.970 g, 81% with respect to [NEt$_4$][Nb(CO)$_6$]} (Found: C, 56.0; H, 6.8; Cl, 6.0; Nb, 15.3; P, 10.5. $C_{28}H_{40}ClNbO_2P_2$ 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 [NEt$_4$][Nb(CO)$_6$]}. The bromide derivatives **2a** and **2b** and the iodide derivatives **3a**–**3c** were prepared accordingly, using the corresponding starting solution and the same molar ratios of reagents. Yields {with respect to [NEt$_4$][Nb(CO)$_6$]}: **2a**, 77; **2b**, 85 (Found: C, 43.9; H, 7.3; Br, 14.6; Nb, 16.8; P, 11.3. $C_{20}H_{40}BrNbO_2P_2$ **2b** 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 cm^3) 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 cm^3). Addition of hexane (10 cm^3) 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 cm^3). 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 cm^3) and cooled to about -10 °C. Addition of cold (0 °C) hexane (20 cm^3) 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, $\alpha = 80.07(1)$, $\beta = 78.59(1)$, $\gamma = 75.50(1)°$, $U = 2570(7)$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000)$ 992, dark pink slightly air-sensitive plates, approximate crystal dimensions $0.96 \times 0.47 \times 0.20$ mm, μ(Mo-Kα) = 17.6 cm^{-1}.

Data collection and processing. Syntex $P2_1$ diffractometer, Mo-Kα radiation, range $4.5 < 2\theta < 55.0°$; 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 $w = 2.2185/(\sigma^2 F_o + 0.000\ 50 F_o)$ 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.

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