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Synthesis, structure and reactions of seven-coordinate, phosphine-supported, halide-activated carbonyl- and alkyne-complexes of niobium(I) *

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Abstract

The complexes $(Hal)Nb(CO)_3(PR_3)_3$ ($PR_3 = PEt_3$, Hal = I; $PR_3 = PMe_2Ph$, Hal = Cl, Br, I) and $(Hal)Nb(CO)_{4/2}(dppe)_{1/2}$ (Hal = Br, I) have been prepared by oxidative halogenation of carbonylniobate with pyridinium halides (Hal = Cl, Br) or iodine (Hal = I). In the tricarbonyls, one CO and one PR_3 are labile and can be displaced by a four-electron donating alkyne to give *all-trans*-$[(Hal)Nb(CO)_2(RCCR')(PR_3)_2]$ ($PR_3 = PMe_2Ph$; Hal = Cl, Br, I: R, R′ = H, Et, Ph; R = H, R′ = Ph. $PR_3 = PEt_3$, Hal = I: R, R′ = Pr; R = H, R′ = Bu, Ph; R = Me, R′ = Et). In the case of acetylene, $INb(CO)(HCCH)_2(PEt_3)_2$ is also formed. PR_3 can be displaced by $P(OMe)_3$. In the tetracarbonyls, two CO ligands are replaced by two isonitriles to form $INb(CO)_2(CNR)_2dppe$ (R = ^tBu, Cy), or by one alkyne to form $(Hal)Nb(CO)_2(PhCCPh)dppe$ (Hal = Br, I). In these complexes, the remaining CO ligands occupy *cis* positions. The structure of $BrNb(CO)_2(dppe)_2 \cdot THF$, $INb(CO)_2(dppe)_2 \cdot$ hexane and $INb(CO)_2(PEt_3)_2(MeC{\equiv}CEt)$ have been determined by a single crystal X-ray diffraction study. The alkyne complexes are best regarded as octahedral with the centre of the alkyne ligand occupying the positions *trans* to the halide and the $C{\equiv}C$ axis aligned with the OC–Nb–CO axis. The complexes $(Hal)Nb(CO)_2(dppe)_2$ adopt a trigonal prismatic structure with the halide capping the tetragonal face spanned by the four phosphorus functions. The crystal structure of a by-product, $Br_2Nb(CO)(H_2CPhPCH_2CH_2PPh_2)_2 \cdot 1/2THF$ has also been determined. The geometry is pentagonal bipyramidal, with one of the bromine atoms and the CO on the axis. Some ^{93}Nb NMR data for the Nb^I complexes are presented, and preliminary observations on the reactions between the π-alkyne complexes and H_2 or H^- are reported.

Key words: Niobium; Carbonyl; Alkyne; Crystal structure; Nb-93 NMR; Halide

1. Introduction

The importance of alkynes in organometallic chemistry has been highlighted recently [1]. Alkyne complexes of the Group 5 metals in low oxidation states are of interest in the context of their possible intermediate formation in the catalytic cycle in various reactions involving alkynes. Thus, alkynes undergo cyclotrimerisation or reductive protonation (to *Z*-alkenes) in the presence of MCl_5/Zn (M = Nb, Ta) [2a]. The reaction of alkynes with aldehydes in the presence of MCl_5/Zn yields *E*-allylalcohols, if M = Ta, or 1,3-dienes, if M = Nb [2b]. Other examples of the application of these systems in organic synthesis are the coupling between alkynes and 1,2-aryldialdehydes in the presence of $NbCl_3(DME)$ [3], and the polymerization of 1-alkynes with $NbCl_3(OR)_2$ [4]. In all these reactions it is likely that as the initial step the substrate alkyne coordinates to a low valent metal centre generated by the action of the reductant, thus activating the alkyne. A V^I complex, *viz.* $BrV(ROC{\equiv}COR)(dmpe)_2$ ($R = Me_3Si$), has recently been isolated and structurally characterized [5]. The alkyne in this complex can be hydrogenated to the *Z*-alkene [5], indicating that π-alkyne complexes of V, Nb and Ta may be regarded as models for active intermediates. Other alkyne complexes of the Group 5 metals have been reported; among these are the $M^{III}(d^2)$ complexes $[(Hal)_4M(alkyne)py]^-$ (M = Ta, Hal = Cl, alkyne = tolane [6]; M = Nb, Hal = Br, alkyne = $F_3CC{\equiv}CCF_3$ [7]) and $(Hal)_3NbL_n(alkyne)$ [8], the mononuclear $M^I(d^4)$ complexes $(Hal)M(CO)_xL_y(alkyne)$ (M = V [9], Nb [10], Ta [10b,10c,11]), and the dinuclear Nb^I complexes $\{Nb(CO)_2(alkyne)_2\}_2(\mu\text{-}Hal)_2$ [12].

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In most cases, the M^I complexes were prepared by reductive coupling of CO or CNR in carbonyl or isocyanide precursor complexes [5,10b,10c,11b,13], or by replacement of substitution-labile CO and phosphine ligands [9,10a]. Labilization of these ligands is particularly effective in the seven-coordinated precursor complexes (Hal)M(CO)$_{6-n}$p$_n$ [14], where p$_n$ represents a tridentate or, in the case of $n = 3$, three monodentate phosphines or, in the case of $n = 2$ or 4, one or two bidentate phosphines. In the present study, we have employed these complexes to prepare alkyne complexes of niobium. A preliminary report has appeared [10a].

2. Results and discussion

2.1. *The precursor complexes (Hal)Nb(CO)$_{6-n}$p$_n$, and Br$_2$Nb(CO)p$_4$*

2.1.1. *Preparation, and reaction with isonitriles*

The hepta-coordinated Nb^I complexes were prepared as described earlier [14a] by oxidation of $[Nb(CO)_6]^-$ with pyridinium-halides (Hal = Br, Cl), or iodine in the presence of phosphines, as shown in eqns. (1) and (2); the Nb^{II} complex $Br_2Nb(CO)p_4$ (p_4 is the linear tetraphosphine [tetraphos] $[CH_2PPhCH_2CH_2PPh_2]_2$) is formed as a by-product along with $BrNb(CO)_2p_4$ (eqn. (3)), and can be isolated by fractional crystallization from a THF solution.

$$[Nb(CO)_6]^- + 3PMe_2Ph + 2[Hpy]Cl/Br \longrightarrow Cl/BrNb(CO)_3(PMe_2Ph)_3 + H_2 + Cl^-/Br^- + 2py + 3CO \quad (1)$$

$$[Nb(CO)_6]^- + 2/3PMe_2Ph + I_2 \longrightarrow INb(CO)_{4/3}(PMe_2Ph)_{2/3} + I^- + 2/3CO \quad (2)$$

$$[Nb(CO_6)]^- + p_4 + [Hpy]Br \longrightarrow BrNb(CO)_2p_4 \text{ and } Br_2Nb(CO)p_4 \quad (3)$$

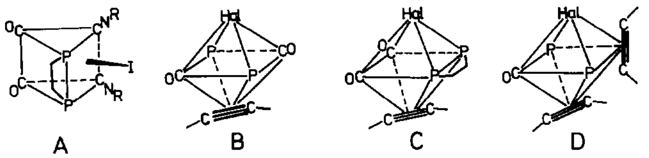
The compounds exhibit the ν(CO) pattern reported earlier for this type of complex [10,14]; *i.e.* two bands at *ca.* 1840vs and 1750s cm^{-1} for the dicarbonyl complexes, and three bands at *ca.* 1945vs, 1890s and 1870s cm^{-1} for the tricarbonyl complexes. Where (usually small) amounts of the tetracarbonyl complexes are present along with the tricarbonyl complexes, additional bands at *ca.* 2030, 1835 and 1705 cm^{-1} are observed, with a fourth band possibly hidden [14c]. These patterns are consistent with the face-capped, trigonal-prismatic arrangement revealed by X-ray structure analysis (see [14a] and below), although other structures, such as the face-capped octahedron, a possible alternative in solution, is also in accord with the data. The value of ν(CO) for $Br_2Nb(CO)p_4$, a pentagonal-bipyramidal complex (see below), is 1677 cm^{-1}.

With dppe as the phosphine the di- and tetracarbonyl complexes have been isolated [14c]. In the latter species two of the CO ligands are labile and may be replaced at ambient temperatures by alkynes (see ref. 10a and below) or by isonitriles CNR (eqn. (4)). Isonitriles form seven-coordinate dicarbonyl complexes, comparable to the monocarbonyl complexes of composition ClNb(CO)(CNR)(dmpe)$_2$, produced by the photo-catalysed reaction between ClNb(CO)$_2$(dmpe)$_2$ and CNR [13b].

TABLE 1. Crystal data

	BrNb(CO)$_2$(dppe)$_2$ [a]	INb(CO)$_2$(dppe)$_2$ [b]	Br$_2$Nb(CO)p$_4$ [c]	INb(CO)$_2$(2-pentyne)(PEt$_3$)$_2$
Formula	$C_{58}H_{56}BrNbO_3P_4$	$C_{60}H_{62}INbO_2P_4$	$C_{47}H_{48}Br_2NbO_{1.5}P_4$	$C_{19}H_{38}INbO_2P_2$
M(g mol^{-1})	1097.72	1158.79	951.42	580.27
Cryst. Syst.	triclinic	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a(Å)	12.438(8)	12.167(3)	9.569(5)	10.117(2)
b(Å)	13.206(10)	14.413(3)	11.578(6)	12.101(2)
c(Å)	13.307(8)	17.227(3)	20.809(10)	21.658(4)
α(°)	89.54(5)	72.69(2)	99.33(4)	
β(°)	99.99(4)	87.47(2)	93.16(4)	
γ(°)	115.30(4)	76.79(2)	99.91(4)	
Z	2	2	2	4
V(Å^3)	2816(3)	2806.9(10)	2233(2)	2651.5(8)
ρ(calcd.)(g cm^{-3})	1.285	1.371	1.460	1.453
F(000)	1112	1184	988	1168

[a] Crystallizes with one molecule of THF. [b] Crystallizes with one molecule of hexane.
[c] Crystallizes with 0.5 THF per formula unit.



Scheme 1.

$$\mathrm{INb(CO)_4dppe + 2CNR \longrightarrow}$$
$$\mathrm{INb(CO)_2(CNR)_2dppe;\ R = {}^tBu,\ Cy} \quad (4)$$

The orange coloured dicarbonyl complexes INb-$(CO)_2(CNR)_2$(dppe) show two almost equally intense ν(CO) bands at 1860 and 1800 cm^{-1}, and two almost equally intense ν(CN) bands at *ca.* 2133 and 2118 cm^{-1}, hence there is a cisoid arrangement of the two ligands in the complex. There is only one ^{31}P resonance (at $\delta(^{31}P) = 54$ ppm), indicating that the two phosphorus functions are equivalent. A plausible structure based on these observations is shown in Scheme 1, A. In this, the basic polyhedron is a face-capped trigonal prism, with the iodine capping a rectangular face and the two carbonyls occupying an opposite edge [15] (see Scheme 1).

2.1.2. X-ray structures

The crystal and molecular structures of $BrNb(CO)_2(dppe)_2 \cdot THF$, $Nb(CO)_2(dppe)_2 \cdot$ hexane and $Br_2Nb(CO)p_4 \cdot 0.5THF$ were determined. Crystal data are given, together with those for the alkyne complex discussed in Section 2.2. in Table 1 and details of the data collection and refinement are given in the experimental section. Fractional coordinates are listed in Tables 2–4. The molecular structures and the numbering schemes of the three halogeno complexes are given in Fig. 1, and selected bond lengths and angles in Table 5.

As in the structurally characterized complexes of the series $(Hal)ML_6$ (see *e.g.* $ClNb(CO)_2(dppe)_2$ [14a], $ITa(CO)_4dppe$ [14c], and $ITa(CO)_3(PMe_3)_3$ [16]), the basic structural unit in $BrNb(CO)_2(dppe)_2$ and $INb(CO)_2(dppe)_2$ is the $\{ML_6\}$ fragment in a trigonal prismatic arrangement with the halogen capping the tetragonal face opposite to the edge occupied by the carbonyls. They are therefore structurally different from the seven-coordinate complexes HML_6 (M = V, Nb, Ta), for which a pentagonal bipyramidal geometry has been found in the case of $HV(CO)_4dppe$ [17a], $HTa(PPh_2)_2(dmpe)_2$ [17b] and $HTa(CO)_2(dppe)_2$ [17c], and a capped octahedral geometry in the case of $HM(CO)_2(dmpe)_2$ (M = Nb, Ta) [18]. The four P atoms in $(Hal)Nb(CO)_2(dppe)_2$ occupy the four corners of the capped face and the two CO groups are in the remaining two positions of the prism, *i.e.* in *cis* positions, as already revealed by the ν(CO) pattern. Bond lengths and bond angles are comparable with those for other $(Hal)NbL_6$ complexes. The capping halide forms Hal–Nb–P angles with an average of *ca.* 80°.

The molecular structure of the dibromo complex $Br_2Nb(CO)p_4$ is best described as a slightly distorted pentagonal bipyramid, with the four phosphorus atoms and one of the bromines, Br2, in the pentagonal plane. Nb is displaced towards the axial Br1 from this plane by only 0.062 Å. The angles at Nb in the plane are almost the ideal 72° (with $\sphericalangle$Br2–Nb–P1 = 76.0(1)° slightly larger). The second ligand in an axial position is a carbonyl group. The Br(1)–Nb–CO link is not linear, the angle Br1–Nb–C1 being 164.1(6)°. The carbonyl–Nb fragment is slightly bent, the angle O1–C1–Nb being 171.6(1)°. The two Nb–Br bond-lengths are in the range observed for other bromoniobium complexes [19]. The same is true for the Nb–P distances [14a,c].

2.2. Alkyne complexes

2.2.1. Preparation and characterization

The alkyne complexes were prepared from the precursor complexes $(Hal)Nb(CO)_{6-n}(PR_3)_n$ (n = 2, 3) or $(Hal)Nb(CO)_4dppe$ by treatment with a slight excess of alkyne in THF at room temperature as shown in eqns. (5) and (6). The reactions, which were monitored by IR spectroscopy, took hours to days, with reaction rates especially low for alkynes bearing phenyl substituents, and in cases where both CO and PR_3 have to be replaced (eqn. (5a)). In contrast to the corresponding (green) vanadium complexes [9], the (red) niobium complexes were also obtained in satisfactory yields from phenylacetylene and tolane. The remaining two CO ligands are not replaced except when acetylene is used; in this case a monocarbonyl-bis(alkyne) complex is formed along with the dicarbonylmono(alkyne) species (eqn. (5b)). In precursor complexes containing dppe the alkyne replaces two CO groups (eqn. (6)). With an excess of phosphite, the monophosphines are displaced (eqn. (7)).

$$\mathrm{(Hal)Nb(CO)_3(PR_3)_3 + RCCR' \longrightarrow}$$
$$\mathrm{(Hal)Nb(CO)_2(RCCR')(PR_3)_2 + PR_3 + CO} \quad (5a)$$

$$\mathrm{INb(CO)_3(PEt_3)_3 + HCCH \longrightarrow}$$
$$\mathrm{INb(CO)_2(HCCH)(PEt_3)_2}$$
$$\mathrm{+\ INb(CO)(HCCH)_2(PEt_3)_2} \quad (5b)$$

$$\mathrm{(Hal)Nb(CO)_4dppe + RCCR' \longrightarrow}$$
$$\mathrm{(Hal)Nb(CO)_2(RCCR')dppe + 2CO} \quad (6)$$

$$\mathrm{(Hal)Nb(CO)_2(RCCR')(PEt_3)_2 + 2P(OMe)_3 \longrightarrow}$$
$$\mathrm{(Hal)Nb(CO)_2(RCCR')\{P(OMe)_3\}_2 + 2PEt_3} \quad (7)$$

TABLE 2. Fractional coordinates ($\times 10^4$) and isotropic thermal factors ($Å^2 \times 10^4$) for the non-hydrogen atoms [a] in $BrNb(CO)_2(dppe)_2 \cdot THF$

Atom	x	y	z	U_{eq}
Nb	1791.6(7)	3821(6)	2190(9)	285(7)
Br	−126.1(9)	3601.1(8)	1392.0(5)	428(10)
P1	3251(2)	5633(2)	2182(12)	360(2)
P3	252(2)	1303(2)	1869(13)	360(2)
P4	2145(2)	2689(2)	958(12)	360(2)
P2	1155(2)	4406(2)	3086(12)	350(2)
CO1	3412(9)	3475(6)	2624(4)	400(9)
CO2	1688(8)	2516(8)	3052(5)	420(9)
O1	4345(6)	3535(6)	2945(4)	560(8)
O2	1677(7)	2010(6)	3559(3)	580(8)
C1	3039(8)	6355(7)	2919(5)	390(9)
C2	1679(9)	5891(7)	2910(5)	500(10)
C3	867(7)	1337(7)	569(5)	460(10)
C4	−266(9)	1024(8)	907(5)	450(10)
C12	5482(10)	6267(10)	1755(6)	610(13)
C13	67731(11)	6599(12)	1887(9)	900(2)
C14	7386(12)	6805(11)	2535(8)	700(2)
C15	6811(12)	6654(11)	3097(8)	800(2)
C16	5555(10)	6280(10)	2992(6)	610(13)
C21	−442(8)	3916(7)	3098(5)	360(9)
C22	2132(9)	6111(9)	924(5)	430(10)
C23	1919(10)	6816(10)	430(6)	580(12)
C24	2671(11)	7961(10)	521(6)	640(13)
C25	3630(11)	8378(10)	1074(6)	600(13)
C26	3852(10)	7695(8)	1549(6)	480(11)
C31	3068(9)	6531(8)	1475(5)	420(10)
C32	−1128(10)	4459(10)	2812(5)	580(12)
C33	−2351(10)	4020(12)	2821(6)	680(14)
C34	−2911(11)	3045(12)	3132(7)	700(2)
C35	−2284(10)	2495(10)	3399(6)	610(13)
C36	−1060(10)	2919(9)	3380(6)	580(12)
C41	1786(9)	4602(8)	4038(5)	440(10)
C42	2817(8)	4441(8)	4291(5)	440(10)
C43	3326(11)	4668(10)	4986(6)	610(13)
C44	2868(11)	5104(10)	5452(6)	580(13)
C45	1866(11)	5279(10)	5215(6)	650(13)
C45	1344(10)	5021(9)	4504(5)	540(11)
C51	−1142(9)	706(8)	2223(6)	470(10)
C52	−1190(10)	178(9)	2854(6)	600(12)
C53	−2262(12)	−304(10)	3116(7)	670(14)
C54	−3256(12)	−273(11)	2750(8)	700(2)
C55	−3283(10)	246(10)	2120(7)	680(15)
C56	−2218(9)	741(9)	1850(6)	540(12)
C61	789(9)	209(7)	2020(5)	450(10)
C62	2000(9)	509(9)	2268(6)	520(11)
C63	2387(12)	−371(11)	2308(8)	900(2)
C64	1608(14)	−1449(10)	2113(8)	900(2)
C65	419(15)	1740(9)	1872(7)	800(2)
C66	−21(11)	−925(9)	1821(6)	580(12)
C71	3403(10)	2340(8)	849(5)	510(11)
C72	4321(10)	2469(9)	1366(5)	590(12)
C73	5214(11)	2141(11)	1260(7)	750(15)
C74	5162(11)	1692(10)	604(7)	800(2)
C75	4215(12)	1559(10)	50(7)	800(2)
C76	3346(11)	1891(9)	156(6)	600(12)
C81	2204(8)	3621(7)	258(5)	330(8)
C82	3329(9)	4500(9)	184(5)	510(11)
C83	3411(11)	5242(9)	−327(6)	610(12)
C84	2380(10)	5170(8)	−758(5)	520(11)
C85	1276(11)	4341(9)	688(5)	570(12)
C86	1186(9)	3572(8)	−185(5)	400(3)
C111	5430(3)	1540(3)	4740(2)	490(10)
C112	5370(4)	1590(4)	5480(2)	640(12)
C113	437(4)	184(4)	558(2)	620(12)
C114	390(5)	201(5)	491(2)	1100(2)
C115	426(3)	153(3)	4390(2)	560(11)
C121	460(4)	1630(4)	5620(2)	590(12)
C122	3850(4)	1990(4)	5230(2)	590(12)
C123	4260(4)	2080(4)	4570(2)	780(15)
C124	5070(4)	1630(4)	4500(2)	730(14)
C125	4640(4)	1970(4)	5220(2)	800(2)
C211	330(4)	1380(4)	5780(2)	660(12)
C212	−30(4)	1770(4)	5100(2)	660(13)
C213	−77(4)	2350(3)	5320(2)	490(10)
C214	−970(5)	2140(4)	6010(2)	800(2)
C215	−570(4)	1310(4)	6160(3)	790(15)
C221	−1460(4)	1620(4)	5790(2)	710(14)
C222	−290(4)	2380(4)	6020(2)	640(12)
C223	350(6)	2140(6)	5540(4)	1300(3)
C224	−330(6)	960(6)	5410(4)	1400(2)
C225	−1200(6)	1440(6)	5100(3)	1200(2)

[a] C111 to C225 refer to the fourfold disordered THF (O and C not distinguished).

The alkynes are bonded in the η^2 mode and act as 4-electron donors. This is shown [12,20] by the ^1H NMR resonance of the proton(s) attached to the triply bonded carbon(s) (see Table 6), which appears at *ca.* 11.2 ppm (*i.e.* deshielded by *ca.* 9 ppm with respect to the uncoordinated alkyne), and also by the ^{13}C NMR resonances (see Table 7 for selected values). The $\delta(^{13}C)$ values are around 209 ppm, and hence close to the range for coordinated CO (227 ppm). They are slightly broadened by the neighbouring quadrupolar nucleus ^{93}Nb. The values of $\delta(^1H)$ for the alkyne protons are comparable with that of 11.2 ppm for the cyclopropenylium ion, suggesting an analogy between the π delocalization in $[cyclo\text{-}C_3R_3]^+$ and that in the (cyclo-)MC_2R_2 fragment. On the other hand, in the case of the acetylene complex $INb(CO)(HCCH)_2(PEt_3)_2$, the corresponding value of $\delta(^1H)$, 9.88 ppm, is in accord with the acetylene acting as a 3-electron donor on an average scale, as in the binuclear bis(alkyne) complexes $\{Nb(CO)_2(alkyne)_2\}_2(\mu\text{-}Hal)_2$ [12].

The ^{31}P NMR spectra exhibit broad resonances at room temperature as a consequence of partial coupling between the nuclei ^{31}P and ^{93}Nb. The resonances sharpen as relaxation decoupling becomes more effective with decreasing temperature, and satisfactory resolution is achieved at *ca.* 210 K (for data, see Table 6). The complexes $(Hal)Nb(CO)_2(alkyne)(PR_3)_2$, *i.e.* those containing two monodentate phosphines, give rise to a single ^{31}P resonance, while the complexes containing the bidentate dppe, viz. $(Hal)Nb(CO)_2(alkyne)dppe$,

TABLE 3. Fractional coordinates ($\times 10^4$) and isotropic thermal factors ($Å^2 \times 10^4$) for the non-hydrogen atoms [a] in $INb(CO)_2(dppe)_2 \cdot$hexane

Atom	x	y	z	U_{eq}
Nb	2645(1)	1365(1)	2475(1)	430
I	615(1)	2062(1)	1367(1)	580(1)
P1	1732(4)	−121(3)	3412(§)	540(3)
P2	1110(4)	2144(3)	3345(3)	520(3)
P3	3768(4)	294(3)	1500(2)	510(3)
P4	3375(4)	2623(3)	1263(2)	500(3)
C1	4062(16)	637(11)	3165(9)	480(13)
O1	4856(11)	271(9)	3555(8)	780(10)
O2	3744(11)	2742(9)	3195(7)	730(10)
C2	3334(14)	2258(12)	2914(11)	490(11)
C3	497(15)	355(13)	3954(9)	640(13)
C4	−35(14)	1431(14)	3557(10)	650(11)
C5	4357(15)	1116(12)	645(10)	610(12)
C6	3553(16)	2151(12)	374(10)	650(15)
C11	1174(15)	−788(13)	2835(9)	530(12)
C12	77(18)	−464(13)	2537(11)	740(17)
C13	−375(21)	−976(19)	2078(12)	930(19)
C14	262(24)	−1767(20)	1920(15)	970(21)
C15	1368(24)	2116(17)	2204(14)	990(23)
C16	1802(19)	−1593(15)	2632(11)	810(16)
C21	2493(17)	−1102(12)	4282(10)	620(15)
C22	3282(21)	−921(17)	4717(13)	1060(22)
C23	3744(25)	−1559(21)	5459(14)	1380(32)
C24	3440(17)	−2479(18)	5713(12)	890(15)
C25	2604(22)	−2684(14)	5308(13)	1030(25)
C26	2135(18)	−1986(14)	4598(12)	860(17)
C31	355(17)	3453(14)	2956(11)	670(14)
C32	855(19)	4179(14)	3050(12)	840(17)
C33	344(23)	5174(17)	2774(17)	1160(21)
C34	−688(29)	5462(23)	2402(18)	1300(31)
C35	−1288(24)	4769(21)	2314(17)	1210(22)
C36	−688(19)	3755(17)	2600(13)	940(17)
C41	1455(15)	2047(12)	4402()	550(12)
C42	2458(17)	1519(16)	4777(11)	810(14)
C43	2675(21)	1361(19)	5593(12)	1060(18)
C44	1842(23)	1765(19)	6030(13)	980(20)
C45	860(22)	2299(19)	5684(13)	980(19)
C46	663(18)	2464(15)	4867(11)	780(16)
C51	5017(14)	−686(12)	1928(11)	560(11)
C52	4936(16)	−1363(13)	2681(11)	670(14)
C53	5786(20)	−2213(15)	2979(14)	890(19)
C54	6714(20)	−2381(20)	2529(17)	1060(17)
C55	6866(21)	−1707(19)	1826(17)	1020(19)
C56	6017(17)	−851(16)	1527(13)	770(14)
C61	3094(15)	−349(12)	938(9)	510(13)
C62	2094(17)	139(14)	470(10)	720(15)
C63	1657(18)	−339(17)	8(11)	830(16)
C64	2163(20)	−1274(18)	2(12)	830(19)
C65	3122(21)	−1788(17)	44113()	950(20)
C66	3543(16)	−1329(13)	930(10)	650(12)
C71	4829(14)	2825(11)	1304(10)	540(13)
C72	5598(16)	2118(14)	1897(11)	660(13)
C73	6700(18)	2244(16)	1885(12)	85(16)
C74	7048(17)	3010(18)	1351(13)	84(13)
C75	6258(20)	3659(15)	751(12)	81(18)
C76	5171(15)	3567(12)	772(11)	61(12)
C81	2561(13)	3893(12)	896(9)	51(11)
C82	2600(16)	4537(13)	132410()	66(14)
C83	1984(19)	5519(15)	1089(13)	93(18)
C84	1291(20)	5892(16)	420(14)	97(21)
C85	1275(15)	5255(15)	−37(11)	75(13)
C86	1882(15)	4256(12)	198(11)	73(14)
C101	5376(25)	5828(21)	1721(20)	147(26)
C102	5092(44)	5279(26)	2591(19)	195(63)
C103	4243(30)	5322(40)	3213(45)	336(30)
C104	3355(63)	5147(34)	3988(26)	222(11)
C105	2914(40)	4533(32)	4897(38)	2190(39)
C106	1753(39)	4820(28)	5199(28)	2230(40)

[a] C101 to C106 refer to hexane.

show two resonances. Assumption of an essentially octahedral geometry, with the alkyne regarded as a monodentate ligand with its centre occupying one of the corners in the octahedron, leads to the overall ligand arrangements shown in Scheme 1 for the bis(monophosphine) (**B** in Scheme 1) and dppe complexes (**C**), respectively, i.e. there is an *all-trans* arrangement in **B** and a *cis* arrangement for the CO groups in **C**. This picture is supported by the IR pattern in the CO stretching region (Table 6): The complexes containing monodentate phosphines give rise to one very strong and one weak ν(CO) band, in accord with a slight distortion of the idealized C_{2v} symmetry of structure **B**. The dppe complexes (structure *C*, C_s symmetry) give rise to two absorptions of medium and strong intensity. For the bis(alkyne) complex $INb(CO)(HCCH)_2(PEt_3)_2$, an *all-trans* structure, as shown in **D** in Scheme 1, is assumed by analogy to that of the bis(carbonyl) complexes $(Hal)Nb(CO)_2(alkyne)(PR_3)_2$.

Although the range of ν(CO) values is quite small, it can be seen that the complexes containing alkylacetylenes give bands at lower wave numbers than the acetylene and phenylacetylene complexes. A possible cause of this is the +I effect of the alkyl groups in the former, which leads to an increase in electron density in the triple bond and so on the niobium centre, and thus to enhanced back-donation into π*(CO) orbitals. Further, phenylacetylenes can be assumed to be better π acceptor ligands than the alkyl analogues by virtue of the extension of electron delocalization into the phenyl-π system. No significant changes in the positions of the ν(CO) bands are observed as the halogen or the auxiliary ligand (phosphine *vs.* phosphite) are varied. We could not detect the ν(C≡C) band in the IR spectra of the complexes containing asymmetrically substituted acetylenes; for the 4-electron donating alkynes, these are to be expected in the region 1400 to 1700 cm^{-1} [5,21,22]. However, even $INb(CO)_2(2\text{-}^{13}C\text{-}phenylethyne)(PEt_3)_2$ did not show even a weak ν(C≡C) band in this region. Owing to their colour (dark red),

TABLE 4. Fractional coordinates and isotropic thermal factors (Å^2) for the non-hydrogen atoms [a] in $Br_2Nb(CO)p_4 \cdot 0.5THF$

Atom	x	y	z	U_{eq}
Nb1	0.5637(2)	0.24988(12)	0.23013(7)	0.032(2)
Br2	0.2874(2)	0.1918(2)	0.25807(9)	0.054(2)
Br1	0.5413(2)	0.4760(2)	0.28829(9)	0.060(2)
P1	0.5830(5)	0.1591(4)	0.3399(2)	0.041(5)
P2	0.8386(5)	0.2907(4)	0.2734(2)	0.044(5)
P3	0.7129(5)	0.3619(4)	0.1487(2)	0.039(5)
P4	0.4067(5)	0.2201(4)	0.1178(2)	0.036(5)
O1	0.6880(13)	0.0361(10)	0.1571(6)	0.050(14)
C1	0.636(2)	0.103(2)	0.1823(10)	0.07(3)
C2	0.523(2)	0.2088(14)	0.0497(7)	0.05(2)
C3	0.634(2)	0.325(2)	0.0620(7)	0.06(2)
C4	0.877(2)	0.304(2)	0.1387(8)	0.06(2)
C5	0.949(2)	0.285(2)	0.2018(8)	0.06(2)
C6	0.870(2)	0.162(2)	0.3108(9)	0.06(2)
C7	0.771(2)	0.155(2)	0.3665(9)	0.06(2)
C12	0.5164(12)	0.2170(10)	0.4192(4)	0.05(2)
C13	0.4469(12)	0.3142(10)	0.4260(4)	0.06(2)
C14	0.3989(12)	0.3554(10)	0.4861(4)	0.08(3)
C15	0.4203(12)	0.2993(10)	0.5393(4)	0.07(3)
C16	0.4899(12)	0.2021(10)	0.5325(4)	0.07(3)
C11	0.5379(12)	0.1609(10)	0.4725(4)	0.06(2)
C22	0.5619(12)	−0.0886(11)	0.2968(6)	0.08(3)
C23	0.4946(12)	−0.2078(11)	0.2838(6)	0.10(4)
C24	0.3543(12)	−0.2395(11)	0.2986(6)	0.07(3)
C25	0.2812(12)	−0.1521(11)	0.3264(6)	0.08(3)
C26	0.3485(12)	−0.0329(11)	0.3394(6)	0.07(3)
C21	0.4889(12)	−0.0012(11)	0.3246(6)	0.05(2)
C32	0.3307(10)	−0.0284(11)	0.0916(6)	0.05(2)
C33	0.2366(10)	−0.1373(11)	0.0815(6)	0.07(3)
C34	0.0900(10)	−0.1402(11)	0.0759(6)	0.08(3)
C35	0.0375(10)	−0.0343(11)	0.0803(6)	0.07(3)
C36	0.1316(10)	0.0746(11)	0.0904(6)	0.05(2)
C31	0.2781(10)	0.0776(11)	0.0961(6)	0.04(2)
C42	0.2944(11)	0.4313(9)	0.1438(4)	0.04(2)
C43	0.2282(11)	0.5223(9)	0.1276(4)	0.05(2)
C44	0.1714(11)	0.5162(9)	0.0637(4)	0.05(2)
C45	0.1807(11)	0.4189(9)	0.0159(4)	0.06(2)
C46	0.2469(11)	0.3279(9)	0.0321(4)	0.05(2)
C41	0.3037(11)	0.3340(9)	0.0960(4)	0.04(2)
C52	0.6644(12)	0.5923(12)	0.1447(6)	0.07(3)
C53	0.6994(12)	0.7164(12)	0.1558(6)	0.10(3)
C54	0.8329(12)	0.7737(12)	0.1856(6)	0.10(4)
C55	0.9316(12)	0.7070(12)	0.2042(6)	0.09(3)
C56	0.8966(12)	0.5829(12)	0.1931(6)	0.07(3)
C51	0.7630(12)	0.5256(12)	0.1633(6)	0.05(2)
C62	1.0872(14)	0.4385(12)	0.3388(7)	0.07(3)
C63	1.1644(14)	0.5277(12)	0.3872(7)	0.08(3)
C64	1.0932(14)	0.5955(12)	0.4314(7)	0.09(3)
C65	0.9447(14)	0.5740(12)	0.4272(7)	0.08(3)
C66	0.8675(14)	0.4847(12)	0.3788(7)	0.07(3)
C61	0.9388(14)	0.4170(12)	0.3346(7)	0.05(2)
C71	0.00(2)	−0.060(15)	0.430(6)	0.17(6)
C72	0.094(14)	0.04(2)	0.475(9)	0.20(13)
C73	0.000(12)	0.094(8)	0.518(7)	0.12(5)
C74	−0.119(6)	0.00000(0)	0.523(3)	0.11(2)
C75	−0.136(13)	−0.077(11)	0.458(4)	0.18(7)
C81	0.078(13)	0.097(7)	0.470(5)	0.10(4)
C82	0.014(9)	0.00000(0)	0.419(3)	0.07(3)
C83	−0.07(3)	−0.094(10)	0.449(7)	0.2(3)
C84	−0.04(3)	−0.05(2)	0.520(6)	0.18(8)
C85	0.06(4)	0.06(2)	0.532(5)	0.3(2)

the compounds decomposed when subjected to Raman studies.

2.2.2. ^{93}Nb-NMR spectra

The nucleus ^{93}Nb (nuclear spin = 9/2, quadrupole moment = −0.28 barn, natural abundance 100%, relative receptivity (^{1}H = 1) = 0.48) belongs to the medium category quadrupolar nuclei of high receptivity. Relaxation times in all but those compounds that exhibit cubic or C_{3v} symmetry are in the ms to μs region, and half-widths $W_{1/2}$ therefore usually around several kilohertz. The $\delta(^{93}Nb)$ values range over *ca.* 3000 ppm (see ref. 23 for recent reviews). Table 8 contains data for selected alkyne complexes, and Fig. 2 relates $\delta(^{93}Nb)$ values for the alkyne complexes to those for other carbonylniobium compounds. The alkyne ligand has a large deshielding effect, a feature also observed for other transition metal nuclei in complexes when CO is replaced by alkynes [23,24]. This deshielding effect indicates that alkynes must be classed as relatively weak ligands in a magnetochemical series of ligand strengths [24]. In contrast to observations on (Hal)Nb(CO)$_3$(PR$_3$)$_3$ [10a], but in accord with what is normally observed in open-shell complexes, shielding of the ^{93}Nb nucleus in (Hal)Nb(CO)$_2$(alkyne)(PR$_3$)$_2$ increases in the series Cl < Br < I; *i.e.* there is a "normal halogen dependence of metal shielding" [23,24a] paralleling increasing polarizability of the halide. Relaxation times for the compounds noted in Table 8 are $6–9 \cdot 10^{-6}$ s thus shorter by one order of magnitude than those for the precursor complexes (Hal)Nb(CO)$_3$(PR$_3$)$_2$ (*ca.* $5 \cdot 10^{-5}$ s [10a]).

2.2.3. X-ray structure determination of INb(CO)$_2$(MeCCEt)(PEt$_3$)$_2$

Crystal data, together with those for the alkyne-free halogen complexes are listed in Table 1 (Section 2.1), bonding parameters in Table 9, and fractional coordinates and thermal factors in Table 10. The molecular structure and numbering scheme is depicted in Fig. 3.

The 2-pentyne complex crystallizes in the orthorhombic space group $P2_12_12_1$. The coordination sphere of Nb is close to octahedral, with the η^2-bound pentyne occupying one of the octahedral positions. The centre of the C≡C triple bond is exactly *trans* to the iodine, and the C≡C axis is aligned with the axis OC–Nb–CO (z direction), hence providing optimum conditions for effective $d_{xz/yz} \rightarrow \pi^*$ (CO) back-bond-

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Notes to table 4:

[a] C71 to C85 refer to the twofold disordered THF (O and C not distinguished).

TABLE 5. Selected bond lengths and bond angles in the halogeno complexes

	$BrNb(CO)_2$-$(dppe)_2$	$INb(CO)_2$-$(dppe)_2$	Br_2Nb-$(CO)p_4$
Bond lengths (Å)			
Nb–Br(1)/I	2.731(2)	2.982(2)	2.749(3)
Nb–Br2			2.732(3)
Nb–P1	2.744(3)	2.701(5)	2.675(5)
Nb–P2	2.620(3)	2.606(5)	2.670(5)
Nb–P3	2.593(3)	2.599(4)	2.633(5)
Nb–P4	2.727(3)	2.729(4)	2.648(5)
Nb–C1	2.003(10)	2.03(2)	2.07(2)
Nb–C2	1.993(9)	2.01(2)	
C1–O1	1.182(12)	1.13(2)	1.08(2)
C2–O2	1.187(11)	1.16(2)	
Bond angles (°)			
Br(1)/I–Nb–C1	166.5(2)	168.5(4)	164.1(6)
Br/I–Nb–C2	124.1(3)	124.6(4)	
Br1–Nb–Br2			84.31(8)
Br(1)/I–Nb–P1	91.52(8)	89.42(11)	97.0(1)
Br(1)/I–Nb–P2	77.30(8)	77.96(11)	90.3(1)
Br(1)/I–Nb–P3	78.27(8)	80.41(11)	83.7(1)
Br(1)/I–Nb–P4	86.09(8)	90.64(11)	102.8(1)
Br2–Nb–P1			76.0(1)
C1–Nb–C2	69.3(4)	66.6(6)	
C1–Nb–P1	78.2(2)	85.0(4)	88.0(6)
C2–Nb–P1	124.4(3)	124.0(4)	
P1–Nb–P2	73.77(9)	72.70(14)	72.5(2)
P1–Nb–P3	165.69(9)	164.54(14)	143.8(1)
P1–Nb–P4	97.95(8)	95.38(14)	141.89(4)
P2–Nb–P3	113.00(9)	115.9(2)	71.3(2)
P2–Nb–P4	161.07(9)	163.4(2)	138.5(1)
P3–Nb–P4	71.61(9)	73.29(14)	71.4(1)
Nb–C1–O1	173.6(7)	176.8(14)	171.6(1)
Nb–C2–O2	177.1(8)	177.3(13)	

ing. The CO ligands again are almost ideally *trans* to each other ($\sphericalangle$ C1–Nb–C2 = 177°), while the phosphines are bent slightly towards one of the COs ($\sphericalangle$ P1–Nb–P2 = 169°) and away from the ethyl substituent on the acetylene. The Nb–C(alkyne) and $C\equiv C$ bond lengths are very much the same as those in $INb(CO)_2(MeCCMe)(PEt_3)_2$ [10a], $ClNb(Me_3SiOC\equiv CO$-$SiMe_3)(dmpe)_2$ [25] and $[Br_4Nb(py)(F_3CC\equiv CCF_3)]^-$ [7]. The bonds are shorter than in CpNb(alkyne) complexes containing 2-electron donating alkynes [22b], and slightly longer than those in the isosteric Mo^{II} complexes with 4-electron donating alkynes [26].

2.2.4. Reactions with hydrogen

In view of the possibility that the alkyne complexes can be regarded as models for active intermediates in various catalytic reactions involving alkynes (see Introduction), we carried out preliminary studies on the reaction pattern of our complexes. It was shown earlier [27] that treatment of the d^4 complex $(RS)_2Mo(CNR)_2$-$(PhCCPh)$ with $Na[BH_4]$ results in practically complete conversion of tolane into a 1 : 1 mixture of *cis*- and *trans*-stilbene. The tolane complex $INb(CO)_2(PhCC$-$Ph)(PEt_3)_2$ also undergoes such a reaction; use of a twenty-fold excess of the tetrahydroborate (as a source of H^-), followed by hydrolytic (H^+) work-up, yielded *cis/trans*-stilbene in medium yields. The corresponding reactions with alkylacetylenes afforded hexacarbonylniobate as the only detectable reduction products. The reduction of coordinated tolane may initially involve

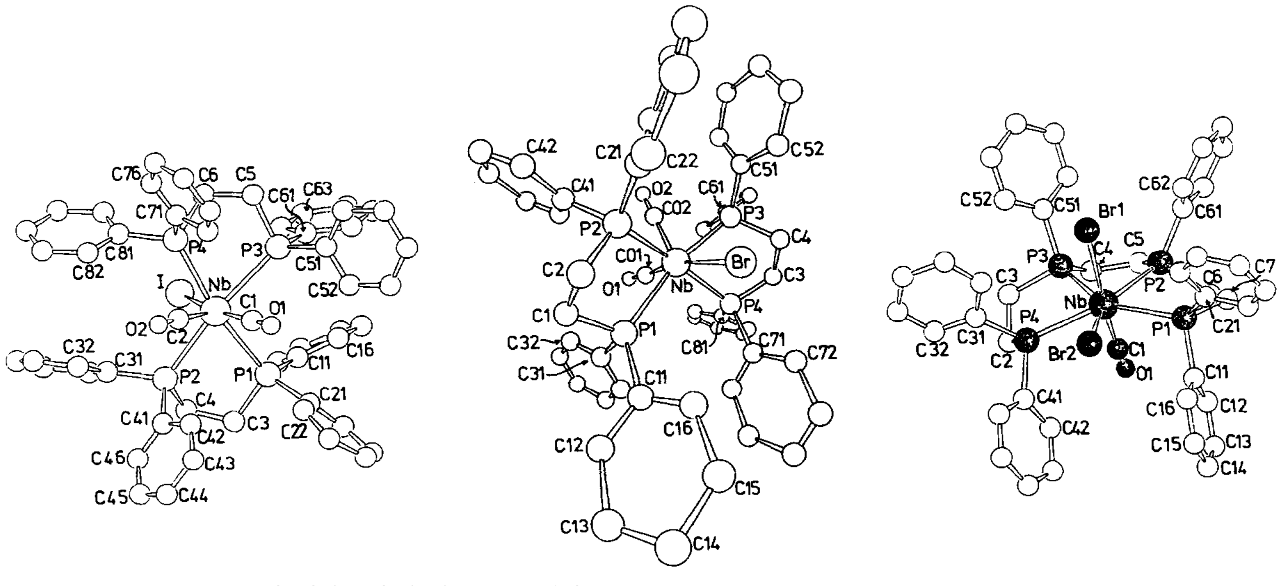


Fig. 1. SCHAKAL plots of $INb(CO)_2(dppe)_2$ (left), $BrNb(CO)_2(dppe)_2$ (centre) and $Br_2Nb(CO)p_4$ (right).

TABLE 6. Selected IR, ^1H NMR and ^{31}P NMR data for η^2-alkyneniobium complexes

Complex	$\nu(CO)$	(cm^{-1}) [a]	$\delta(^1H)$ (ppm)	$\delta(^{31}P)$ (ppm) [b]
$ClNb(CO)_2(HCCPh)(PMe_2Ph)_2$	1990	1920	11.29	NO [e]
$ClNb(CO)_2(EtCCEt)(PMe_2Ph)_2$	1980	1895		−3.2
$BrNb(CO)_2(EtCCEt)(PMe_2Ph)_2$	1992	1923		−7.1
$BrNb(CO)_2(PhCCPh)dppe$	2065	2020		37.4, 41.2
$INb(CO)_2(HCCPh)(PMe_2Ph)_2$	1991	1920	11.14	NO
$INb(CO)_2(EtCCEt)(PMe_2Ph)_2$	1980	1895		−11.9
$INb(CO)_2(PhCCPh)(PMe_2Ph)_2$	2005	1935		NO
$INb(CO)_2(HCCH)(PEt_3)_2$	1997	1920	11.32	7.4
$INb(CO)_2(HCCBu)(PEt_3)_2$	1988	1907	10.88 [c]	7.9
$INb(CO)_2(HCCPh)(PEt_3)_2$	1996	1920	11.34	6.9
$INb(CO)_2(MeCCEt)(PEt_3)_2$	1980	1901		NO
$INb(CO)_2(PrCCPr)(PEt_3)_2$	1975	1906 [d]		NO
$INb(CO)_2(PhCCPh)dppe$	2060	2015		32.2, 36.9
$INb(CO)_2(MeCCMe)\{P(OMe)_3\}_2$	1979	1897		143.2
$INb(CO)_2(EtCCEt)\{P(OMe)_3\}_2$	1976	1893		NO
$INb(CO)(HCCH)_2(PEt_3)_2$	1930		9.88, 9.87	27.3

[a] In THF. The intensities of the bands for the (*trans* configurated) complexes with monophosphines are *w* and *vs*, for the dppe complexes (*cis*) *m-s* and *vs*. [b] In THF at 210 K. [c] Triplet; $^4J(^1H-^1H) = 0.8$ Hz. [d] In Nujol. [e] NO, not observed.

TABLE 7. Selected $\delta(^{13}C)$ values (in CD_2Cl_2) of selected alkyne complexes [a]

Complex	R [b]	C≡C	CO
$INb(CO)_2(HCCBu)(PEt_3)_2$	14.0, 22.9, 33.5, 36.6	211.8	235.9
$INb(CO)_2(HCCPh)(PEt_3)_2$	– [c]	207.7	226.2
$INb(CO)_2(MeCCEt)(PEt_3)_2$	14.3, 20.9; 30.1(Me)	208.0	226.3
$INb(CO)_2(PrCCPr)(PEt_3)_2$	15.5, 23.9, 29.3	206.3	227.0
$ClNb(CO)_2(EtCCEt)(PEt_3)_2$ [d]	14.8, 29.6	209.0	226.9
$BrNb(CO)_2(EtCCEt)(PEt_3)_2$ [d]	14.9, 29.8	209.0	227.1
$INb(CO)_2(EtCCEt)(PEt_3)_2$ [d]	14.9, 29.8	207.7	226.5

[a] The resonances for the ethyl groups of the PEt_3 are at *ca.* 8 (methyl) and 20 ppm (methylene; triplets with $^1J(^{13}C-^{31}P) = 8–9$ Hz); see also experimental section. [b] R denotes the substituent on the acetylenic carbons. The first entry is for the terminal carbon, followed by the next-to-terminal etc. (where appropriate). [c] For the phenyl carbons see experimental section. [d] From ref. 10(a).

formation of a hydride intermediate, which is followed by the generation of a σ-alkenyl complex by hydride transfer to the alkyne and protolytic removal of the ligand from the metal centre. The formation of alkenyl complexes by hydrometalation of the alkyne has been demonstrated for the system $HV(CO)_{6-n}p_n$/alkyne [28]. Hydrogenation of $INb(CO)_2(PhC{\equiv}CH)(PEt_3)_2$ at atmospheric pressure yields organic carbonyl com-

TABLE 8. ^{93}Nb NMR data for selected alkyne–niobium complexes

Complex	$\delta(^{93}Nb)$ [a] (ppm)	$W_{1/2}$ [b] (kHz)
$ClNb(CO)_2(EtCCEt)(PEt_3)_2$ **1**	−799	44
$BrNb(CO)_2(PhCCPh)(PEt_3)_2$ **2**	−795	45
$BrNb(CO)_2(EtCCEt)(PEt_3)_2$ **3**	−834	33
$INb(CO)_2(EtCCEt)(PEt_3)_2$ **4**	−931	35
$INb(CO)_2(MeCCMe)(PEt_3)_2$ **5**	−967	49

[a] In THF, relative $[NbCl_6]^-$. [b] Width at half-height.

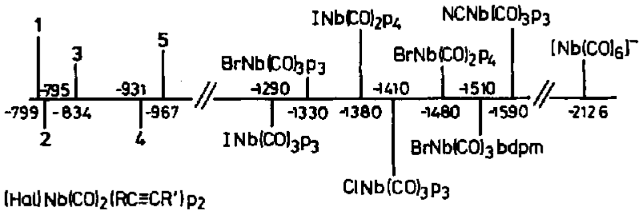


Fig. 2. $\delta(^{93}Nb)$ values (relative to $[NbCl_6]^-$) for carbonylniobium complexes. $p_2 = 2\ PEt_3$, $p_3 = 3\ PMe_2Ph$, $p_4 = [Ph_2P(CH_2)_2PPh\text{-}CH_2]_2$, bdpm = $MeP(CH_2CH_2CH_2PMe_2)_2$. For data see Table 8 and ref. 23.

TABLE 9. Selected bond lengths and bond angles in $INb(CO)_2(MeC{\equiv}CEt)(PEt_3)_2$.

Bond lengths (Å)		*Bond angles (°)*	
Nb–I	2.913(2)	I–Nb–P1	85.1(1)
Nb–P1	2.629(6)	I–Nb–P2	84.2(1)
Nb–P2	2.635(5)	I–Nb–C1	90.1(5)
Nb–C1	2.161(20)	I–Nb–C2	87.1(5)
Nb–C2	2.104(21)	I–Nb–C3	162.1(5)
Nb–C3	2.095(17)	I–Nb–C4	162.3(6)
Nb–C4	2.076(19)	P1–Nb–P2	169.3(2)
C1–O1	1.105(25)	P1–Nb–C1	90.5(5)
C2–O2	1.139(27)	P1–Nb–C2	90.6(6)
C3–C4	1.261(27)	P1–Nb–C3	92.7(5)
C3–C5	1.543(28)	P1–Nb–C4	91.6(6)
C4–C6	1.485(28)	C1–Nb–C2	176.9(7)
		C3–Nb–C4	35.2(8)
		Nb–C1–O1	173.7(18)
		Nb–C3–C5	147.5(16)
		Nb–C4–C6	150.3(17)

TABLE 10. Fractional coordinates ($\times 10^4$) and isotropic temperature factors ($Å^2 \times 10^3$) of the non-hydrogen atoms in $INb(CO)_2(MeC{\equiv}CEt)(PEt_3)_2$

	x	y	z	$U_{(eq)}$
Nb	2645(1)	1365(1)	2475(1)	43(1)
I	615(1)	2062(1)	1367(1)	58(1)
P(1)	1732(4)	−121(3)	3412(3)	54(3)
P(2)	1110(4)	2144(3)	3345(3)	52(3)
P(3)	3768(4)	294(3)	1500(2)	51(3)
P(4)	3375(4)	2623(3)	1263(2)	50(3)
O(1)	4856(11)	271(9)	3555(8)	78(10)
C(1)	4062(16)	637(11)	3165(9)	48(13)
O(2)	3744(11)	2742(9)	3195(7)	73(10)
C(2)	3334(14)	2258(12)	2914(9)	49(11)
C(3)	497(15)	355(13)	3954(9)	64(13)
C(4)	−35(14)	1431(14)	3557(10)	65(11)
C(5)	4357(15)	1116(12)	645(10)	61(12)
C(6)	3553(16)	2151(12)	374(10)	65(15)
C(11)	1174(15)	−788(13)	2835(9)	53(12)
C(12)	77(18)	−464(13)	2537(11)	74(17)
C(13)	−375(21)	−976(19)	2078(12)	93(19)
C(14)	262(24)	−1767(20)	1920(15)	97(21)
C(15)	1368(24)	−2116(17)	2204(14)	99(23)
C(16)	1802(19)	−1593(15)	2632(11)	81(16)
C(21)	2493(17)	−1102(12)	4282(10)	62(15)
C(22)	3282(21)	−921(17)	4717(13)	106(22)
C(23)	3744(25)	−1559(21)	5459(14)	138(32)
C(24)	3440(17)	−2479(18)	5713(12)	89(15)
C(25)	2604(22)	−2684(14)	5308(13)	103(25)
C(26)	2135(18)	−1986(14)	4598(12)	86(17)
C(31)	355(17)	3453(14)	2956(11)	67(14)
C(32)	855(19)	4179(14)	3050(12)	84(17)
C(33)	344(23)	5174(17)	2774(17)	116(21)
C(34)	−688(29)	5462(23)	2402(18)	130(31)
C(35)	−1228(24)	4769(21)	2314(17)	121(22)
C(36)	−675(19)	3755(17)	2600(13)	94(17)
C(41)	1455(15)	2074(12)	4402(10)	55(12)
C(42)	2458(17)	1519(16)	4777(11)	81(14)
C(43)	2675(21)	1361(19)	5593(12)	106(18)
C(44)	1842(23)	1765(19)	6030(13)	98(20)
C(45)	860(22)	2299(19)	5684(13)	98(19)
C(46)	663(18)	2464(15)	4867(11)	78(16)
C(51)	5017(14)	−686(12)	1928(11)	56(11)
C(52)	4936(16)	−1363(13)	2681(11)	67(14)
C(53)	5786(20)	−2213(15)	2979(14)	89(19)
C(54)	6714(20)	−2381(20)	2529(17)	106(17)
C(55)	6866(21)	−1707(19)	1826(17)	102(19)
C(56)	6017(17)	−851(16)	1527(13)	77(14)
C(61)	3094(15)	−349(12)	938(9)	51(13)
C(62)	2094(17)	139(14)	470(10)	72(15)
C(63)	1657(18)	−339(17)	8(11)	83(16)
C(64)	2163(20)	−1274(18)	2(12)	83(19)
C(65)	3122(21)	−1788(17)	441(13)	95(20)
C(66)	3543(16)	−1329(13)	930(10)	65(13)
C(71)	4829(14)	2825(11)	1304(10)	54(12)
C(72)	5598(16)	2118(14)	1897(11)	66(13)
C(73)	6700(18)	2244(16)	1885(12)	85(16)
C(74)	7048(17)	3010(18)	1351(13)	84(13)
C(75)	6258(20)	3659(15)	751(12)	81(18)
C(76)	5171(15)	3567(12)	772(11)	61(12)
C(81)	2561(13)	3893(12)	896(9)	51(11)
C(82)	2600(16)	4537(13)	1324(10)	66(14)
C(83)	1984(19)	5519(15)	1089(13)	93(18)
C(84)	1291(20)	5892(16)	420(14)	97(21)
C(85)	1275(15)	5255(15)	−37(11)	75(13)
C(86)	1882(15)	4256(12)	198(11)	73(14)
C(101)	5376(25)	5828(21)	1721(20)	147(26)
C(102)	5092(44)	5279(26)	2591(19)	195(63)
C(103)	4243(30)	5322(40)	3213(45)	336(30)
C(104)	3355(63)	5147(34)	3988(26)	222(110)
C(105)	2914(40)	4533(32)	4897(38)	219(39)
C(106)	1753(39)	4820(28)	5199(28)	223(40)

pounds, the formation of which can be understood on the basis of hydroformylation reactions.

3. Conclusion

The primary oxidation product of the reaction between hexacarbonylniobate and iodine or pyridinium halides (eqns. (1)–(3) in Section 2.1.1) is the dinuclear Nb^1 complex $[\{Nb(CO)_4\}_2(\mu\text{-Hal})_3]^-$ [29], which plays a key role in further conversions, as summarized in Scheme 2: In the presence of monophosphines the halide complexes $(Hal)Nb(CO)_3(PR_3)_3$ are formed, and then react with alkynes to produce mononuclear monoalkyne complexes or, in the case of acetylene and Hal = I, the mononuclear bis(alkyne) complexes $INb(CO)(HCCH)_2(PR_3)_2$. Reaction of $[\{Nb(CO)_4\}_2(\mu\text{-Hal})_3]^-$ with alkynes in the absence of phosphines affords dinuclear bis(alkyne) complexes [12], which

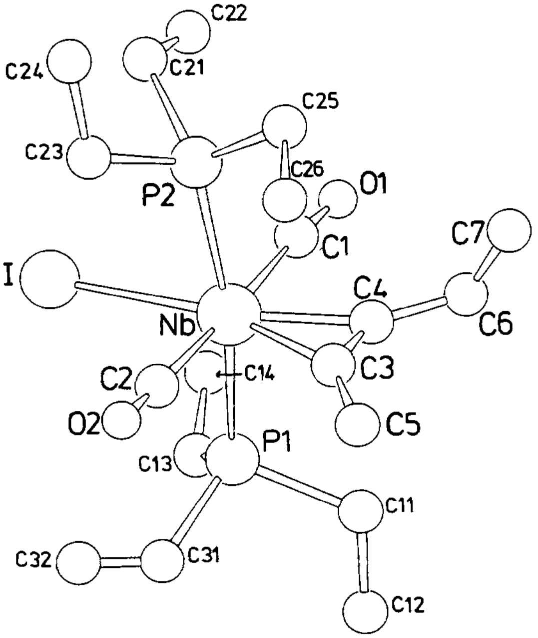
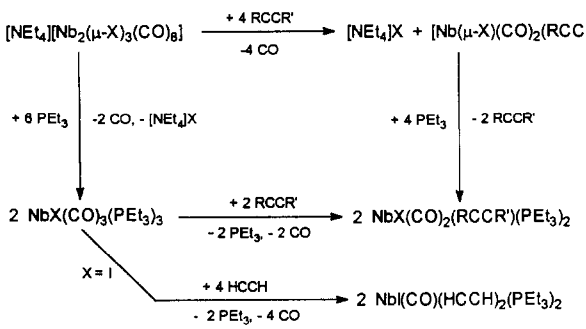


Fig. 3. SCHAKAL plot of $INb(CO)_2(2\text{-pentyne})(PEt_3)_2$.



Scheme 2.

upon addition of phosphine yield (Hal)Nb(CO)$_2$(alkyne)(PR$_3$)$_2$. This route to alkyne-niobium complexes, which is alternative to the generation of functionalized alkyne complexes by reductive C–C coupling at the metal centre [10b,10c,11b], is widely applicable to non-functionalized alkyl-and phenyl-acetylenes, and has also been employed in the preparation of the corresponding vanadium [9] and tantalum complexes [30]. Hence a variety of well characterized alkyne complexes of the Group 5 metals is available, allowing model studies of reactions in which alkynes are introduced in organic syntheses involving the presence of Group 5 catalyst systems.

4. Experimental details

4.1. General

All operations were carried out in inert gas atmosphere and absolute solvents using standard Schlenk techniques. Alkynes, phosphines, phosphites, isonitriles and pyridinium chloride were obtained from commercial sources. Pyridinium bromide was prepared from equimolar amounts of pyridine and HBr, recrystallized from ethanol, and kept under N_2 after being dried under high vacuum. [Et$_4$N][Nb(CO)$_6$] was prepared in a synthesis at atmospheric pressure as described by Calderazzo *et al.* [31]. The following complexes were prepared as previously described. (Hal)Nb(CO)$_4$(dppe) [14c]; (Hal)Nb(CO)$_3$(PMe$_2$Ph)$_3$ [14a]; (Hal)Nb(CO)$_2$-(RCCR)(PEt$_3$)$_2$, Hal = Cl, Br and I, R = Et; Hal = Br, R = Ph; Hal = I, R = Me [10a].

The IR spectra were obtained on a Perkin Elmer 1720 FT spectrometer for THF solutions in 0.1 mm CaF$_2$ cuvettes. NMR spectra were recorded on a Bruker AM 360 spectrometer for samples in deuterated solvents under the following conditions: ^{1}H: 5 mm vials, ambient temperatures, reference TMS; ^{13}C: 90.55 MHz, ^{1}H broad band decoupling, ambient temperatures, 10 mm vials, reference TMS; ^{31}P: 145.8 MHz, ^{1}H broad band decoupling, 210(2) K, 10 mm vials, reference 80% aqueous H$_3$PO$_4$. ^{93}Nb NMR spectra were scanned on a modified Varian SWL 3-100 broad-line spectrometer at 16 MHz and $B_0 = 1.542$ T in non-rotating 14 mm diameter vials; reference saturated acetonitrile solution of [Et$_4$N][NbCl$_6$].

4.2. X-ray structure analyses

The data were collected with a Syntex $P2_1$ diffractometer (MoK$_\alpha$, graphite monochromator) at ambient temperatures in the $\theta/2\theta$ scan mode. Table 11 contains details of the data collection and refinement of the structures. The program systems SHELXS-68 and SHELXTL PLUS [32] were used throughout. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included with common isotropic temperature factors in the last cycles of the refinement.

In the case of BrNb(CO)$_2$(dppe)$_2$ · THF, a fourfold disorder (1 : 1 : 1 : 1) model for the THF molecule was

TABLE 11. Details of data collection and structure refinement [a]

	BrNb(CO)$_2$(dppe)$_2$ · THF	INb(CO)$_2$(dppe)$_2$ · hexane	Br$_2$Nb(CO)p$_4$ · 0.5THF	INb(CO)$_2$(2-pentyne)(PEt$_3$)$_2$
Crystal dimensions (mm^3)	0.6 × 0.2 × 0.2	0.8 × 0.35 × 0.3	0.5 × 0.3 × 0.2	0.95 × 0.25 × 0.2
Absorption coefficient (cm^{-1})	10	0.9	21	1.7
2θ range (°)	4.5–45	4.5–45	4.5–55	4.5–60
hkl range	$0 < h < 14$, $-15 < k < 15$, $-21 < l < 21$	$0 < h < 13$, $-15 < k < 15$, $-18 < l < 18$	$0 < h < 11$, $-13 < k < 13$, $-24 < l < 24$	$0 < h < 14$, $0 < k < 17$, $0 < l < 30$
Symmetry-independent reflcns.	10240	8052	8193	4505
Unique reflctns	9628	7380	6792	4330
Significant reflctns ($F > 4\sigma(F)$)	7305	3755	4369	1638
R_{int}	0.0690	0.1133	0.0761	0.0271
Refined parameters	640	615	427	274
R value	0.0896	0.084	0.097	0.0540
Min. difference hole (eÅ^{-3})	−1.78	−0.469	−1.147	−0.41
Max. difference peak (eÅ^{-3})	1.46	0.651	1.672	0.68

[a] See also Table 1.

employed. Hydrogen atoms of THF were not included in the refinement. The crystal was of low quality; and so 68 reflections with $\sigma > 3.5$ and 23 reflections with $F_o > 5\sigma F_c$ were eliminated. An empirical absorption correction was made [33]. In the case of $Br_2Nb(CO)p_4 \cdot 0.5THF$, the THF molecule was included as a 1:1 disorder model. The hydrogens of the THF were not included.

Tables of thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

4.3. Preparation of Complexes

4.3.1. $ClNb(CO)_3\{P(C_2H_5)_3\}_3$, $BrNb(CO)_3\{P(C_2H_5)_3\}_3$ and $INb(CO)_3\{P(C_2H_5)_3\}_2$

0.474 g (4.10 mmol) of pyridinium chloride, 0.782 g (2.00 mmol) of $[Et_4N][Nb(CO)_6]$ and 0.82 ml (6.20 mmol) of PEt_3 were suspended or dissolved in 25 ml of THF. Visible evolution of CO and H_2 began after *ca.* 1 h of stirring at room temp. After 16 h time the red solution was filtered to remove $[Et_4N]Cl$, and the filtrate was evaporated to dryness. The excess of PEt_3 was removed *in vacuo*. The oily, red residue (ν(CO) (THF) = 1935, 1854, 1832 cm^{-1} of about equal intensities) was redissolved in 20 ml of THF and the solution used directly after filtration for the generation of alkyne complexes (*vide infra*). The bromo complex was prepared analogously from 0.648 g (2.00 mmol) of pyridinium bromide, 0.782 g (2.00 mmol) of $[Et_4N][Nb(CO)_6]$, and 0.83 ml (6.28 mmol) of PEt_3. Reaction time: 24 h. ν(CO) (THF): 1930, 1845 and 1820 cm^{-1}.

For the preparation of the iodo complex, a solution of 0.782 g (2.00 mmol) of $[Et_4N][Nb(CO)_6]$ and 0.82 ml (6.20 mmol) of PEt_3 in 25 ml of THF was cooled to −78°C then treated with 0.501 g (1.97 mmol) of iodine. Immediate evolution of gas indicated the onset of the reaction. After 2 h, the mixture was warmed to room temperature and stirred for a further 5 h. $[Et_4N]I$ was filtered off and the dark, red filtrate containing $INb(CO)_3(PEt_3)_3$(ν(CO) (THF) = 1925, 1840 and 1815 cm^{-1}) used for further reactions.

4.3.2. $BrNb(CO)_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2$ and $INb(CO)_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2$

A suspension of 0.320 g (2.00 mmol) of pyridinium bromide and 0.797 g (2.00 mmol) of dppe in 15 ml of THF was treated with 0.398 g (1.02 mmol) of $[Et_4N][Nb(CO)_6]$. Evolution of gas commenced after *ca.* 45 min. After 24 h the orange coloured solution was filtered and the filtrate slowly evaporated to yield a bright red oil. This was washed with 10 ml of hexane and dissolved in 10 ml of toluene. Hexane was added to the solution until it became turbid. The solution was kept for 5 days at 2°C to give crystals of $BrNb(CO)_2(dppe)_2$, which were filtered off and dried under vacuum. Yield 0.311 g = 51%. Crystals of $BrNb(CO)_2(dppe)_2 \cdot THF$ suitable of the X-ray structure determination were obtained by adding hexane to a solution of the complex in THF/toluene 1/1.

For the preparation of the corresponding iodo complex, a solution of 0.399 g (1.02 mmol) of $[Et_4N][Nb(CO)_6]$ in 15 ml of THF was cooled to −78°C and treated with 0.254 g (1.00 mmol) of iodine. Immediate evolution of CO and a colour change from yellow to red indicated the formation of the anion $[\{Nb(CO)_4\}_2(\mu - I)_3]^-$. The solution was allowed to warm to −50°C during 15 min and 0.797 g (2.00 mmol) of dppe were then added, whereupon enhanced evolution of CO was observed and the solution turned turbid (separation of $[Et_4N]I$). The mixture was warmed to room temperature during 30 min and stirred for additional 4 h. Filtration and evaporation yielded a sticky, red oil, which was washed with 10 ml of hexane and redissolved in 10 ml of toluene. The solution was treated with hexane until the complex began to precipitate out. The solution was kept at 2°C for 3 weeks to yield red crystals. Yield = 0.457g = 42%. Crystals of $INb(CO)_2(dppe)_2 \cdot$ hexane suitable for an X-ray structure analysis were selected under a microscope.

4.3.3. $Br_2Nb(CO)p_4$, $p_4 = [(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2]_2$

A suspension of 0.645 g (4.03 mmol) and 0.665 g (0.99 mmol) of the tetraphosphine in 15 ml of THF was treated with 0.398 g (1.02 mmol) of $[Et_4N][Nb(CO)_6]$. After 5 h stirring at room temp., $BrNb(CO)_2p_4$ had been formed (IR spectrum). The mixture was warmed to 50°C giving rise to a new ν(CO) at 1677 cm^{-1}, belonging to $Br_2Nb(CO)p_4$; the intensity of this band increased at the expense of the ν(CO) bands of $BrNb(CO)_2p_4$ (1837 and 1750 cm^{-1}) during two days of stirring. No more of the dibromo complex was formed after that time. The solution was cooled to room temperature, filtered, and concentrated to half of its volume and hexane was added to the point of turbidity. The solution was kept at 1–2°C for 2 weeks to yield orange rhomboidal crystals of $Br_2Nb(CO)p_4 \cdot 0.5THF$. These were separated from the mother liquor which contained the monobromo complex and dried in a N_2 stream. Yield 0.099 g = 11%.

4.3.4. $NbI(CO)_2(RNC)_2(Ph_2PCH_2CH_2PPh_2)$, $R = {}^tC_4H_9$, cyclo-C_6H_{11}

A THF solution (30 ml) of $INb(CO)_4dppe$, prepared from 0.391 g (1 mmol) of $[Et_4N][Nb(CO)_6]$, 0.396 g (0.993 mmol) dppe and 0.245 g (1 mmol) of iodine, was cooled to −78°C and treated with 0.23 ml (2 mmol) of *tert*·butylisonitrile. The mixture was stirred for 14 h and the solution was allowed to warm slowly to 10°C and then over a further 2 h to room temp. The solution was evaporated to dryness, and the orange-brown, solid residue was dissolved in 20 ml of toluene. The solution was filtered and hexane was added to precipitate the orange–brown INb(CO)$_2$(^{t}BuNC)$_2$dppe. IR(THF): ν(CO) = 1858, 1798; ν(NC) = 2131, 2113 cm^{-1}. δ(^{31}P) = 54.0 ppm.

The related complex INb(CO)$_2$(CyNC)$_2$dppe was prepared analogously with a different work-up. Thus, the residue obtained after evaporation was dissolved in 20 ml of toluene, the solution was filtered, the filtrate evaporated, and the residue washed with hexane and redissolved in hexane/toluene 1/3. The solution was concentrated, and cooled to −15°C to yield the orange crystals. IR (THF): ν(CO) = 1861, 1799; ν(NC) = 2135, 2121 cm^{-1}. δ(^{31}P) = 54.3 ppm.

4.3.5. *INb(CO)$_2$(alkyne)(PR$_3$)$_2$*

The following description for the preparation of INb(CO)$_2$(CH$_3$C≡CCH$_2$CH$_3$){P(C$_2$H$_5$)$_3$}$_2$ also applies to other complexes with PEt$_3$ or PMe$_2$Ph ligands. A solution (25 ml) of INb(CO)$_3$(PEt$_3$)$_3$, prepared as described in Section 4.3.1. and containing *ca.* 1.8 mmol of this complex, was treated at room temperature with stirring with 0.19 ml (2 mmol) of 2-pentyne, whereupon the solution became slightly turbid and turned dark red. After 16 h stirring the solution was filtered and the filtrate evaporated to dryness to leave a red solid, which was redissolved in 10 ml of warm hexane. The solution was filtered, concentrated *in vacuo* and kept at −15°C for 1 h to give red crystal. Yield 0.45 g = 39%. Analysis: C$_{19}$H$_{38}$INbO$_2$P$_2$ (580.27) Calcd. C, 39.33; H, 6.60; I, 21.87; P, 10.68; Nb, 16.01. Found C, 39.20; H, 6.53; I, 21.9; P, 10.5; Nb, 16.0. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.91 (m, 18H, PCH$_2$C*H*$_3$), 1.23 [t (^3J(HH) = 7.48 Hz), 3H, C*H*$_3$CH$_2$CCH$_3$], 1.32 (m, 12H, PC*H*$_2$CH$_3$), 2.82 (s, 3H, CH$_3$CH$_2$CCC*H*$_3$), 3.21 [q, (^3J(HH) = 7.48 Hz), 2H, CH$_3$C*H*$_2$CCCH$_3$] ppm. ^{13}C NMR (CDCl)$_3$: δ = 8.17 (s, PCH$_2$CH$_3$), 14.34 (s, CH$_3$CCCH$_2$*C*H$_3$), 20.00 [t, J(PH) = 8.78 Hz), P*C*H$_2$CH$_3$], 20.89 (s, CH$_3$CC*C*H$_2$CH$_3$), 30.09 (s, *C*H$_3$CCCH$_2$CH$_3$), 202.95 (s, CH$_3$*C*CCH$_2$CH$_3$), 207.95 (s, CH$_3$C*C*CH$_2$CH$_3$), 226.25 (s, *C*O) ppm.

The yields for other alkyne complexes varied between 19% (ClNb(CO)$_2$(PhCCH)(PMe$_2$Ph)$_2$) and 86% (INb(CO)$_2$(EtCCEt)(PMe$_2$Ph)$_2$). Elemental analyses and spectroscopic data for two selected complexes were as follows: INb(CO)$_2$(PhC≡CH)(PEt$_3$)$_2$: Analysis: C$_{22}$H$_{36}$INbO$_2$P$_2$ (614.29) Calcd. C, 43.02; H, 5.89; I, 20.66; P, 10.08; Nb, 15.12. Found C, 43.32; H, 5.98; I, 21.6; P, 6.9; Nb, 15.2%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.92 (m, 18H, PCH$_2$C*H*$_3$), 1.39 (m, 12H, PC*H*$_2$CH$_3$), 7.25–7.49 (m, 5H, Ph), 11.34 (s, 1H, *H*CCPh) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 8.11 (s, PCH$_2$*C*H$_3$), 20.35 [t (J(PC) = 9.15 Hz), P*C*H$_2$CH$_3$], 128.37, 129.04 and 129.36 (all Ph), 14.23 (s, *ipso-C* of Ph), 199.70 (s, H*C*CPh), 207.68 (s, HC*C*Ph), 226.19 and 228.76 (s, *C*O) ppm. INb(CO)$_2$(4-octyne)(PEt$_3$)$_2$: Analysis: C$_{22}$H$_{44}$INbO$_2$P$_2$ (622.35) Calcd. C, 42.46; H, 7.13; I, 20.39; P, 9.95; Nb, 14.93. Found C, 42.37; H, 7.14; I, 20.4; P, 9.8; Nb, 14.9%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.94 (m, 18H, PCH$_2$C*H*$_3$), 1.03 [t(^3J(HH) = 1.29 Hz), 6H, C*H*$_3$(CH$_2$)$_2$CC(CH$_2$)$_2$C*H*$_3$], 1.34 (m, 12H, PC*H*$_2$CH$_3$), 1.58 (m, 4H, CH$_3$C*H*$_2$CH$_2$CCCH$_2$C*H*$_2$CH$_3$), 3.22 (m, 4H, CH$_3$CH$_2$C*H*$_2$CCC*H*$_2$CH$_2$CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 8.26 (s, PCH$_2$*C*H$_3$), 15.49 (s, -CC(CH$_2$)$_2$*C*H$_3$), 20.05 [t (J(PH) = 8.83 Hz), P*C*H$_2$-CH$_3$], 23.88 (s, -CCCH$_2$*C*H$_2$CH$_3$), 39.25 (s, -CC-*C*H$_2$CH$_2$CH$_3$), 206.32 (s, -*CC*-, 227.04 (s, *C*O) ppm.

The complex INb(CO)$_2$(HCCH)(PEt$_3$)$_2$ was prepared from a solution of INb(CO)$_3$(PEt$_3$)$_3$ (see Section 4.3.1), cooled to −15°C, and subjected to 1 atm. pressure of acetylene (purified by passage through concentrated H$_2$SO$_4$ and molecular sieves). Evolution of CO started after a few minutes, and the solution turned dark red. After 2 h the solution was filtered at −15°C and evaporated to dryness, still at −15°C. The dark red, syrupy residue was dried *in vacuo* and dissolved in 5 ml of THF, and the solution transferred to a 1 cm column of Celite (pretreated under high vacuum and loaded with N$_2$) and eluted with 5 ml of THF. Addition of hexane and storage at −30°C afforded red, crystals INb(CO)$_2$(HCCH)(PEt$_3$)$_2$, which were filtered off and dried *in vacuo* for 1 h. Yield 0.290 g = 27%.

Treatment with further acetylene for longer times yielded INb(CO)(HCCH)$_2$(PEt$_3$)$_2$, which was not isolated.

4.3.6. *Reaction of INb(CO$_2$)(EtCCEt)(PEt$_3$)$_2$ with phosphites*

A solution of 0.299 g (0.51 mmol) of INb(CO)$_2$(EtCCEt)(PEt$_3$)$_2$ in 20 ml of THF, was treated under one atmosphere of carbon monoxide with 0.645 ml (2.55 mmol) of trimethylphosphite. After 4 h stirring at room temp., the IR spectrum indicated the formation of INb(CO)$_2$(EtCCEt)(PEt$_3$)P(OMe)$_3$. After a further 24 h the solution was filtered and evaporated to dryness, and the residue washed with two 5 ml portions of cold (0°C) hexane. Two recrystallizations of the residue from 10 ml of warm (40°C) hexane afforded raspberry-red, crystalline INb(CO)$_2$(EtCCEt){P(OMe)$_3$}$_2$. Yield 0.161 g = 52%.

Reaction of INb(CO)$_2$(MeCCMe)(PEt$_3$)$_2$ with P(OMe)$_3$ yielded INb(CO)$_2$(MeCCMe){P(OMe)$_3$}$_2$ in 46% yield.

4.3.7. Reaction of $INb(CO)_2(PhCCPh)(PEt_3)_2$ with $Na[BH_4]$

A solution of 0.508 g (0.74 mmol) of $INb(CO)_2(PhCCPh)(PEt_3)_2$ in 15 ml of THF was treated with an excess (0.224 g, 5.92 mmol) of sodium tetrahydroborate and stirred at room temp. for 7 days, during which the initially red solution faded to become almost colourless, and at the same time the intensity of the ν(CO) bands in the IR spectrum decreased. The solution was filtered, the solvent removed *in vacuo*, and the residue treated with 10 ml of water (slightly exothermic reaction). The aqueous phase was extracted three times with diethyl-ether, and the combined extracts dried over magnesium sulphate. Decantation, and evaporation of the ether afforded 0.026 g of a white oily product consisting of a 1:1 mixture of *cis*- and *trans*-stilbene (^1H evidence).

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