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Alkyne-niobium(I) complexes with functionalized alkynes: synthesis, structure and reactivity

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Abstract

The reaction between $INb(CO)_3(PR_3)_3$ and diynes yielded the complexes *all-trans*-$[INb(CO)_2(PR_3)_2\text{diyne}]$ ($PR_3 = PEt_3$; diyne = 2,4-hexadiyne (**1a**), 1,5-hexadiyne (**1b**). $PR_3 = PMe_2Ph$, diyne = 2,6-octadiyne (**1c**)). Only one of the acetylenic bonds coordinates. Reaction of $INb(CO)_3(PMe_2Ph)_3$ with $Ph_2PC{\equiv}CPPh_2$ generated $INb(CO)_2(PMe_2Ph)_2(Ph_2PC{\equiv}CPPh_2)$ (**2**), again with the ligands mutually *trans*. The UV-induced reaction between **2** and $W(CO)_6$ led to *fac*-$[W(CO)_3(PMe_2Ph)_3]$ (**3**). **1a**, **2** and **3** were characterized by X-ray structure analyses.

Keywords: Niobium; Carbonyl; Alkyne; Phosphaalkyne

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1. Introduction

Catalyst systems such as MCl_5–Zn–H^+ (M = Nb or Ta) enable the reduction, coupling and polymerization of alkynes [1]. Alkyne complexes of low-oxidation-state Nb and Ta are very likely intermediates in these reactions. In addition, biogenic catalysts such as vanadium-nitrogenase from nitrogen fixing bacteria are able to promote the reductive protonation of acetylene to ethane [2]. Again, an alkyne complex is possibly the active intermediate. We have started a programme designed to model these intermediates and to evaluate their reactivity. In previous studies, we have reported on simple alkyne complexes of the type $XM(CO)_2(PR_3)_2(\text{alkyne})$ (M = Nb or V) [3–5], $[\mu\text{-}XNb(CO)_2(\text{alkyne})_2]_2$ [6], where X is a halogen, preferentially Br or I, and the Nb(III) complex $[NbBr_4(F_3CC{\equiv}CCF_3)(\text{pyr})]^-$ [7]. These complexes are most conveniently prepared from seven-coordinated complexes of the type $XM(CO)_3(PR_3)_3$ which carry both a labile CO and phosphine. An alternative route to alkyne complexes, by reductive coupling of CO or CNR, has been described by Lippard and coworkers [8–10]. In this paper we present results of experiments on complexes with diphosphaacetylene and diynes, i.e. alkynes which posess, in addition to the coordinating triple bond, additional functional groups, viz. two PPh_2 groups or a second acetylenic bond, respectively. The structure of an unprecedented reaction product, *fac*-$[W(CO)_3(PMePh_2)_3]$, is also described.

2. Results and discussion

2.1. Preparation and structure of diyne complexes

Preparation was carried out via the precursor complexes $INb(CO)_3(PR_3)_3$ ($PR_3 = PEt_3$, PMe_2Ph) in THF at ambient temperature according to Eq. (1) to form red–brown to violet, products usually in the form of pastes. The precursor complexes were generated in vitro from $[Et_4N][Nb(CO)_6]$, PR_3 and I_2 [5]. Only one of the acetylenic bonds coordinates; no bidentate binding or bridging mode has so far been verified for the diynes employed. The $\delta(^{13}C)$ values for the coordinated –C≡C– are broadened by the adjacent quadrupolar ^{93}Nb nucleus (nuclear spin 9/2) and appear at low field (Table 1) in a region typical of four-electron donation [6,11,12]. The coordination shifts $\Delta\delta = \delta(\text{coordinated alkyne}) - \delta(\text{free alkyne})$ in $INb(CO)_2(PEt_3)_2$(2,4-hexadiyne) (**1a**) amount to 119.9 and 148.8 ppm for the C atoms forming the coordinated triple bond and 49.6 and 6.7 ppm for those forming the uncoordinated one, i.e. the uncoordinated –C≡C– is still strongly influ-

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Table 1
IR (ν(CO) region) and selected NMR data of diyne–niobium complexes

Compound	ν(CO) (cm^{-1}) [a]	$\delta(^{31}P)$ [b] (ppm)	$\delta(^{13}C)$ [c]		$\delta(^1H)$ [d]	
			$(-C{\equiv}C-)_{co}$	$(-C{\equiv}C-)_{unco}$	$(Me/HC{\equiv}C)_{co}$	$(Me/HC{\equiv}C)_{unco}$
1a $INb(CO)_2(PEt_3)_2$(2,4-hexadiyne)	1999w 1917vs	7.4	213.2, 191.9	114.1, 78.7	2.82	2.27
1b $INb(CO)_2(PEt_3)_2$(1,5-hexadiyne)	1990w 1907vs	8.0	210.4, 192.4 [e]	143, 127 [f]	10.98, 10.92	[g]
1c $INb(CO)_2(PMe_2Ph)_2$(2,6-octadiyne)	1990w 1907vs	−10.2	206.9, 205.4	79.8, 76.4	2.53	2.45

[a] In THF. [b] In CD_2Cl_2 at 210 K. [c] In THF-d_8 (2,4-hexadiyne) or CD_2Cl_2 (other compounds). [d] In CD_2Cl_2. [e] A second, weak pair of signals at 205.9 and 204.8 ppm is also observed. [f] Plus a second weak pair at 140 and 130 ppm. [g] Not unambiguously assigned due to overlap with other resonances.

enced. There are two pairs of $\delta(^{13}C)$ and $\delta(^1H)$ NMR signals for the acetylenic groups in the case of $INb(CO)_2(PMe_3)_2$(1,5-hexadiyne) (**1b**), indicating the presence of (possibly conformational) isomers. The two CO groups, which are slightly nonequivalent because they are differently influenced by the 1,5-hexadiyne, give rise to two broadened resonances at 227.3 and 225.2 ppm. The respective signals for $INb(CO)_2(PMe_2Ph)_2$(2,6-octadiyne (**1c**) appear at 223.2 and 223.8 ppm. We did not observe in the IR spectrum $\nu(C{\equiv}C)$ bands for the coordinated or uncoordinated triple bonds. The IR spectrum in the ν(CO) region exhibits a weak and a strong band (Table 1) in accordance with a slightly disturbed *trans* position of the two CO groups in an octahedral coordination environment for Nb. There is a single resonance in the ^{31}P NMR spectrum, indicating that the phosphine ligands are also mutually *trans*.

$$INb(CO)_3(PR_3)_3 + \text{diyne} \rightarrow INb(CO)_2(\text{diyne})(PR_3)_2 + CO + PR_3 \quad (1)$$

Support for this arrangement in solution comes from the X-ray structure of **1a**. Fig. 1 is an ORTEP representation of the molecule, Table 2 summerizes the crystal data. Fractional coordinates and isotropic displacement parameters are contained in Table 3, with selected bond lengths and angles in Table 4. The diyne coordinates side-on with one of the acetylenic bonds. The structure is best described as an octahedron with the centre of the diyne triple bond occupying the position *trans* to io-

Table 2
Crystal data for the complexes **1a**, **2** and **3**

	1a	**2**	**3**
Empirical formula	$C_{20}H_{36}INbO_2P_2$	$C_{44}H_{42}INbO_2P_4$	$C_{27}H_{33}O_3P_3W$
Molar mass (g mol^{-1})	590.24	946.47	682.29
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2(1)/m$	$P\bar{1}$	$P2(1)/n$
Cell dimensions			
a (Å)	9.413(2)	10.618(3)	9.575(2)
b (Å)	12.410(2)	10.829(4)	29.87(2)
c (Å)	11.399(2)	21.471(5)	10.665(3)
α (deg)		95.70(3)	
β (deg)	94.40(3)	90.50(2)	111.85(2)
γ (deg)		119.06(2)	
Volume ($Å^3$)	1327.7(4)	2142.7(11)	2831(3)
Z	2	2	4
Calc. density (g cm^{-3})	1.476	1.467	1.601
μ (Mo Kα) (mm^{-1})	1.7	1.2	4.3
F(000)	592	952	1352
Crystal dimensions (mm^3)	0.55 × 0.50 × 0.35	0.2 × 0.2 × 0.3	1.50 × 0.95 × 0.80
θ range (deg)	2.43 to 30.08	2.26 to 25.05	2.39 to 30.07
Index range	$0 < h < 13$, $0 < k < 17$, $-16 < l < 16$	$-12 < h < 12$, $-12 < k < 12$, $-25 < l < 25$	$-2 < h < 13$, $-2 < k < 4$ $-14 < l < 14$
Measured reflections	7565	16529	11613
Independent reflcns	4062	7583	8292
R_{int}	0.2228	0.0483	0.0506
Reflections with $I > 2\sigma(I_0)$	1951	5808	6705
Refined parameters	174	476	318
GOF	0.981	0.950	1.102
$R1$. $wR2$	0.0783, 0.1847	0.0379, 0.0859	0.0521, 0.1253
max./min. residual electron density (e $Å^{-3}$)	2.176/ − 0.880	0.779/ − 0.352	2.499/ − 3.290

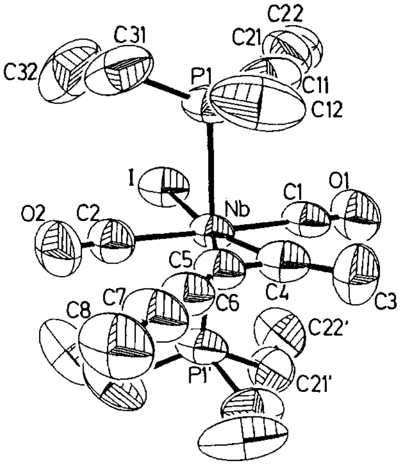

Fig. 1. ORTEP plot (50% probability ellipsoids) and numbering scheme for compound **1a**.

dine. The almost linear OC–Nb–CO fragment (C1–Nb–C2 = 175.6(5)°) is aligned with the triple bond. Nb, I, the 2 CO groups and hexadiyne define a mirror plane. Bonding parameters are in the range common for other complexes of this type [3,5,8–10]. The bond distance of the uncoordinated acetylenic bond, *d*(C6–C7) = 1.193(13) Å, does not deviate significantly from that of the free alkyne, while the coordinated acetylenic bond, *d*(C4–C5), is widened to 1.34(2) Å.

Table 3
Fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{pm}^2 \times 10^{-1}$) for the nonhydrogen atoms of **1a**

	x	*y*	*z*	*U*(eq)
Nb	7711(1)	2500	7453(1)	65(1)
I	9848(1)	2500	5763(1)	92(1)
P(1)	7906(3)	382(2)	7358(2)	89(1)
C(1)	6159(15)	2500	5974(8)	78(4)
O(1)	5277(12)	2500	5267(7)	115(3)
C(2)	9364(15)	2500	8815(9)	84(3)
O(2)	10145(12)	2500	9618(7)	119(3)
C(3)	4133(17)	2500	7978(14)	117(5)
C(4)	5708(16)	2500	8103(8)	82(3)
C(5)	6703(14)	2500	9010(8)	77(3)
C(6)	6761(14)	2500	10240(8)	78(3)
C(7)	6876(19)	2500	11289(8)	107(5)
C(8)	6925(20)	2500	12595(9)	134(6)
C(11)	6364(31)	−287(20)	7870(27)	124(9)
C(21)	6757(27)	−315(16)	6108(16)	106(6)
C(31)	9524(38)	−199(22)	8343(19)	139(11)
C(12)	6011(50)	−252(26)	9009(31)	189(20)
C(22)	7082(15)	−109(10)	4988(9)	130(4)
C(32)	10857(21)	23(15)	8096(12)	175(7)
C(11*)	7168(48)	−247(20)	8627(22)	140(13)
C(21*)	8308(33)	−277(13)	6032(15)	108(8)
C(31*)	9530(27)	−283(18)	7196(19)	120(8)
C(12*)	7027(50)	−1334(35)	8623(36)	290(32)

2.2. Preparation and structure of INb(CO)$_2$(PMe$_2$Ph)$_2$-Ph$_2$PCCPPh$_2$ (2), and its reaction with W(CO)$_6$

The preparation was carried out analogously to that described for the diyne complexes except that the reaction mixture was heated under reflux. **2** gradually precipitates as a green solid. The spectral pattern (ν(CO) = 2028m and 1944vs in THF; 2013w and 1941vs cm^{-1} in CH$_2$Cl$_2$; δ(^{31}P) = −10.81 (PMe$_2$Ph) and 18.6 ppm (unresolved triplet, Ph$_2$PCCPPh$_2$)) points to a structure in which the carbonyls, phosphines, and iodine and the diphosphaacetylene are mutually *trans*. This is also the structure found in the solid state (Fig. 2). Crystal data for **2** are contained in Table 2, with bonding parameters in Table 4, and fractional coordinates and isotropic displacement parameters in Table 5. The geometry is similar to that of **1a**, except that there is no mirror

Table 4
Selected bond lengths and angles for 1**a** and **2** [a]

Bond lengths (Å)			Bond angles		
	1	**2**		**1**	**2**
Nb–I	2.889(2)	2.934(1)	I–Nb–C1	86.8(3)	80.40(10)
Nb–P1	2.638(2)	2.641(2)	I–Nb–C2	88.8(4)	79.74(10)
Nb–P2	2.638(2)	2.618(2)	C1–Nb–C2	175.6(5)	160.08(14)
Nb–C1	2.145(12)	2.128(4)	C1–Nb–C*	72.4(5)	80.94(14)
Nb–C2	2.112(12)	2.167(4)	C2–Nb–C#	74.3(5)	82.09(14)
C1–O1	1.111(14)	1.130(5)	I–Nb–P1	85.33(6)	81.19(4)
C2–O2	1.128(13)	1.126(5)	I–Nb–C*	159.2(3)	160.48(10)
Nb–C*	2.079(14)	2.103(3)	I–Nb–C#	163.1(4)	161.85(10)
Nb–C#	2.077(11)	2.102(4)	C*–Nb–C#	37.7(5)	36.94(14)
C*–C#	1.34(2)	1.332(5)	P1–Nb–P2	180.0	162.15(4)
C3–C4	1.48(2)		C3–C4–C5	135.2(11)	
C5–C6	1.398(13)		C4–C5–C6	138.1(13)	
C6–C7	1.193(13)				
C7–C8	1.486(13)				
P3–C3	1.792(3)		P3–C3–C4		134.9(3)
P4–C4	1.788(4)		P4–C4–C3		137.4(3)

[a] C* and C# indicate the coordinated acetylenic bonds. C* and C# are C4 and C5 in **1** (Fig. 1), and C3 and C4 in **2** (Fig. 2).

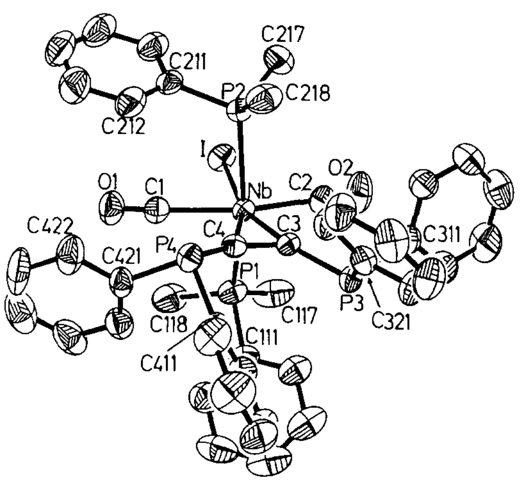

Fig. 2. ORTEP plot (50% probability ellipsoids) and numbering scheme for compound **2**.

plane, and the OC–Nb–CO and R_3P–Nb–PR_3 axes are bent away from linearity by ca. 20° (see Table 4). The dihedral angle P3,C3,C4/P4,C4,C3 amounts to 30.3°.

In order to evaluate the potential coordination behaviour of the free phosphorus functions in **2**, a THF solution of **2** was irradiated with UV light at ca. −60°C in the presence of hexacarbonyltungsten. From this solution, pale yellow *fac*-[$W(CO)_3(PMe_2Ph)_3$] (**3**) was isolated, i.e. instead of generating the expected dinuclear complex **2**-$W(CO)_{5/4}$, UV-induced decomposition of **2** to yield NbI_2 and phosphine transfer to $W(CO)_6$ takes place. Other potential substrates to **2**, such as $W(CO)_5THF$, $W(CO)_4(piperidine)_2$, $Mo(CO)_4$(norbornadiene), $CpNb(CO)_3THF$ and $[Nb_2I_3(CO)_8]^-$ did not react or yielded undefined products. Since at least one of the phosphorus functions of the coordinated diphosphaacetylene should be sterically available (Fig. 2), failure to generate dinuclear complexes by coordination of a coordinatively unsaturated or electron-deficient complex fragment points to a drastically diminished basicity of the phosphorus atoms by electron withdrawal as a consequence of the 4-electron donating mode of the acetylene.

3, although well known [13], has not yet been structurally characterized. We therefore undertook an X-ray structure analysis. **3** crystallizes in the monoclinic space group $P2(1)/n$. The molecular structure is displayed in Fig. 3 (for crystal data see Table 2). Fractional coordinates and thermal factors are given in Table 6, with selected bond distances and angles in Table 7. The molecule attains approximately octahedral geometry; the torsion angle between the $(P)_3$ and $(CO)_3$ faces is 8°. The geometry about the phosphorus atoms corresponds to a flat trigonal pyramid with tungsten at the apex and an average CPC angle of 101.2°. Bond distances d(W–P) and d(W–CO) are in the expected range.

3. Experimental

3.1. General

All operations were carried out in inert gas atmosphere and absolute solvents using standard Schlenk

Table 5
Fractional coordinates ($\times$ 10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for the nonhydrogen atoms of **2**

	x	y	z	U(eq)
I	5107(1)	2259(1)	1156(1)	50(1)
Nb	2898(1)	1533(1)	2075(1)	31(1)
P(1)	2618(1)	−1016(1)	1773(1)	45(1)
P(2)	3586(1)	4199(1)	2050(1)	40(1)
P(3)	1902(1)	964(1)	3743(1)	37(1)
P(4)	−790(1)	926(1)	2439(1)	39(1)
C(1)	1565(4)	1090(5)	1223(2)	42(1)
O(1)	964(4)	889(4)	757(1)	60(1)
C(2)	4745(5)	2092(5)	2677(2)	43(1)
O(2)	5777(4)	2398(5)	2960(2)	75(1)
C(3)	1945(4)	1299(4)	2941(2)	31(1)
C(4)	952(4)	1055(4)	2491(2)	33(1)
C(111)	1302(5)	−2414(5)	2209(2)	46(1)
C(112)	1580(6)	−2317(5)	2846(2)	59(1)
C(113)	637(8)	−3396(7)	3188(3)	77(2)
C(114)	−564(8)	−4516(7)	2915(3)	85(2)
C(115)	−887(6)	−4632(6)	2289(3)	84(2)
C(116)	45(6)	−3582(6)	1935(3)	69(1)
C(117)	4204(6)	−1220(6)	1889(3)	78(2)
C(118)	2049(7)	−1747(5)	953(2)	79(2)
C(211)	2906(5)	4535(4)	1336(2)	44(1)
C(212)	1428(6)	3998(6)	1233(2)	63(1)
C(213)	853(7)	4130(6)	685(3)	79(2)
C(214)	1745(9)	4802(7)	230(2)	80(2)
C(215)	3205(8)	5337(6)	319(2)	77(2)
C(216)	3790(6)	5209(5)	872(2)	59(1)
C(217)	5478(5)	5552(5)	2150(2)	64(1)
C(218)	2817(6)	4873(5)	2661(2)	62(1)
C(311)	3757(4)	2057(5)	4098(2)	39(1)
C(312)	4492(5)	3524(5)	4179(2)	51(1)
C(313)	5859(5)	4284(6)	4476(2)	62(1)
C(314)	6484(6)	3568(7)	4697(3)	75(2)
C(315)	5784(7)	2116(7)	4630(3)	83(2)
C(316)	4425(6)	1363(6)	4334(2)	61(1)
C(321)	1061(4)	1893(4)	4175(2)	39(1)
C(322)	556(5)	2716(5)	3925(2)	47(1)
C(323)	−122(5)	3305(5)	4293(2)	57(1)
C(324)	−311(5)	3077(6)	4909(2)	58(1)
C(325)	202(5)	2281(6)	5168(2)	58(1)
C(326)	873(5)	1693(5)	4801(2)	51(1)
C(411)	−1839(4)	−316(4)	2995(2)	38(1)
C(412)	−1635(5)	−1429(5)	3149(2)	45(1)
C(413)	−2481(5)	−2329(5)	3567(2)	55(1)
C(414)	−3540(6)	−2130(6)	3847(2)	68(1)
C(415)	−3750(6)	−1037(7)	3705(2)	74(2)
C(416)	−2910(5)	−132(6)	3287(2)	59(1)
C(421)	−1620(4)	−168(5)	1680(2)	44(1)
C(422)	−2219(5)	345(6)	1271(2)	66(2)
C(423)	−2826(6)	−456(9)	681(3)	93(2)
C(424)	−2782(7)	−1691(9)	515(3)	95(2)
C(425)	−2197(6)	−2178(6)	921(2)	74(2)
C(426)	−1621(5)	−1429(5)	1503(2)	54(1)

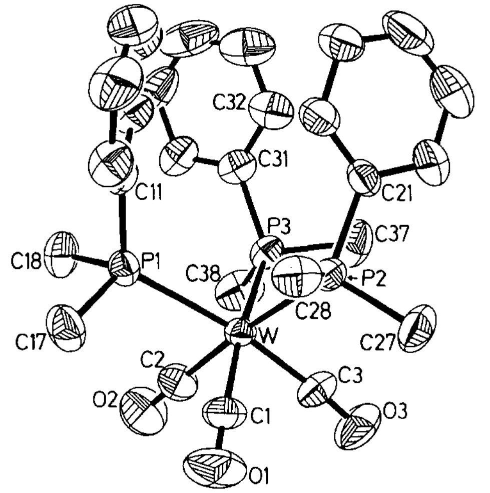

Fig. 3. ORTEP plot (50% probability ellipsoids) and numbering scheme for compound **3**.

techniques. Alkynes, phosphines and $W(CO)_6$ were obtained from commercial sources. $Mg/Zn[Nb(CO)_6]_2$ was prepared from $NbCl_5$ in pyridine by normal pressure synthesis [14], converted to $Na[Nb(CO)_6]$ with NaOH and precipitated as $[Et_4N][Nb(CO)_6]$ [3].

IR spectra were obtained on a Perkin Elmer 1720 spectrometer as THF solutions in 0.1 mm CaF_2 cuvettes. ^{31}P NMR spectra were recorded at 145.8 MHz on a Bruker AM 360 spectrometer. Low temperatures (ca. 210 K) were employed in order to enhance relaxation decoupling of the nuclei ^{31}P and ^{93}Nb to obtain reasonably sharp resonance lines. ^1H and ^{13}C NMR spectra were run on the same instrument at ambient temperatures with the usual measuring conditions.

The UV irradiation was carried out with a high pressure mercury lamp (Philips HPK 125) in a quartz immersion well placed close to the Duran Schlenk tube containing the reaction mixture.

3.2. X-ray structure analysis

Table 6
Fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for the nonhydrogen atoms of **3**

	x	*y*	*z*	*U*(eq)
W	1555(1)	1232(1)	9432(1)	35(1)
P(1)	726(2)	1949(1)	8131(2)	39(1)
P(2)	3820(2)	1082(1)	8829(2)	43(1)
P(3)	−312(2)	734(1)	7698(2)	39(1)
C(1)	2926(8)	1571(2)	10947(7)	50(2)
O(1)	3693(8)	1755(2)	11900(6)	84(2)
C(2)	44(9)	1364(3)	10203(7)	54(2)
O(2)	−785(9)	1435(3)	10745(8)	92(2)
C(3)	2075(10)	705(3)	10578(7)	61(2)
O(3)	2399(11)	395(2)	11276(7)	103(3)
C(11)	1209(7)	2105(2)	6694(6)	44(1)
C(12)	2373(11)	2396(3)	6805(10)	73(2)
C(13)	2755(14)	2486(4)	5726(13)	98(4)
C(14)	2014(14)	2284(4)	4527(11)	88(3)
C(15)	847(11)	2004(3)	4359(9)	68(2)
C(16)	451(9)	1919(3)	5461(7)	53(2)
C(17)	1274(11)	2436(2)	9185(8)	67(2)
C(18)	−1289(8)	2023(3)	7447(7)	55(2)
C(21)	3748(7)	867(3)	7214(7)	48(1)
C(22)	3540(9)	1151(3)	6127(9)	64(2)
C(23)	3425(10)	989(5)	4921(10)	81(3)
C(24)	3488(10)	541(6)	4723(10)	94(4)
C(25)	3678(10)	252(4)	5746(12)	89(4)
C(26)	3808(8)	412(3)	7007(9)	61(2)
C(27)	5076(10)	686(4)	9996(9)	74(3)
C(28)	5083(9)	1550(3)	9084(11)	72(2)
C(31)	−1112(7)	856(2)	5898(6)	41(1)
C(32)	−245(8)	782(3)	5115(7)	52(2)
C(33)	−754(10)	906(3)	3783(8)	66(2)
C(34)	−2134(12)	1110(4)	3219(9)	80(3)
C(35)	−3020(10)	1165(3)	3916(10)	78(3)
C(36)	−2520(7)	1043(3)	5284(8)	55(2)
C(37)	326(9)	159(2)	7689(9)	60(2)
C(38)	−1985(8)	644(3)	8086(9)	62(2)

Data were collected on a Syntex $P2_1$ diffractometer at 293(2) K, Mo Kα irradiation ($\lambda = 0.71073$ Å), graphite monochromator, in the $\theta/2\theta$ scan mode. Crystal parameters and details of the data collection and refinement are collated in Table 2 (vide supra). The programs SHELXS-86 and SHELXL 93 [15] were used throughout. All nonhydrogen 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.

Table 7
Bonding parameters for **3**

Bond distances (Å)		Bond angles (deg)			
W–C1	1.943(7)	C1–W–P1	89.6(2)	av. C–P1–C	101.3
W–C2	1.952(7)	C1–W–P2	85.7(2)	av. C(alkyl)–P1–W	113.1
W–C3	1.941(7)	C2–W–P3	89.6(2)	av. C(arom)–P–W	124.2
W–P1	2.515(2)	C3–W–P3	85.9(3)	av. C–O–W	176.5
W–P2	2.522(2)	P1–W–P3	96.09(7)		
W–P3	2.524(2)	P1–W–P2	97.75(6)		
C1–O1	1.148(8)	P2–W–P3	98.62(5)		
C2–O2	1.161(9)	C1–W–P3	172.3(2)		
C3–O3	1.154(9)	C2–W–P2	170.5(2)		
		C3–W–P1	173.1(3)		

In the case of **1**, the disordered ethyl carbons C11, C12, C21 and C31 were treated with a 1 : 1 disorder model.

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

3.3. *Preparation of complexes*

3.3.1. *$INb(CO)_2\{P(C_2H_5)_3\}_2(CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_3)$, **1a**, and related diyne complexes*

$[Et_4N][Nb(CO)_6]$ (0.782 g, 2 mmol) was dissolved in 25 ml of THF and treated with 0.82 ml (6.2 mmol) of PEt_3. The solution was cooled to dry-ice temperature and 0.501 g (1.97 mmol) of iodine was added. Slow overnight warming of the mixture to room temperature resulted in a red solution of $INb(CO)_3(PEt_3)_3$ (plus small amounts of $INb(CO)_4(PEt_3)_2$) and a precipitate of $[Et_4N]I$, which was filtered off. The filtrate was treated with 0.156 g (2 mmol) of 2,4-hexadiyne. After stirring for 24 h the reaction was completed (IR control, Table 1) and a deep violet solution of **1a** had formed. The solvent was removed in vacuo and the residue was redissolved in hexane, filtered, concentrated to saturation and placed at −25°C for 1d to yield violet crystals of **1a**. Yield: 75%. **1a** is soluble in THF, CH_2Cl_2 and n-hexane. Analysis: $C_{20}H_{36}INbO_2P_2$ (590.26) Calc. C, 40.70; H, 6.15; O, 5.42%. Found C, 40.49; H, 6.30; O, 5.60%. ^1H NMR (CD_2Cl_2): $\delta = 0.95$ (m, 18H, PCH_2CH_3), 1.36 (m, 12H, PCH_2CH_3), 2.27 (s, 3H, $H_3C{-}C{\equiv}C{-}$ uncoordinated), 2.82 (s, 3H, $-C{\equiv}C{-}CH_3$ coordinated). ^{13}C NMR (THF-d_8): $\delta = 6.72$ (s, C3), 9.04 (s, PCH_2CH_3), 21.41 (t, ($J_{PC} = 9.1$ Hz), PCH_2CH_3), 22.77 (s, C8), 78.73 (s, C7), 114.04 (s, C6), 191.88 (s, C4), 213.21 (s, C5).

The complexes $INb(CO)_2(PR_3)_2$(diyne) (with diyne = 1,5-hexadiyne, $PR_3 = PEt_3$ **1b**) and 2,6-octadiyne ($PR_3 = PMe_2Ph$), **1c** were prepared in similar fashion. The complexes were recovered in the form of viscous oils after vacuum evaporation of the solvent. The oils were washed with three 10 ml portions of n-hexane, redissolved in CH_2Cl_2 and evaporated to dryness. Drying under high vacuum yielded brown–violet (**1b**, yield 90%) or dark red–brown (**1c**, yield 96%) polycrystalline powder. ^{13}C NMR (CD_2Cl_2), **1b**: $\delta = 8.0$ (PCH_2CH_3), ca. 19 ($-C{\equiv}C{-}CH_2{-}$ uncoord.), 20.2 (t, PCH_2CH_3), 38.5 ($-C{\equiv}C{-}CH_2{-}$ coord.), 127.2 and 142.7 ($-C{\equiv}C{-}$ uncoord.), 192.4 and 210.4 ($-C{\equiv}C{-}$ coord.), = 225.2 and 227.3 (CO); **1c**: $\delta = 14.9$ ($-C{\equiv}C{-}CH_3$ uncoord.), 20.6 ($-C{\equiv}C{-}CH_3$ coord.), 36.2 ($-C{\equiv}C{-}CH_2{-}$uncoord.), 37.0 ($-C{\equiv}C{-}CH_2{-}$coord.), 13.3 (unresolved t, $P(CH_3)Ph$), 76.4 and 79.8 ($-C{\equiv}C{-}$uncoord.), 128.6 to 140.0 (m, $PMe_2C_6H_5$), 205.4 and 206.9 ($-C{\equiv}C{-}$ coord.), 223.2 and 223.8 (CO). For selected ^1H NMR data see Table 1.

3.3.2. *$INb(CO)_2\{P(CH_3)_2C_6H_5\}_2\{(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2\}$, 2*

$[Et_4N][Nb(CO)_6]$ (0.782 g, 2 mmol) was dissolved in 20 ml of THF and treated with 0.85 ml (6 mmol) of PMe_2Ph. The solution was cooled to dry-ice temperature, 0.501 g (1.97 mmol) of iodine was added, and the mixture allowed to warm to room temperature overnight. $[Et_4N]I$ was removed by filtration, and 0.789 g (2 mmol) of 1,1,4,4-tetraphenyl-1,4-diphospha-2-butyne was added to the red filtrate containing $INb(CO)_3(PMe_2Ph)_3$ and a small amount of $INb(CO)_4(PMe_2Ph)_2$. The mixture was heated under reflux for 2.5 h to yield an olive coloured solution from which green **2** gradually precipitated. Complete in vacuo removal of the solvent yielded a residue which was redissolved in 20 ml of CH_2Cl_2. Filtration, concentration until the beginning turbidity and addition of 3 ml of hexane gave crystalline **2** in 75% yield. Analysis: $C_{44}H_{42}INbO_2P_4$ (946.52) Calc. C, 55.84; H, 4.47; O, 3.38%. Found C, 55.29; H, 4.64; O, 3.85%. ^1H NMR (CD_2Cl_2): $\delta = 1.73$ (t($J_{PH} = 3.4$ Hz), 12H, $P(CH_3)_2Ph$), 6.80–7.55 (m, 30H, C_6H_5). ^{13}C NMR (CD_2Cl_2): $\delta = 19.39$ (t ($J_{PC} = 11.9$ Hz), $P(CH_3)_2Ph$), 128.69–139.93 (m, C_6H_5), 211.60 (d($J_{PC} = 64.48$ Hz), $-PCCP-$), 227.79 (s, CO). ^{31}P NMR (THF-d_8): $\delta = -10.8$ (s, 2P, PMe_2Ph), 18.6 (unresolved triplet, 2P, $Ph_2PCCPPh_2$).

3.3.3. *Reaction between 2 and $W(CO)_6$: fac-$[W(CO)_3\{P(CH_3)_2C_6H_5\}_3]$, 3*

$W(CO)_6$ (0.352 g, 1 mmol) and 0.946 g (1 mmol) of **2** were dissolved in 25 ml of THF, cooled to −60°C and irradiated for 4 d. Within this period, the two strong ν(CO) bands typical of $W(CO)_6$ (1973 cm^{-1}) and **2** (2010 cm^{-1}) were gradually replaced by those of *fac*-$[W(CO)_3(PMe_2Ph)_3]$ (1931 and 1833 cm^{-1}). The solution was filtered, the filtrate treated with 3 ml of hexane and kept at −15°C. Suitable crystals for an X-ray structure analysis were obtained from this solution after 1 week. ^{31}P NMR ($CDCl_2$, 210 K): $\delta = -24.1$, ^{183}W satellites: $J(^{31}P{-}^{183}W) = 108$ Hz. ^{13}C NMR (CD_2Cl_2): 20.5 to 21.1 (2 d, $P(CH_3)_2Ph$), 130.0 to 128.5 (m, $PMe_2C_6H_5$).

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