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Synthesis, crystal structures and spectroscopic properties of cationic carbyne complexes of molybdenum and tungsten supported by tripodal nitrogen, phosphorus and sulphur donor ligands

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Abstract

Reaction of the tridentate ligands $HCpy_3$ or Ppy_3 (py = 2-pyridyl) with $Cl(CO)_2py_2M{\equiv}CPh$ (M = Mo, W) in THF at elevated temperature followed by metathesis with $NaBPh_4$ in CH_3CN affords $[(\eta^3\text{-}Xpy_3)(CO)_2M{\equiv}CPh]^+$ (M = W, X = P (**2**), HC (**3**); M = Mo, X = P (**4**)) in high yield. Interaction between 1,1,1-tris(diphenylphosphinomethyl)ethane ($CH_3C(CH_2PPh_2)_3$) or 1,4,7-trithiacyclononane (TTCN) and $Cl(CO)_2py_2W{\equiv}CPh$ in the presence of $AgPF_6$ in refluxing CH_3CN gives $[\{CH_3C(CH_2PPh_2)_3\}(CO)_2W{\equiv}CPh]PF_6$ (**5**) and $[(TTCN)(CO)_2W{\equiv}CPh]PF_6$ (**6**), respectively. These complexes exhibit intense absorption bands at 320–340 nm and weak absorptions in the 400–500 nm region, while excitation at 330 nm in dichloromethane give intense orange to red emission. The structure of the product (**1**) from reaction of Ppy_3 with $Cl(CO)_2py_2W{\equiv}CPh$ was established by X-ray crystallography and shows that only two of the pyridine rings in Ppy_3 are bound to the metal center. The crystal structures of **2**·EtOH and **3**·EtOH show that the W–N distance *trans* to the carbyne moiety is significantly longer than those which are *cis*, and this is attributed to the strong *trans* influence of CPh compared to CO.

Keywords: Carbyne complexes; Crystal structures; Molybdenum; Photoluminescence; Tripodal ligands; Tungsten.

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1. Introduction

The chemistry of cationic carbyne complexes of group 6 metals [1] is less developed than their neutral counterparts [2,3], while the incorporation of neutral tridentate ligands into these systems is rare. We recently reported on the cationic carbyne complexes of group 6 metals bearing facial nitrogen donor ligands and these illustrated the strong σ-donating strengths of 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN) and 1,4,7-triazacyclononane (TACN) [4].

In an attempt to study the effects of different neutral facial ligands with various donor atoms, namely nitrogen, phosphorus and sulphur, on the reactivity of the carbyne moiety and complex as a whole, cationic phenylcarbyne derivatives of the type $[(\eta^3\text{-}L')M(CO)_2({\equiv}CPh)]^+$ (M = Mo, W; η^3-L' = tris(2-pyridyl)methane ($HCpy_3$), tris(2-pyridyl)phosphine (Ppy_3), 1,1,1-tris(diphenylphosphinomethylethane ($CH_3C(CH_2PPh_2)_3$) and 1,4,7-trithiacyclononane (TTCN) were prepared. Characterization of these complexes by X-ray crystallography was undertaken to allow for structural comparisons. It is noteworthy that the strength of the donor atom *trans* to the carbyne moiety in related tungsten–carbyne complexes can affect the strength [5] and hence the reactivity [6] of the $W{\equiv}C$ bond.

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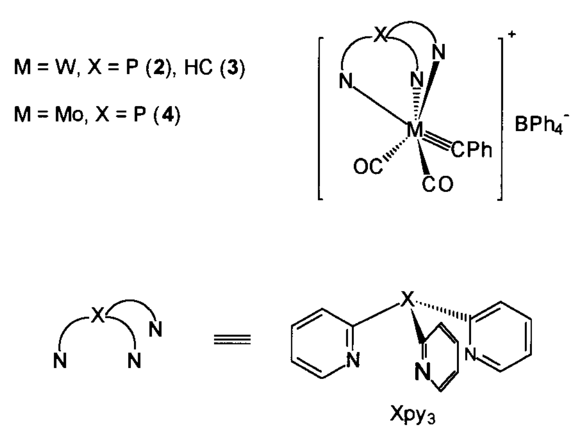
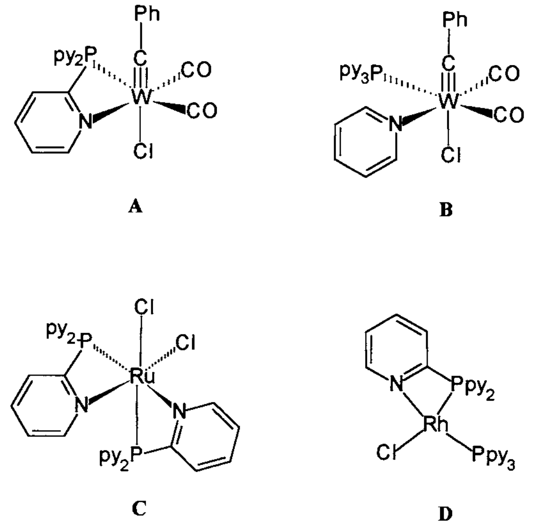
2. Results and discussion

Reactions of the tridentate ligands $HCpy_3$ and Ppy_3 with $Cl(CO)_2py_2M{\equiv}CPh$ (M = Mo, W) in THF at elevated temperature yielded yellow solids which are soluble in acetonitrile but insoluble in dichloromethane. The structure of the product using Ppy_3 in the case of tungsten was established by X-ray crystallography as $[Cl(\eta^2\text{-}Ppy_3)(CO)_2W{\equiv}CPh]$ (**1**), where one pyridine ring does not coordinate to the tungsten atom. We envisaged that metathesis of the chloride group with a non-coordinating anion would result in tridentate coordination of the facial ligand. Hence, addition of sodium tetraphenylborate to the yellow solids in warm acetonitrile afforded the corresponding cationic complexes $[(\eta^3\text{-}Xpy_3)(CO)_2M{\equiv}CPh]^+$ (M = W, X = P (**2**), HC (**3**); M = Mo, X = P (**4**)) (Scheme 1). It is notable that for the triamine ligand Me_3TACN, the macrocyclic effect is manifested in the unassisted displacement of the chloride ligand from the metal center [4].

The coordination mode of Ppy_3 in molybdenum and tungsten carbyne derivatives merits further discussion. Although 2,2′-bipyridine (bpy) and 1,2-bis-(diphenylphosphino)ethane (dppe) respectively, react with $Cl(CO)_2py_2W{\equiv}CPh$ to form $Cl(L\text{–}L)(CO)_2W{\equiv}CPh$ [7] (L–L = bpy, dppe), complexes of the types **A** and **B** (Scheme 2) with mixed N/P coordination have not been reported. Wilkinson and co-workers [8] reported that reaction of $RuCl_2(PPh_3)_3$ and $RhCl(PPh_3)_3$ with excess Ppy_3 gave the products **C** and **D**, respectively, (Scheme 2) with both P and N as donor atoms.



Scheme 1.



Scheme 2.

On the contrary, the reaction of $[Ru(DMF)_6](OTs)_2$ [9] with 2 equivalents of Ppy_3 affords $[(\eta^3\text{-}Ppy_3)_2Ru]^{2+}$ with only N donors. Therefore, it is apparent that Ppy_3 can replace 'soft' donors such as triphenylphosphine to give complexes containing P donors but displaces 'hard' ligands to afford species with N donors only. The latter situation is observed in this work where Ppy_3 coordinates solely via nitrogen atoms in complexes **1**, **2** and **4**.

Refluxing $CH_3C(CH_2PPh_2)_3$ or TTCN with $Cl(CO)_2py_2W{\equiv}CPh$ in CH_3CN showed no observable change. However, with the addition of one equivalent of silver hexafluorophosphate, the cationic complexes $[\{CH_3C(CH_2PPh_2)_3\}(CO)_2W{\equiv}CPh]^+$ (**5**) and $[(TTCN)(CO)_2W{\equiv}CPh]^+$ (**6**) respectively, were obtained in high yields. The TTCN derivative is relatively unstable: decomposition occurs in aerobic CH_3CN after 3 days with the appearance of free TTCN ligand. The unstable nature of **6** may be accredited to the low coordinating strength of TTCN. In summary, $Cl(CO)_2py_2M{\equiv}CPh$ (M = Mo, W) are good precursors for the preparation of cationic carbyne complexes containing neutral facial ligands such as Ppy_3, $HCpy_3$, $CH_3C(CH_2PPh_2)_3$ and TTCN.

Selected NMR and IR spectral data of complexes **1**–**6** and related carbyne complexes are summarized in Table 1. The ^1H- and $^{13}C\{^1H\}$-NMR data suggest that in solution complexes **1–6** contain a mirror plane along the metal–carbyne bond which bisects the tridentate ligand and the terminal carbonyl groups. The ^{13}C chemical shifts of the carbyne carbon atoms are within the range expected for Group 6 complexes [3]. A comparison of the $^{13}C\{^1H\}$-NMR spectral data should reveal the influence of the metal atoms and the facial ligands upon the $M{\equiv}C$ and metal-bound $C{\equiv}O$ moieties.

The ^{13}C $\delta(\underline{C}Ph)$ values of $Cl(CO)_2py_2W{\equiv}CPh$, $Cl(\eta^2\text{-}Ppy_3)(CO)_2W{\equiv}CPh$ (**1**) and $Cl(CO)_2(bpy)W{\equiv}CPh$ are

Table 1
Selected IR and $^{13}C\{^1H\}$-NMR data for related Group 6 carbyne complexes

Complex	$\nu(CO)^a$ (cm^{-1})	$\delta(\underline{C}Ph)^c$ (ppm)	$\delta(CO)^c$ (ppm)	References
$[Cl(\eta^2\text{-}Ppy_3)(CO)_2W{\equiv}CPh]$, **1**	1980s, 1885s	266.3	223.2	
$[(\eta^3\text{-}Ppy_3)(CO)_2W{\equiv}CPh]BPh_4$, **2**	1984s, 1899s	286.3	221.1	
$[(\eta^3\text{-}HCpy_3)(CO)_2W{\equiv}CPh]BPh_4$, **3**	1988s, 1894s	288.1	222.0	
$[(\eta^3\text{-}Ppy_3)(CO)_2Mo{\equiv}CPh]BPh_4$, **4**	1998s, 1918s	297.2	223.1	
$[\{\eta^3\text{-}CH_3C(CH_2PPh_2)_3\}(CO)_2W{\equiv}CPh]PF_6$, **5**	1999s, 1934s	294.8	211.6	
$[(TTCN)(CO)_2W{\equiv}CPh]PF_6$, **6**	2007s, 1925s	293.1	214.0	
$[(Me_3TACN)(CO)_2Mo{\equiv}CPh]BPh_4$	1980s, 1906s	298.0^d	225.2^d	[4]
$[(TACN)(CO)_2Mo{\equiv}CPh]BPh_4$	1997s, 1914s	294.3^d	225.8^d	[4]
$[(Me_3TACN)(CO)_2W{\equiv}CPh]BPh_4$	1975s, 1879s	288.0^d	224.6^d	[4]
$[Cl(CO)_2py_2W{\equiv}CPh]$	1985s, $1897s^b$	262.7^e	220.4^e	[7]
$[Cl(CO)_2(bpy)W{\equiv}CPh]$	1986s, $1899s^b$	265.8^e	222.2^e	[7]

[a] KBr unless specified otherwise.
[b] In CH_2Cl_2.
[c] In CD_3CN unless specified otherwise.
[d] In d_6-acetone.
[e] In $CDCl_3$.

Table 2
Absorption and emission data

Compounds	UV–vis^a nm (log ε_{max})	Emission λ_{max},^{b} nm (τ, μs)	Quantum yield $\Phi_{em} \times 10^{-5}$
$[Cl(\eta^2\text{-}Ppy_3)(CO)_2W{\equiv}CPh]$, **1**	315 (4.19)		
$[(\eta^3\text{-}Ppy_3)(CO)_2W{\equiv}CPh]BPh_4$, **2**	342 (4.01) 420 (3.74)	633 (0.25)	23
$[(\eta^3\text{-}HCpy_3)(CO)_2W{\equiv}CPh]BPh_4$, **3**	339 (4.11) 488sh (2.95)	626 (0.21)	33
$[(\eta^3\text{-}Ppy_3)(CO)_2Mo{\equiv}CPh]BPh_4$, **4**	350 (3.69) 496 (3.26)	614 (0.11)	20
$[\{\eta^3\text{-}CH_3C(CH_2PPh_2)_3\}(CO)_2W{\equiv}CPh]PF_6$, **5**	336 (3.87) 488 (3.17)	669 (0.009)	11
$[(TTCN)(CO)_2W{\equiv}CPh]PF_6$, **6**	336 $(2.53)^b$ 472 (2.94)		

[a] In CH_3CN unless otherwise stated.
[b] In CH_2Cl_2.

comparable since the electronic effect of the py_2, η^2-Ppy_3 and bpy ligands on the W≡C moiety should be similar. However, replacement of the chloride in **1** by a pyridyl group leads to a downfield shift for the carbyne carbon in **2** (286.3 cf. 266.3 ppm for **1**). Corresponding $\nu(CO)$, $\delta(\underline{C}Ph)$ and $\delta(CO)$ values were found for **2** and **3**; $HCpy_3$ and Ppy_3 are both σ-donors and π-acceptors and evidently exhibit similar chelating properties. Changing from tungsten in **2** to molybdenum in **4** causes downfield ^{13}C $\delta(\underline{C}Ph)$ and $\delta(CO)$ shifts plus higher IR $\nu(CO)$ values. This can be rationalized by the higher electron density of the third row transition metal which leads to greater metal–carbonyl π-back bonding.

Complexes **5** and **6** bearing P and S donor atoms respectively, display more downfield $\delta(\underline{C}Ph)$ signals and higher $\nu(CO)$ values than derivatives with nitrogen-donor ligands. Hence $CH_3C(CH_2PPh_2)_3$ and TTCN appear to be weaker σ-donors and/or better π-acceptors than $HCpy_3$ and Ppy_3.

The UV-visible absorption and emission data for the carbyne complexes are summarized in Table 2. Complexes **2**–**6** exhibit intense absorption bands at 320–340 nm and weak absorptions in the 400–500 nm region. The large extinction coefficients observed for the high energy bands suggest that they originate from charge transfer transitions which are presumably MLCT [10]. With reference to previous studies [10–12], the low energy absorptions at $\lambda > 400$ nm with low ε_{max} are assigned to $d_{xy} \rightarrow d_{\pi}^{*}$ transition (where d_{π}^{*} is comprised of d_{xz}, d_{yz} and π^{*} of the phenylcarbyne moiety). Excitation of the complexes **2**–**5** at 330 nm in dichloromethane give intense orange to red emissions. The large difference between the energies of the emission and lowest allowed absorption plus the relatively long emission lifetimes suggest that the transitions involved are spin-forbidden processes [12]. The emissive state is likely to be $^3[(d_{xy})^1(d_{\pi}^{*})^1]$.

Complexes **1**, **2**, **3** and **5** have been characterized by X-ray diffraction methods in order to probe the antici-

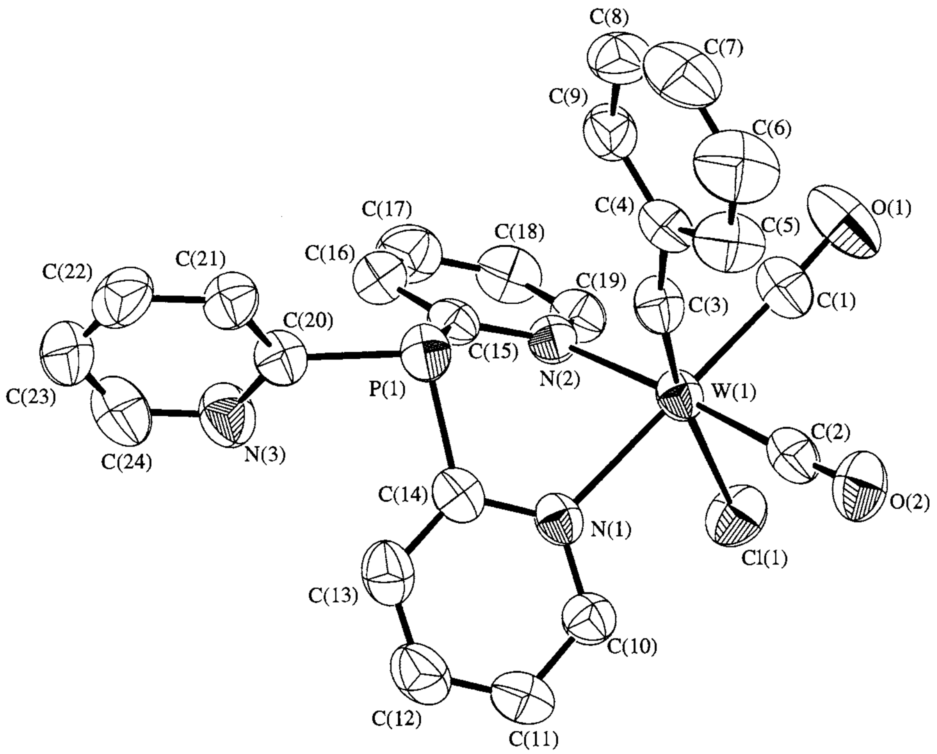


Fig. 1. Perspective view of [Cl(η^2-Ppy$_3$)(CO)$_2$W≡CPh] (40% probability ellipsoids).

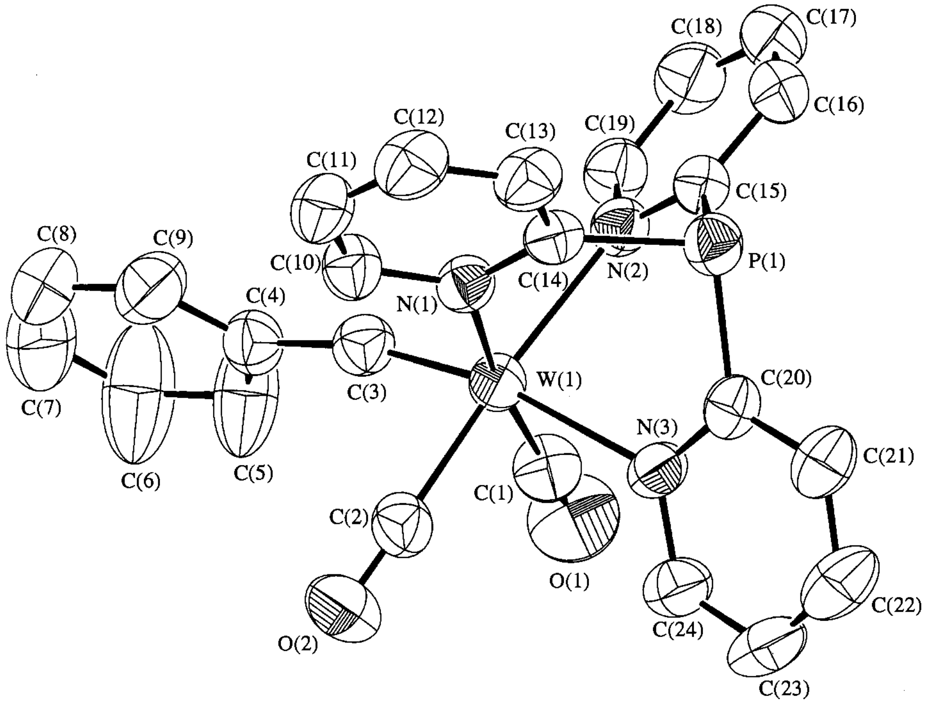


Fig. 2. Perspective view of [(η^3-Ppy$_3$)(CO)$_2$W≡CPh]$^+$ (40% probability ellipsoids).

pated changes in structural parameters imposed by different donor atoms and ligands. The perspective views of the cations in **1**, **2**, **3** and **5** with atomic numbering schemes are shown in Figs. 1–4 while crystal data and selected bond lengths and angles are listed in Tables 3–7, respectively. The W(1)–C(3) distances and W(1)–C(3)–C(4) angles in complexes **1**, **2**, **3** and **5** are comparable to related derivatives (Table 8) and fall within the range previously observed for tungsten–carbon triple bonds [3]. The structure of **1** consists of one diethyl ether molecule for two complex molecules. The Ppy$_3$ ligand coordinates to the metal atom via only two

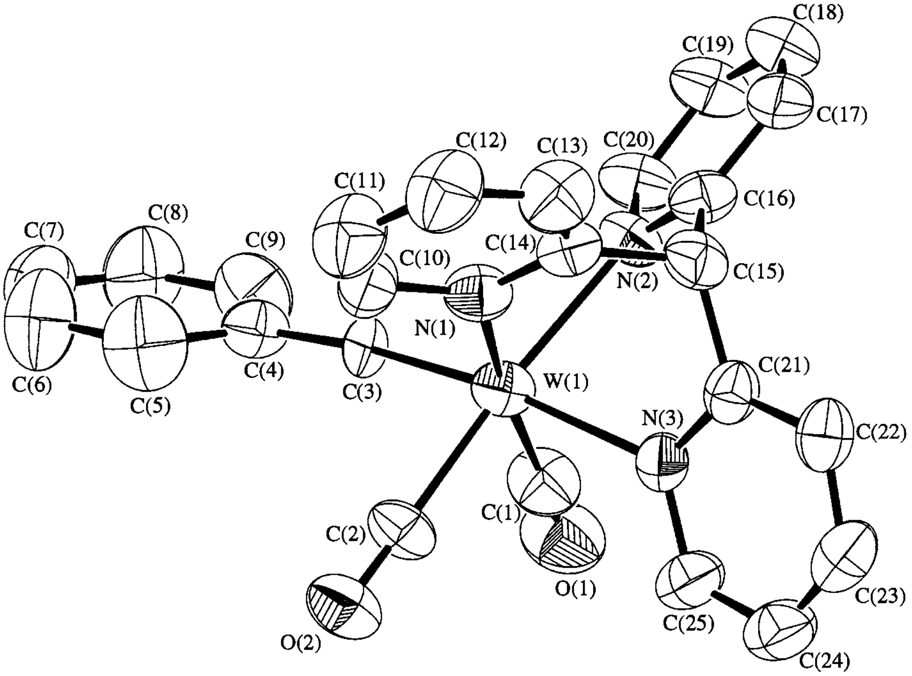


Fig. 3. Perspective view of $[(\eta^3\text{-HCpy}_3)(CO)_2W{\equiv}CPh]^+$ (50% probability ellipsoids).

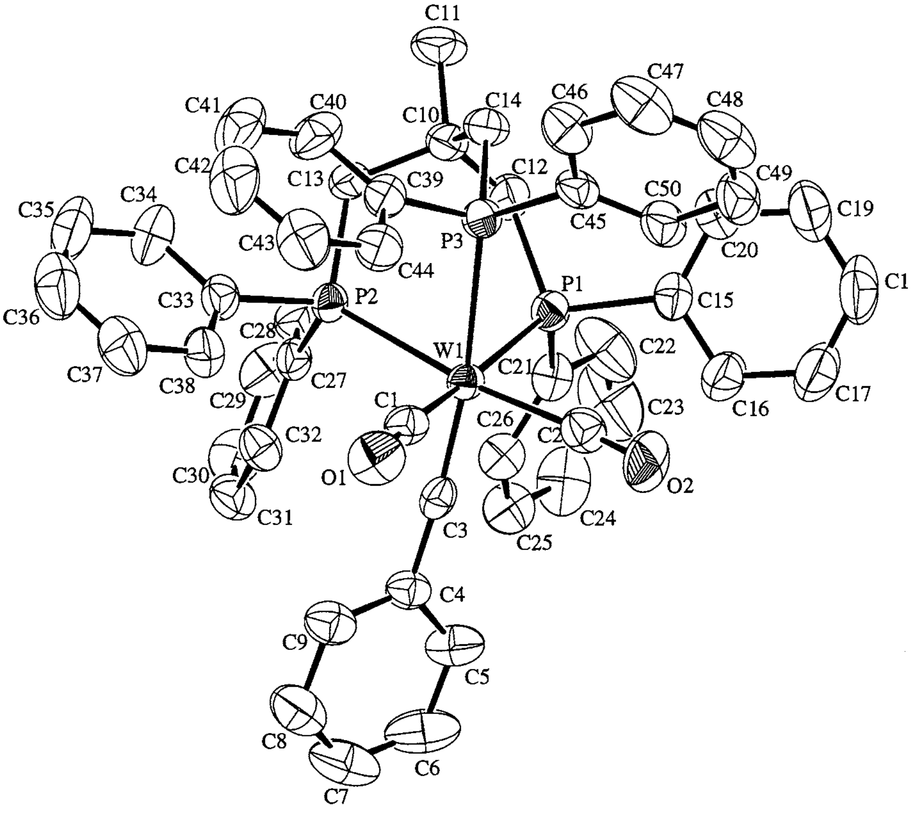


Fig. 4. Perspective view of $[\{CH_3C(CH_2PPh_2)_3\}(CO)_2W{\equiv}CPh]^+$ (40% probability ellipsoids).

pyridyl nitrogen atoms. The crystal structures of **2** and **3** both consist of one ethanol molecule per complex cation. The W atoms are in distorted octahedral environments and are bonded to two carbonyl groups, one phenylcarbyne moiety and three Ppy_3 or $HCpy_3$ nitrogen atoms, respectively. The W(1)–N(3) bond distances in **2** and **3** are significantly longer than the W(1)–N(1) and W(1)–N(2) contacts, and this is attributed to the

Table 3
Crystal data for **1**·$0.5Et_2O$, **2**·EtOH, **3**·EtOH and **5**

	1·$0.5Et_2O$	**2**·EtOH	**3**·EtOH	**5**
Formula	$C_{26}H_{22}ClN_3O_{2.5}PW$	$C_{50}H_{43}BN_3O_3PW$	$C_{51}H_{44}BN_3O_3W$	$C_{50}H_{44}F_6O_2P_4W$
M_r	666.76	959.54	941.59	1098.63
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	12.188(3)	13.256(2)	14.170(9)	12.39 6(4)
b (Å)	12.532(3)	14.450(3)	14.304(2)	13.60 9(3)
c (Å)	10.255(3)	12.863(1)	11.638(1)	27.62 0(4)
α (°)	109.19(2)	102.50(1)	107.62(1)	
β (°)	111.90(2)	102.09(1)	94.41(2)	91.86(2)
γ (°)	101.80(2)	101.91(3)	83.83(3)	
V (Å^3)	1273.2(7)	2268.9(7)	2232(1)	4656(1)
Z	2	2	2	4
D_c (g cm^{-3})	1.666	1.404	1.401	1.567
μ (Mo–K$_\alpha$) (cm^{-1})	47.40	26.27	26.34	26.84
F(000)	650	964	948	2192
No. of parameters refined	298	532	532	604
R, wR	0.029, 0.037	0.032, 0.044	0.065, 0.078	0.031, 0.037

stronger *trans* influence exerted by the carbyne moiety compared to CO. The W–C(carbyne) distance in **2** (1.811(7) Å) is slightly shorter than that in **3** (1.835(8) Å), while correspondingly, the *trans* W(1)–N(3) contact in **2** (2.326(5) Å) is marginally longer than that in **3** (2.278(9) Å). However, the two remaining W–N(pyridyl) distances are similar in **2** and **3**. This is in accordance with the observation by Mayr that changes in the interaction along the X–W≡CPh axis does not significantly affect the bonding parameters between the metal and the four ligands perpendicular to the X–W≡CPh axis [3b].

The octahedral geometry around the tungsten atom in **5** is highly distorted. Complex **5** is a rare example of a structurally characterized group 6 cationic complex containing a phosphine donor atom *trans* to a carbyne group. The crystal structures of [*trans*-$(Ph_3P)(CO)_4Cr{\equiv}CNEt_2$]$BF_4$ [13] and [*trans*-$(Me_3P)(CO)_4Cr{\equiv}CMe$]$BCl_4$ [14] have been reported. The highly flexible tripodal ligand $CH_3C(CH_2PPh_2)_3$ allows optimum orientation of the phosphine substituents and phenyl rings such that repulsion between CPh and the three PPh_2 groups is minimized. The W–P bond *trans* to CPh is significantly longer than the remaining *cis*-(W–P) bonds as expected. These W–P contacts are similar to those in $Cl(CO)_2(dppf)W{\equiv}CPh$ (2.583(2) and 2.585(2) Å; dppf = 1,1'-bis(diphenylphosphino)ferrocene) [15] and *trans*-Br(CO)$_2${*o*-Ph-(PPh$_2$)$_2$}W≡CC$_6$H$_4$Me-4 (2.512(1) and 2.528(2) Å) [16], hence the cationic charge on complex **5** does not appear to have a significant impact on the W–P interaction.

Table 4
Selected bond lengths (Å) and angles (°) for **1**·$0.5Et_2O$

W(1)–Cl(1)	2.542(2)		
W(1)–N(1)	2.254(5)		
W(1)–N(2)	2.255(5)		
W(1)–C(1)	1.993(8)		
W(1)–C(2)	1.988(8)		
W(1)–C(3)	1.806(6)		
Cl(1)–W(1)–N(1)	86.6(1)	Cl(1)–W(1)–N(2)	86.1(1)
Cl(1)–W(1)–C(1)	91.1(2)	Cl(1)–W(1)–C(2)	89.3(2)
Cl(1)–W(1)–C(3)	171.9(2)	N(1)–W(1)–N(2)	82.5(2)
N(1)–W(1)–C(1)	176.7(2)	N(1)–W(1)–C(2)	95.7(2)
N(1)–W(1)–C(3)	100.1(2)	N(2)–W(1)–C(1)	95.0(3)
N(2)–W(1)–C(2)	175.1(2)	N(2)–W(1)–C(3)	99.1(2)
C(1)–W(1)–C(2)	86.6(3)	C(1)–W(1)–C(3)	82.3(3)
C(2)–W(1)–C(3)	85.7(3)	W(1)–C(3)–C(4)	167.5(5)
W(1)–N(1)–C(10)	119.1(4)	W(1)–N(1)–C(14)	122.3(4)
W(1)–N(2)–C(19)	118.8(4)	W(1)–N(2)–C(15)	122.0(4)
W(1)–C(1)–O(1)	174.5(7)	W(1)–C(2)–O(2)	177.3(6)

Table 5
Selected bond lengths (Å) and angles (°) for **2**·EtOH

W(1)–N(1)	2.237(5)	W(1)–N(2)	2.231(5)
W(1)–N(3)	2.326(5)	W(1)–C(1)	1.989(8)
W(1)–C(2)	1.974(7)	W(1)–C(3)	1.811(7)
P(1)–C(14)	1.838(6)	P(1)–C(15)	1.829(7)
P(1)–C(20)	1.835(7)		
N(1)–W(1)–N(2)	83.0(2)	N(1)–W(1)–N(3)	85.2(2)
N(1)–W(1)–C(1)	173.1(2)	N(1)–W(1)–C(2)	95.6(2)
N(1)–W(1)–C(3)	101.6(2)	N(2)–W(1)–N(3)	87.2(2)
N(2)–W(1)–C(1)	93.1(2)	N(2)–W(1)–C(2)	174.2(2)
N(2)–W(1)–C(3)	103.3(2)	N(3)–W(1)–C(1)	89.0(2)
N(3)–W(1)–C(2)	87.1(2)	N(3)–W(1)–C(3)	168.1(2)
C(1)–W(1)–C(2)	87.8(3)	C(1)–W(1)–C(3)	84.7(3)
C(2)–W(1)–C(3)	82.5(3)	W(1)–C(3)–C(4)	168.3(5)
W(1)–N(1)–C(10)	118.7(4)	W(1)–N(1)–C(14)	124.4(4)
W(1)–N(2)–C(15)	123.0(4)	W(1)–N(2)–C(19)	119.1(4)
W(1)–N(3)–C(20)	122.0(4)	W(1)–N(3)–C(24)	120.0(5)
W(1)–C(1)–O(1)	179.0(7)	W(1)–C(2)–O(2)	177.1(6)

Table 6
Selected bond lengths (Å) and angles (°) for **3**·EtOH

W(1)–N(1)	2.227(9)	W(1)–N(2)	2.229(9)
W(1)–N(3)	2.278(9)	W(1)–C(1)	2.02(1)
W(1)–C(2)	2.00(1)	W(1)–C(3)	1.835(8)
C(14)–C(15)	1.53(2)	C(15)–C(16)	1.53(2)
C(15)–C(21)	1.53(2)		
N(1)–W(1)–N(2)	80.9(4)	N(1)–W(1)–N(3)	80.8(4)
N(1)–W(1)–C(1)	171.8(4)	N(1)–W(1)–C(2)	96.3(5)
N(1)–W(1)–C(3)	105.9(5)	N(2)–W(1)–N(3)	80.3(4)
N(2)–W(1)–C(1)	94.6(4)	N(2)–W(1)–C(2)	172.0(5)
N(2)–W(1)–C(3)	101.2(5)	N(3)–W(1)–C(1)	91.8(4)
N(3)–W(1)–C(2)	91.8(5)	N(3)–W(1)–C(3)	173.3(4)
C(1)–W(1)–C(2)	87.2(5)	C(1)–W(1)–C(3)	81.6(5)
C(2)–W(1)–C(3)	86.7(6)	W(1)–C(3)–C(4)	174(1)
W(1)–N(1)–C(10)	121.2(8)	W(1)–N(1)–C(14)	122.0(8)
W(1)–N(2)–C(16)	122.6(8)	W(1)–N(2)–C(20)	120.6(9)
W(1)–N(3)–C(21)	122.2(7)	W(1)–N(3)–C(25)	123.2(8)
W(1)–C(1)–O(1)	178(1)	W(1)–C(2)–O(2)	175(1)

3. Experimental details

3.1. General procedures

All operations were carried out using standard Schlenk techniques under an atmosphere of argon. Details for purification of solvents have been given elsewhere [4]. $Cl(CO)_2py_2M\equiv CPh$ (M = Mo, W) were prepared as described for the bromo analogue [7] except oxalyl chloride was used. Water was doubly distilled over potassium permanganate. $HCpy_3$ and Ppy_3 were prepared by literature methods [9]. TTCN and $CH_3C(CH_2PPh_2)_3$ were purchased from Aldrich.

Elementary analyses were performed by the Butterworth Laboratory, UK. IR spectra were recorded on a BIO-RAD FTS-7 FTIR spectrophotometer. ^1H-, ^{13}C- and ^{31}P-NMR spectra were recorded on Bruker SPX300 or SPX500 Spectrometers. Chemical shifts were referenced to tetramethylsilane (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Expected coupling constants are omitted. Assignments for ^{13}C-NMR data were made with reference to related compounds [7]. FAB Mass spectra were obtained from a Finnigan Mat 95 mass spectrometer. UV/VIS absorption spectra were measured on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Steady-state emission spectra were recorded on a SPEX 1681 FLUOROLOG-2 series F111AI spectrometer. The emission lifetimes were determined and flash-photolysis measurements were performed with a Quanta Ray DCR-3 pulsed Nd-YAG laser system (pulse output 355 nm, 8 ns). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope.

Table 7
Selected bond lengths (Å) and angles (°) for **5**

W(1)–P(1)	2.568(1)	W(1)–P(2)	2.550(1)
W(1)–P(3)	2.646(1)	W(1)–C(1)	2.027(6)
W(1)–C(2)	2.009(5)	W(1)–C(3)	1.836(5)
P(1)–W(1)–P(2)	82.57(4)	P(1)–W(1)–P(3)	80.62(4)
P(1)–W(1)–C(1)	172.6(1)	P(1)–W(1)–C(2)	99.1(1)
P(1)–W(1)–C(3)	96.9(1)	P(2)–W(1)–P(3)	85.28(4)
P(2)–W(1)–C(1)	91.6(2)	P(2)–W(1)–C(2)	172.6(1)
P(2)–W(1)–C(3)	104.6(1)	P(3)–W(1)–C(1)	94.5(1)
P(3)–W(1)–C(2)	87.9(1)	P(3)–W(1)–C(3)	169.5(1)
C(1)–W(1)–C(2)	86.1(2)	C(1)–W(1)–C(3)	88.9(2)
C(2)–W(1)–C(3)	82.3(2)	W(1)–C(3)–C(4)	171.4(4)
W(1)–P(1)–C(12)	114.6(1)	W(1)–P(1)–C(15)	119.3(2)
W(1)–P(1)–C(21)	112.1(1)	W(1)–P(2)–C(13)	115.1(2)
W(1)–P(2)–C(27)	117.1(2)	W(1)–P(2)–C(33)	113.8(2)
W(1)–P(3)–C(14)	111.6(2)	W(1)–P(3)–C(39)	121.9(2)
W(1)–P(3)–C(45)	110.2(2)	W(1)–C(1)–O(1)	176.0(5)
W(1)–C(2)–O(2)	173.1(4)		

3.2. $Cl(\eta^2\text{-}Ppy_3)(CO)_2W\equiv CPh$ (1)

A solution of Ppy_3 (0.11 g, 0.40 mmol) and $Clpy_2(CO)_2W\equiv CPh$ (0.21 g, 0.40 mmol) in THF (8 ml) was stirred at 50°C for 6 h. The orange solution turned cloudy with subsequent formation of a yellow precipitate, which was collected upon cooling and washed with cold THF (1 ml) to remove trace amounts of pyridine. The product was recrystallized by diffusion of diethyl ether into an ethanol solution to afford yellow crystals. Yield: 90% (0.23 g). FAB-MS: *m/z* 594 (M^+–Cl). ^1H-NMR (CD_3CN): δ 9.36 (d, 2H, H_6-py); 8.89 (d, 1H, $H_{6'}$-py); 8.10, 8.01 (m, 3H, $H_{3,3'}$-py); 7.75 (m, 2H, H_5-py); 7.60 (m, 1H, $H_{5'}$-py); 7.45–7.26 (m, 8H, $H_{4,4'}$-py and CPh). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 266.3, (W≡C); 223.2 (CO), 158.9, 157.7 ($C_{6,6'}$-py); 153.6 (br, $C_{2,2'}$-py); 150.4 (*ipso*-CPh); 143.1, 142.2 (d, $C_{3,3'}$-py, J_{C-P} = 17.2 Hz); 130.4, 130.3, 129.6 (*o,m,p*-CPh); 128.6, 128.1 ($C_{5,5'}$-py); 126.9, 124.6 ($C_{4,4'}$-py). $^{31}P\{^1H\}$-NMR (CD_3CN): δ 5.2. IR (KBr, cm^{-1}): 1980s, 1885s ν(CO). UV-VIS λ_{max}, nm (log ε_{max}) in CH_3CN: 315 (4.19). Anal. Calcd. for $C_{24}H_{17}ClN_3O_2PW$: C, 45.75; H, 2.70; N, 9.37. Found: C, 45.81; H, 2.77; N, 9.32%.

3.3. $[(\eta^3\text{-}Ppy_3)(CO)_2W\equiv CPh]BPh_4$ (2)

$NaBPh_4$ (0.22 g, 0.64 mmol) was added to $Cl(\eta^2\text{-}Ppy_3)(CO)_2W\equiv CPh$ (0.40 g, 0.64 mmol) in CH_3CN (10 ml) and the mixture was stirred at 50°C for 2 h to yield a bright orange solution and white precipitate. After cooling to ambient temperature, the solution was filtered and all volatile components were removed in vacuo. The solid residue was extracted with acetone and the filtrate was evaporated to dryness. Red crystals were obtained by diffusion of diethyl ether into an ethanol solution. Yield: 86% (0.50 g). FAB-MS: *m/z* 594 $((Ppy_3)(CO)_2W\equiv CPh)^+$; 538 $((Ppy_3)W\equiv CPh)^+$. ^1H-NMR ($CDCl_3$): δ 9.67 (dd, 2H, H_6-py); 9.17 (d, 1H, $H_{6'}$-py); 8.39 (m, 3H, $H_{3,3'}$-py); 8.10 (m, 2H, H_5-py);

Table 8
Selected structural parameters of related Group 6 carbyne complexes

Compounds	M–(carbyne), Å	M–X, Å (*trans* to carbyne)	Carbyne angle, °	Reference
$[(Me_3TACN)(CO)_2Mo{\equiv}CPh]BPh_4$	1.797(6)	N:2.351(4)	174.7(5)	[4]
$[(Me_3TACN)(CO)_2W{\equiv}CPh]BPh_4$	1.800(6)	N:2.316(5)	174.4(4)	[4]
$[\{\eta^3\text{-}B(pz)_4\}(CO)_2W{\equiv}CC_6H_4Me\text{-}4]$	1.821(7)	N:2.284(6)	164.0(6)	[20]
$[Cl(\eta^2\text{-}Ppy_3)(CO)_2W{\equiv}CPh]$, **1**	1.806(6)	Cl:2.542(2)	167.5(5)	
$[(\eta^3\text{-}Ppy_3)(CO)_2W{\equiv}CPh]BPh_4$, **2**	1.811(7)	N:2.326(5)	168.3(5)	
$[(\eta^3\text{-}HCpy_3)(CO)_2W{\equiv}CPh]BPh_4$, **3**	1.835(8)	N:2.278(9)	174(1)	
$[\{\eta^3\text{-}CH_3C(CH_2PPh_2)_3\}(CO)_2\text{-}W{\equiv}CPh]PF_6$, **5**	1.836(5)	P:2.646(1)	171.4(4)	

8.00 (m, 1H, $H_{5'}$-py); 7.60–7.45 (m, 8H, $H_{4,4'}$-py and CPh); 7.26, 6.99, 6.89 (m, 20H, BPh). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 286.3 (W≡C); 221.1 (CO); 158.9, 157.8 ($C_{6,6'}$-py); 152.9, 152.4 (d, $C_{2,2'}$-py, $J_{C-P} = 18.1$ Hz); 149.6 (*ipso*-CPh); 143.0, 142.2 (d, $C_{3,3'}$-py, $J_{C-P} = 17.3$ Hz); 136.7 (B-Ph); 130.7 (*o*-CPh); 130.5 (*m*-CPh); 129.6 (*p*-CPh); 128.8, 128.1 ($C_{5,5'}$-py); 126.6 (br, B-Ph and $C_{4,4'}$-py); 122.8 (B-Ph). $^{31}P\{^1H\}$-NMR (CD_3CN): δ 7.1. IR (KBr, cm^{-1}): 1984s, 1899vs ν(CO). UV-VIS λ_{max}, nm (log ε_{max}) in CH_3CN: 274 (4.46); 342 (4.01); 420 (3.74). Anal. Calcd. for $C_{48}H_{37}BN_3O_2PW$: C, 63.09; H, 4.05; N, 4.60. Found: C, 63.15; H, 4.18; N, 4.48%.

3.4. $[(\eta^3\text{-}HCpy_3)(CO)_2W{\equiv}CPh]BPh_4$ (3)

$HCpy_3$ (0.094 g, 0.38 mmol) was added to a solution of $Clpy_2(CO)_2W{\equiv}CPh$ (0.20 g, 0.38 mmol) in THF (10 ml) at ambient temperature. The clear solution was stirred at 50°C for 6 h to afford a yellow precipitate, which was collected upon cooling and washed with THF (1 ml) and diethyl ether (10 ml × 3). The yellow solid was dissolved in acetonitrile (8 ml) and $NaBPh_4$ (0.13 g, 0.38 mmol) was added. The resulting mixture was heated at 45°C for 3 h to give an orange red solution with white precipitate. The solution was cooled to ambient temperature and filtered. All volatile components were removed in vacuo to give an orange crystalline solid which was washed with diethyl ether and air dried. The product can be recrystallized from ethanol/diethyl ether to give red crystals. Yield: 86% (0.29 g). FAB-MS: m/z 576 $((HCpy_3)(CO)_2W{\equiv}CPh)^+$. ^1H-NMR (CD_3CN): δ 9.55 (d, 2H, H_6-py); 9.05 (d, 1H, $H_{6'}$-py); 8.38 (m, 2H, H_3-py); 8.36 (m, 1H, $H_{3'}$-py); 8.30 (d, 2H, H_5-py); 8.27 (d, 1H, $H_{5'}$-py); 7.70–7.42 (m, 8H, $H_{4,4'}$-py, CPh), 7.26 (m, 8H, BPh), 7.05 (s, 1H, $HCpy_3$), 6.99, 6.89 (m, 12H, BPh). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 288.1 (W≡CPh, $J(^{183}W\text{–}C) = 192$ Hz); 222.0 (CO, $J(^{183}W\text{–}C) = 170$ Hz); 156.7, 155.3 ($C_{6,6'}$-py); 154.1, 153.9 ($C_{2,2'}$-py); 150.1 (*ipso*-CPh); 144.1, 143.4 ($C_{3,3'}$-py), 136.7 (B-Ph), 130.4 (*o*-CPh), 130.3 (*m*-CPh); 129.5 (*p*-CPh); 128.2, 127.6 ($C_{5,5'}$-py); 126.6 (B-Ph), 126.4, 125.9 ($C_{4,4'}$-py); 122.8 (B-Ph), 61.7 ($HCpy_3$). IR(KBr, cm^{-1}): 1988s, 1894s ν(CO). UV-VIS λ_{max}, nm (log ε_{max}) in CH_3CN: 267 (4.46), 339 (4.11) 488sh (2.95). Anal. Calcd. for $C_{49}H_{38}BN_3O_2W$: C, 65.70; H, 4.24; N, 4.69. Found: C, 65.77; H, 4.30; N, 4.60%.

3.5. $[(\eta^3\text{-}Ppy_3)(CO)_2Mo{\equiv}CPh]BPh_4$ (4)

Ppy_3 (0.12 g, 0.46 mmol) was dissolved in THF (10 ml) at ambient temperature and $Cl(CO)_2py_2Mo{\equiv}CPh$ (0.2 g, 0.46 mmol) was added. The resulting orange red solution was stirred at 50°C for 6 h with subsequent formation of a yellow precipitate. The product was filtered after cooling, washed with THF (2ml) and diethyl ether (10 ml × 2) and dried in vacuo. Acetonitrile (10 ml) was added to dissolve the solid and $NaBPh_4$ (0.157 g, 0.46 mmol) was added. The cloudy solution was stirred at 55°C for 2 h. After cooling to ambient temperature, the bright orange-yellow solution was filtered and evaporated to dryness in vacuo. The residue was washed with diethyl ether (10 ml × 3) and recrystallized by diffusion of diethyl ether into an ethanol solution to give a bright yellow microcrystalline solid. Yield: 60% (0.23 g). FAB-MS: m/z 508 $((Ppy_3)(CO)_2Mo{\equiv}CPh)^+$. ^1H-NMR ($CDCl_3$): δ 9.54 (d, 2H, H_6-py); 9.05 (d, 1H, $H_{6'}$-py); 8.31 (m, 3H, $H_{3,3'}$-py); 8.07–7.85 (m, 3H, $H_{5,5'}$-py); 7.57–7.41 (m, 8H, $H_{4,4'}$-py, CPh); 7.27, 6.99, 6.83 (m, 20H, BPh). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 297.2 (Mo≡C); 223.1 (CO); 158.0, 156.4 ($C_{6,6'}$-py); 153.4, 151.3 (d, $C_{2,2'}$-py, $J_{C-P} = 18.2$ Hz); 148.7 (*ipso*-CPh); 141.5, 141.0 (d, $C_{3,3'}$-py, $J_{C-P} = 17.4$ Hz); 136.7 (B-Ph); 131.2 (*o*-CPh); 130.1 (*m*-CPh); 129.5 (*p*-CPh); 128.0, 127.2 ($C_{5,5'}$-py); 126.7, 125.7 ($C_{4,4'}$-py); 126.6, 122.8 (B-Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 9.89. IR(KBr, cm^{-1}): 1998, 1918 ν(CO). UV-VIS λ_{max}, nm (log ε_{max}) in CH_3CN: 252 (4.39); 350 (3.69); 496 (3.26). Anal. Calcd. for $C_{48}H_{37}BMoN_3O_2P$: C, 69.82; H, 4.48; N, 5.09. Found: C, 69.90; H, 4.50; N, 5.01%.

3.6. $[\{CH_3C(CH_2PPh_2)_3\}(CO)_2W{\equiv}CPh]PF_6$ (5)

A mixture of $Cl(CO)_2py_2W{\equiv}CPh$ (0.20 g, 0.38 mmol), $CH_3C(CH_2PPh_2)_3$ (0.24 g, 0.38 mmol) and $AgPF_6$ (0.097 g, 0.39 mmol) in CH_3CN (10 ml) was stirred at 50°C for 18 h to give a brown solution and white precipitate. After filtration, the solvent was removed in vacuo. The residue was washed with diethyl ether (20 ml × 2), extracted with acetonitrile and recrystallized by diffusion of diethyl ether into an acetonitrile solution to yield large orange–yellow crystals. Yield: 80% (0.33 g). FAB-MS: *m*/*z* 953 ($\{CH_3C(CH_2PPh_2)_3\}W(CO)_2(\equiv CPh))^+$. ^{1}H-NMR ($CD_3CN$): δ 7.67 (m, 35H, aromatic H); 2.87–2.63 (m, 6H, CH_2); 1.72 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (CD_3CN): δ 294.8 (m, W≡C); 211.6 (m, CO); 149.8 (br, *ipso*-PPh); 149.7 (*ipso*-CPh); 133.3–129.6 (aromatic C); 39.1 (m, $\underline{C}H_2$); 34.6 (m, $CH_3\underline{C}$); 33.5 (m, $\underline{C}H_3$). $^{31}P\{^1H\}$-NMR (CD_3CN): δ 1.53 ($J_{P-W} = 216$ Hz), 1.43 ($J_{P-W} = 216$ Hz). IR (KBr, cm^{-1}): 1999s, 1934s ν(CO). UV-VIS λ_{max}, nm (log ε_{max}) in CH_3CN: 260 (4.40), 336 (3.87), 488 (3.17). Anal. Calcd. for $C_{50}H_{44}F_6O_2P_4W$: C, 54.64; H, 4.01. Found: C, 54.71; H, 4.11%.

3.7. *[(TTCN)(CO)$_2$W≡CPh]PF$_6$ (**6**)*

A mixture of $Cl(CO)_2py_2W\equiv CPh$ (0.20 g, 0.38 mmol), TTCN (0.068 g, 0.38 mmol) and $AgPF_6$ (0.097 g, 0.39 mmol) in acetonitrile (15 ml) was refluxed for 12 h. After cooling, the orange yellow solution was filtered and evaporated to dryness in vacuo. The residue was washed with diethyl ether and recrystallized by diffusion of diethyl ether into an acetonitrile solution to afford a yellow microcrystalline solid. Yield: 76% (0.19 g). FAB-MS: *m*/*z* 509 ($(TTCN)W(CO)_2(\equiv CPh))^+$; 453, $((TTCN)W\equiv CPh)^+$. ^{1}H-NMR (CH_3CN): δ 7.41 (m, 5H, Ph); 3.58 (m, 4H, CH_2); 3.38 (m, 4H, CH_2); 3.26 (m, 4H, $C\underline{H}_2$). $^{13}C\{^1H\}$-NMR (CH_3CN): δ 293.1 (W≡C); 214.0 (CO); 149.5 (*ipso*-Ph); 131.3 (*o*-Ph); 130.3 (*m*-Ph); 129.3 (*p*-Ph); 37.6, 35.5, 33.8 ($\underline{C}H_2$). IR(KBr, cm^{-1}): 2007s, 1925s ν(CO). UV-VIS λ_{max}, nm (log ε_{max}) in CH_2Cl_2: 250 (4.21), 336 (2.53), 472 (2.94). Anal. Calcd. for $C_{15}H_{17}F_6PO_2S_3W$: C, 27.52; H, 2.60. Found: C, 27.70; H, 2.68%.

3.8. *Structural determination of **1**·0.5Et$_2$O, **2**·EtOH and **3**·EtOH*

Crystal data of **1**. $\{[WClPO_2N_3C_{24}H_{17}]\cdot 0.5Et_2O\}$, orange crystal, dimensions: 0.20 × 0.15 × 0.25 mm, formula weight = 666.76, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.188(3)$, $b = 12.532(3)$, $c = 10.255(3)$ Å, $\alpha = 109.19(2)$, $\beta = 111.90(2)$, $\gamma = 101.80(2)°$, $V = 1273.2(7)$ Å^3, $Z = 2$, $D_c = 1.666$ g cm^{-3}, μ (Mo–K$_\alpha$) = 47.40 cm^{-1}, $F(000) = 650$, $T = 301$ K.

Crystal data of **2**. $\{[WPO_2N_3C_{24}H_{17}]B(C_6H_5)_4\cdot EtOH\}$; red crystal, dimensions: 0.20 × 0.20 × 0.30 mm; formula weight = 959.54, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.256(2)$, $b = 14.450(3)$, $c = 12.863(1)$ Å, $\alpha = 102.50(1)$, $\beta = 102.09(1)$, $\gamma = 101.91(3)°$, $V = 2268.9(7)$ Å^3, $Z = 2$, $D_c = 1.404$ g cm^{-3}, μ (Mo–K$_\alpha$) = 26.27 cm^{-1}, $F(000) = 964$, $T = 301$ K.

Crystal data of **3**. $\{[WO_2N_3C_{25}H_{18}]B(C_6H_5)_4\cdot EtOH\}$; yellow crystal, dimensions 0.30 × 0.20 × 0.30 mm; formula weight = 941.59, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.170(9)$, $b = 14.304(2)$, $c = 11.638(1)$ Å, $\alpha = 107.62(1)$, $\beta = 94.41(2)$, $\gamma = 83.83(3)°$, $V = 2232(1)$ Å^3, $Z = 2$, $D_c = 1.401$ g cm^{-3}, μ (Mo–K$_\alpha$) = 26.34 cm^{-1}, $F(000) = 948$, $T = 301$ K.

Crystal data collection was made at 28°C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega - 2\theta$ scans. Intensity data (in the range $2\theta_{max} = 46$ (**1**); 50 (**2**); 50° (**3**)) were corrected for decay and for Lorentz and polarization effects, and empirical absorption corrections were based on the ψ-scan of five (four for complex **1**) strong reflections. The numbers of unique reflections measured: **1**, 3544; **2**, 7976; **3**, 6018; and the numbers of observed reflections with $I > 3\sigma(I)$: **1**, 3039; **2**, 6588; **3**, 4699; were used in the structural analyses. The space group was determined based on a statistical analysis of intensity distribution and the successful refinement of the structure solved by direct methods (SIR92 [17]), expanded by Fourier method and refined by full-matrix least-squares using the software package TeXsan [18] on a Silicon Graphics Indy computer. For **1**, **2** and **3**, one formula unit constitutes a crystallographic asymmetric unit.

In the least-squares refinement of **1**, all 32 non-H atoms were refined anisotropically, atoms of the diethyl ether were refined isotropically and 22 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 298 variable parameters by least-squares refinement on F with $w = 4\,F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.035\,F_o^2)^2]$ was reached at $R = 0.029$ and $wR = 0.037$ with a goodness-of-fit of 1.16. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.08 and 0.67 e Å^{-3}, respectively.

For **2**, the hydroxyl H atom in the solvent molecule was not found. In the least-squares refinement, all 59 non-H atoms were refined anisotropically and 42 H atoms at calculated positions were not refined. Convergence for 532 variable parameters by least-squares refinement on F with $w = 4\,F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.013\,F_o^2)^2]$ was reached at $R = 0.032$ and $wR = 0.044$ with a goodness-of-fit of 2.37. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.95 and 0.58 e Å^{-3}, respectively.

For **3**, the H atom of the ethanol solvent molecule was not found. In the least-squares refinement, all 59 non-H atoms were refined anisotropically and 43 H atoms at calculated positions were not refined. Convergence for 532 variable parameters by least-squares refinement on F with $w = 4\,F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.033\,F_o^2)^2]$ was reached at $R = 0.065$ and

$wR = 0.078$ with a goodness-of-fit of 2.94. The final difference Fourier map was featureless, with maximum positive and negative peaks of 2.10 and 1.99 e Å^{-3}, respectively.

3.9. Structural determination of *5*

Crystal data. $\{[WP_3O_2C_{50}H_{44}]PF_6\}$; formula weight = 1098.63, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.396(4)$ Å, $b = 13.609(3)$ Å, $c = 27.620(4)$ Å, $\beta = 91.86(2)°$, $V = 4656(1)$ Å^3, $Z = 4$, $D_c = 1.567$ g cm^{-3}, μ (Mo–K$_\alpha$) = 26.84 cm^{-1}, $F(000) = 2192$, $T = 301$ K. An orange crystal of dimensions 0.15 × 0.10 × 0.40 mm mounted on a glass fibre was used for data collection at 28°C on a Nonius-Enraf CAD4 diffractometer with graphite monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega - 2\theta$ scans. Intensity data (in the range $2\theta_{max} = 48°$) were corrected for decay and for Lorentz and polarization effects, and empirical absorption corrections were based on the ψ-scan of four strong reflections. 7096 unique reflections were measured, 5425 reflections of which with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The structure was solved by Patterson and Fourier methods (PATTY [19]) and refinement by full-matrix least squares using the software package TeXsan [18] on a Silicon Graphics Indy computer. The PF_6^- anion was disordered, with the F atoms placed at ten positions, having occupation numbers 1.0, 1.0, 0.65, 0.65, 0.65, 0.75, 0.25, 0.35, 0.35, 0.35, respectively. All non-H atoms were refined anisotropically and 44 H atoms of the complex cation at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 604 variables by least-squares refinement on F with $w = 4F_o^2/\sigma^2\ (F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.033\ F_o^2)^2]$ was reached at $R = 0.031$ and $wR = 0.037$ with a goodness-of-fit of 2.23. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.94 and 1.09 e Å^{-3}, respectively.

4. Supplementary material

Listings of crystal data and refinement, atomic coordinates, calculated coordinates, anisotropic displacement parameters, bond lengths and angles and structure factors for **1**·0.5Et$_2$O, **2**·EtOH, **3**·EtOH and **5** are available as Supplementary Material from the authors.

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