Synthesis, Structural Characterisation and Electrochemical Studies of Neutral Alkenylcarbyne Tungsten Complexes Bearing Chelating Bidentate and Tridentate Phosphanes

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Neutral alkenylcarbyne complexes [X = SCN; *n* = 1 (**2a**), 4 (**2b**). X = OCN; *n* = 1 (**2c**), 4 (**2d**)] were prepared by reaction of the acetonitrile complexes [*n* = 1 (**1a**), 4 (**1b**)] with M[OCN] or M[SCN] (M = Na, K, Bu_4N), and were fully characterised. The synthesis of complex **3**, containing the tridentate phosphane triphos [triphos = $PPh(CH_2CH_2PPh_2)_2$], is also described. The structures of **2b** and **3** were determined by X-ray diffraction methods. In both complexes, the coordination of the W atom was octahedral, with the N-bonded thiocyanate (**2b**) or the chlorine (**3**) anions *trans* to the alkenylcarbyne group. The W–N and W–Cl bond lengths were significant longer than the average found in the literature; this indicates the remarkable *trans* influence of the alkenylcarbyne moiety. The electrochemical behaviour of complexes **2a**–**d** and **3**, as well as that of the related compounds **D** (**2e**: X = F, *n* = 4), (**2f**: X = Cl, *n* = 1), (**2g**: X = $S_2P(OEt)_2$, *n* = 1) and **A** (**4**: *n* = 1) was investigated by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in aprotic media and at a Pt electrode. They underwent irreversible anodic and cathodic processes, the former usually being multi-electronic in the time scale of CPE and involving anodically induced proton dissociation from the alkenylcarbynes. These ligands behave as remarkably strong π-electron acceptors and from the linear relationship between the oxidation potential of the first anodic wave and the electrochemical P_L ligand parameter, it was possible to estimate, for the first time for a carbyne-containing metal centre, that is, the site $\{(dppe)(CO)_2W{\equiv}C{-}R\}$, the values of the electrochemical electron richness (E_s) and the polarisability (β) parameters. These values indicate that this site has low electron richness and low polarisability; this is accounted for by the extensive π-electron acceptance of the alkenylcarbyne ligand. P_L was also estimated for the $S_2P(OEt)_2^-$ ligand, which was shown to act as a rather strong net electron releaser.

Introduction

We have recently reported a systematic methodology for the synthesis of Fischer-type alkenylcarbyne tungsten complexes, which has led to the preparation of a large series of cationic **A**, **B** (L = PMe_3, MeCN), and **C**, and neutral **D** [X = F, Cl, Br, I, CN, κ^1-(*S*)-$S_2P(OEt)_2$] derivatives[1−3] (Scheme 1). Furthermore, we have also studied[3] the synthesis and electrochemical behaviour of dinuclear complexes containing cyanide and diisocyanide bridging ligands **E** [X = CN, 1,4-$(CN)_2C_6H_4$], which are readily generated from the reaction of the labile cationic complexes **B** (L = MeCN) with complexes **D** (X = CN) or the bidentate diisocyanide ligand 1,4-$(CN)_2C_6H_4$. Complexes **E** are unusual examples of dimetallic species bearing long π-conjugated electronic chains involving two terminal α,β-unsaturated carbyne moieties. Molecular systems of this type, containing metallic fragments and extended organic π-systems linked by metal−carbon multiple bonds, are attracting increasing interest. Continuing our work in this field, we were interested to explore the synthesis of novel carbyne complexes displaying related conjugated electronic systems. Since electrochemical studies on metal−carbyne derivatives are rather scarce,[3−8] the synthesis of novel complexes would provide further study subjects for developing the knowledge on the electrochemical behaviour of these types of derivatives, as well as on the electron donor/acceptor character of such ligands, and on the electronic properties of their binding metal centres.

We now report the synthesis and electrochemical studies of novel neutral derivatives of type **D** [dppe = κ^2-(*P*,*P*)-$Ph_2P(CH_2)_2PPh_2$; X = κ-(N)-SCN; *n* = 1 (**2a**), 4 (**2b**). X =

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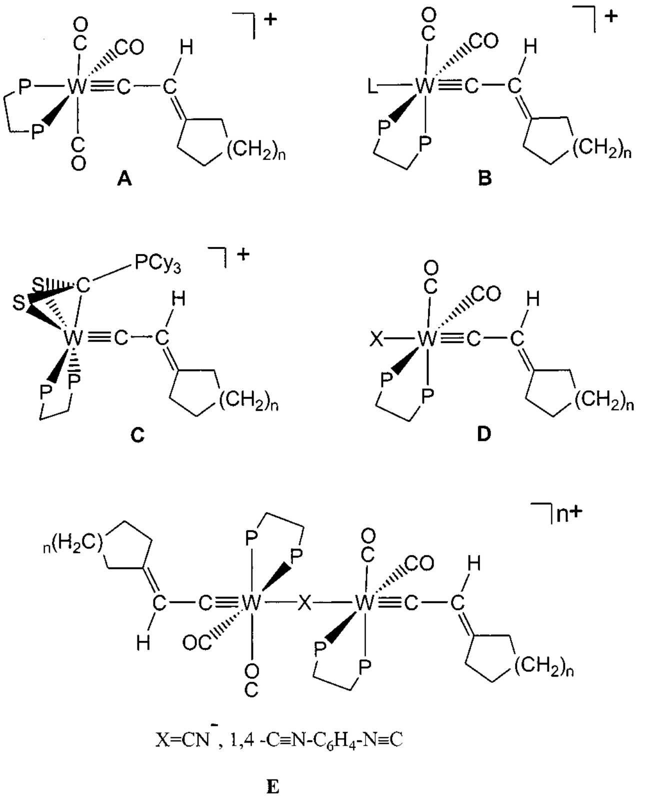
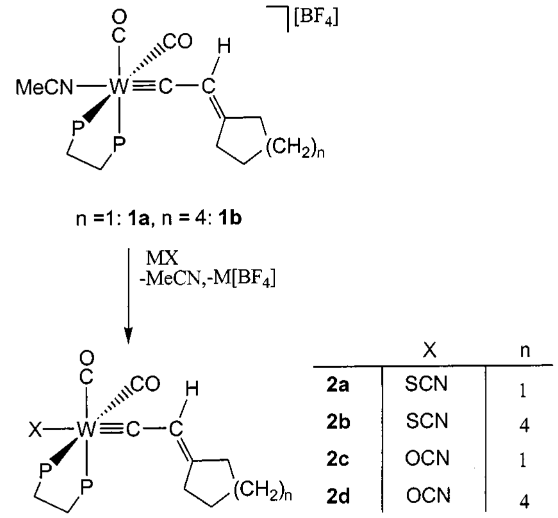


Scheme 1



	X	n
2a	SCN	1
2b	SCN	4
2c	OCN	1
2d	OCN	4

Scheme 2

OCN; *n* = 1 (**2c**), 4 (**2d**)] and **3** (Schemes 2 and 3). The molecular structures of complexes **2b** and **3** were determined by X-ray diffraction. Electrochemical studies by cyclic voltammetry and of controlled potential electrolysis of these and related alkenylcarbyne complexes are also reported.

Results and Discussion

Synthesis and Characterisation of Complexes 2a−d

Complexes **2a−d** were prepared by the reaction of the labile acetonitrile complexes **1a**,**b** with an equimolar amount of KSCN or NaOCN in MeOH (Scheme 2). Alternatively, complexes **2a**,**b** were also formed from the treatment of **1a**,**b** with $[Bu_4N][SCN]$ in CH_2Cl_2. After the resulting solutions were worked up, the desired carbyne complexes were isolated (80−90% yield) as yellow air-stable solids (see Experimental Section) and were characterised by elemental analysis and IR spectroscopy and ^{1}H-, $^{31}P\{^{1}H\}$-, and $^{13}C\{^{1}H\}$-NMR spectroscopy. In addition, the structure of **2b** was determined by X ray diffraction (see below).

The IR spectra (CH_2Cl_2) of **2a−d** contained two strong ν(CO) absorptions (Table 1), as expected for the presence of the *cis*-dicarbonyl arrangement, as also observed for the analogous halide derivatives.[1] Furthermore, IR spectra of **2a**,**b** displayed a very strong absorption at 2064 cm^{-1}, assigned to the CN stretching vibration of the SCN group in accord with most of the N-bonded thiocyanato complexes.[9] This coordination mode was confirmed by the X-ray diffraction structural determination of **2b** (vide infra). Similarly, IR spectra of **2c**,**d** showed another strong absorption at 2212 cm^{-1}, as expected for ν_a(NCO) [consisting mainly of ν(CN) vibration].[9] Since the majority of the cyanato complexes are reported to be N-bonded, we tentatively assigned this linkage to complexes **2c**,**d**. Although the ν_s(NCO) vibration for such a type of linkage is expected to appear in the 1370−1300 cm^{-1} range,[10−11] only a weak band at 1335−1338 cm^{-1} was observed. Other pseudohalide N-bonded Fischer type carbyne complexes have been reported.[12]

The $^{31}P\{^{1}H\}$-NMR spectra (Table 1) of **2a−d** displayed single resonances at ca. $\delta = 40$, indicating the chemical equivalence of the phosphorus atoms of dppe in accordance with the proposed *trans* pseudohalide−carbyne arrangement. *J*(P-W) values of ca. 228 Hz are similar to those found for the analogous halide derivatives.[1] The ^{1}H-NMR spectra (Table 1) showed a broad signal at δ 4.97−5.00 for the alkenyl proton resonance ($=C_{\beta}H-$) of the cyclopentenyl derivatives (*n* = 1, **2a**,**c**), which was shifted to a higher field (δ 4.65−4.68) in cyclooctenyl analogues (*n* = 4, **2b**,**d**). $^{13}C\{^{1}H\}$-NMR spectra (Table 2) were also consistent with the expected resonances in accord with the proposed formulations. In particular, the spectra showed typical carbyne carbon resonances as triplet signals at $\delta = 273.0-279.0$ [$^{2}J(C-P) = 10.0-10.6$ Hz], in addition to the resonances for the C_{β} and C_{γ} nuclei of the alkenylcarbyne chain and the *cis*-dicarbonyl ligands, which appeared as a virtual doublet of doublets. The carbon resonance of the OCN group appeared as a singlet signal at δ 145.0, while that of the SCN group was overlapped by those of the aromatic groups.

We have reported[3] that the analogous cyanide carbyne derivatives of type **D** (X= CN; *n* = 1, 4) (Scheme 1) reacts with complexes **1a**,**b**, affording cyanide-bridged bis(alkenylcarbyne) dinuclear complexes of type **E** (X= CN) (Scheme 1). All attempts directed to the formation of analogous dinuclear μ-NCO and μ-NCS bridging complexes from the reactions of **2a−d** with a stoichiometric amount

Table 1. Selected IR and $^{31}P\{^1H\}$- and ^1H NMR data for the neutral alkenylcarbyne tungsten complexes **2a–d** and **3**

Complexes	IR[a] ν(CO)	ν(CN)	$^{31}P\{^1H\}$[b][c]	^1H[b] $C_\beta H$
2a	2001 (s), 1932 (vs)	2064 (vs)[d]	41.2 s (229.6)	4.97 s,br
2b	2000 (s), 1932 (vs)	2064 (vs)[d]	41.1 s (228.8)	4.65 s,br
2c	1997 (vs), 1927 (vs)	2212 (vs)[e]	39.8 s (227.9)	5.00 s,br
2d	1996 (vs), 1927 (vs)	2212 (vs)[e]	39.7 s (228.3)	4.68 s,br
3	1897 (vs)		84.1 t (8.6,[f] 201.0) 48.2 d (8.6,[f] 294.0)	4.94 s,br

[a] Spectra recorded in CH_2Cl_2, ν (cm^{-1}). Abbreviations: s, strong; vs, very strong. – [b] Spectra recorded in $CDCl_3$, δ in ppm, *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; br, broad. – [c] In parenthesis, *J*(P–W). – [d] ν(SCN). – [e] ν(OCN). – [f] *J*(P–P).

Table 2. Selected $^{13}C\{^1H\}$ NMR data for the neutral alkenylcarbyne tungsten complexes **2a–d** and **3**

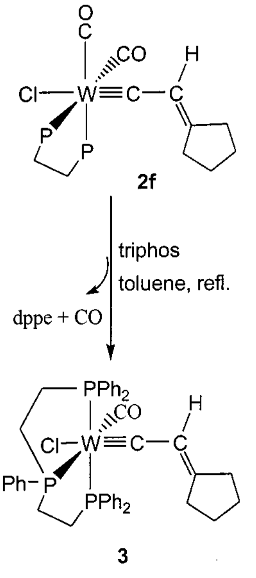
Complexes[a]	C_α [b]	C_β	C_γ[c]	CO[b]	YCN (Y=S,O)
2a	273.0 t (10.2)	[d]	162.6 t (3.2)	213.1 vdd (43.4, 6.8)	[d]
2b	273.1 t (10.3)	135.2 s	161.1 t (3.2)	213.3 vdd (43.5, 6.9)	[d]
2c	279.0 t (10.6)	[d]	164.5 t (3.3)	212.9 vdd (39.7, 6.1)	145.0 s
2d	278.8 t (10.0)	135.0 s	162.8 t (3.3)	212.9 vdd (40.1, 7.1)	145.0 s
3	270.6 dt (9.7, 8.8)	[d]	156.1 s	233.7 dt (88.0, 41.0)	

[a] Spectra recorded in $CDCl_3$, δ in ppm, *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; dt, doublet of triplet; m, multiplet; v, virtual. – [b] Within parenthesis, ^2J(C–P). – [c] Within parenthesis, ^4J(C–P). – [d] Overlapped by aromatic carbon atoms.

of **1a**,**b** or the labile acetone complex *fac*-[W(CO)$_3$(dppe)(Me$_2$CO)][1a,13] were unsuccessful. In all the cases, the starting complexes were recovered unchanged.

Synthesis and Characterisation of Complex 3

The reaction of an equimolar mixture of **2f**[1a] and triphos [PPh(CH$_2$CH$_2$PPh$_2$)$_2$] in refluxing toluene led to the formation of **3**, which was isolated (75% yield) as an orange air-stable solid (Scheme 3). The reaction was monitored by IR spectroscopy in the carbonyl region and was allowed to proceed until the absorptions of the starting *cis*-dicarbonyl complex disappeared. The ^{31}P-NMR spectrum of the resulting solution revealed the presence of free dppe.



Scheme 3

Analytical and spectroscopic data (IR and NMR) of **3** supported this formulation and the structure was confirmed by an X-ray diffraction study (see below). Significantly, the IR spectrum (CH$_2$Cl$_2$) (Table 1), showed a strong ν(CO) absorption at 1897 cm^{-1} and the $^{13}C\{^1H\}$-NMR spectrum (Table 2) displayed the expected resonances for the alkenylcarbyne moiety and the carbonyl group. Thus, carbon carbyne resonances appeared as a doublet of triplet signal at δ = 270.6, characteristic of the AB$_2$X spin system with ^2J(C–P) values of 9.7 and 8.8 Hz arising from the presence in the *cis* positions of two sets of inequivalent phosphorus atoms of the triphos ligand. Carbonyl resonances appeared at δ = 233.7 [dt, ^2J(C–P) = 88.0 and 41.0 Hz], revealing the presence of one *trans* and two *cis* phosphorus nuclei. The $^{31}P\{^1H\}$-NMR spectrum (Table 1) was consistent with the triphos arrangement around the metal centre, showing the resonances typical of an AB$_2$ system [δ = 84.1 (t) and 48.2 (d), *J*(P–W) = 201 and 294 Hz, respectively]. The ^1H-NMR spectrum showed aromatic and proton resonances of the triphos as well as those of the alkenylcarbyne group (see Experimental Section).

X-ray Crystal Structures of Complexes 2b and 3

The structures of complexes **2b** and **3** are shown in Figure 1 and Figure 2 together with the atom numbering scheme. Selected bond lengths and angles are given in Table 3 and Table 4, respectively.

In both complexes, the W atom was coordinated as a distorted octahedron, with the two apical positions occupied by the C atom from the alkenylcarbyne ligand and by the N atom of the isothiocyanate group (**2b**) or by the Cl atom (**3**). In **2b** the coordination was completed by two P atoms from a chelating dppe ligand and by two carbonyl

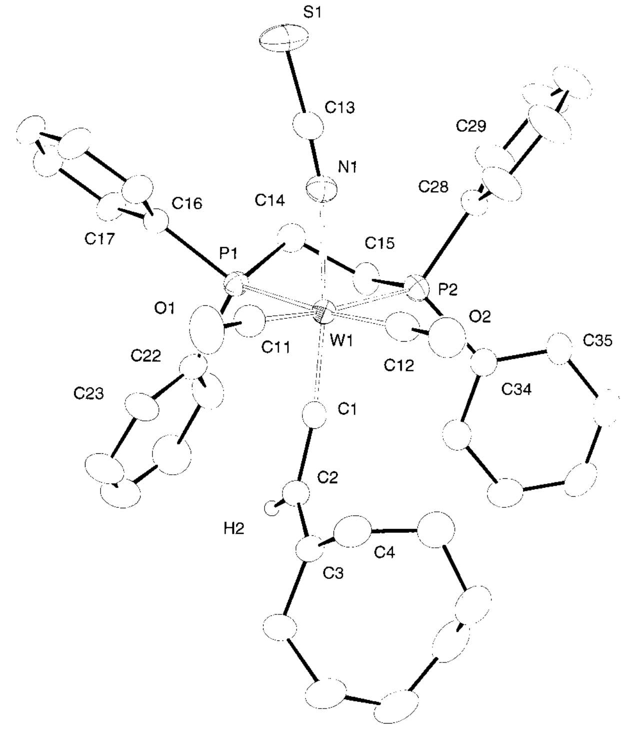


Figure 1. ORTEP view of the molecular structure of complex **2b**, with the atom-numbering scheme, the thermal ellipsoids are drawn at the 30% probability level

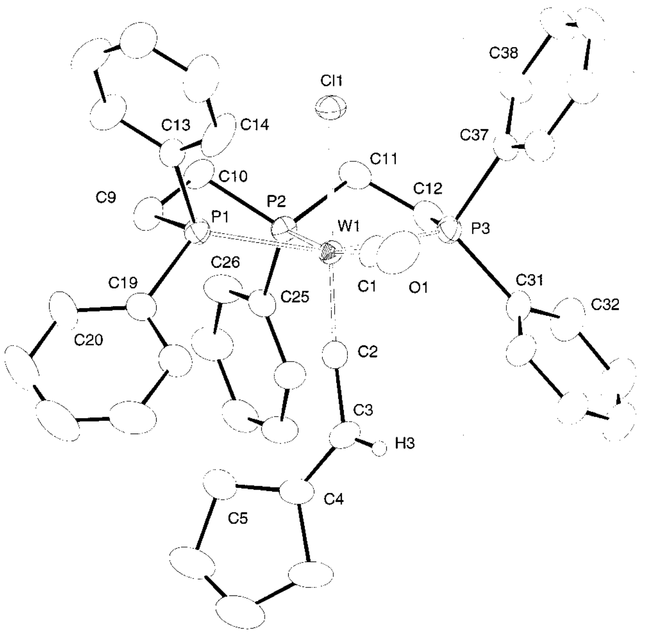


Figure 2. ORTEP view of the molecular structure of complex **3**, with the atom-numbering scheme, the thermal ellipsoids are drawn at the 30% probability level

groups, whereas in **3** the coordination was completed by three P atoms from the triphos ligand and by a carbonyl group. In **2b** the W atom was only slightly, 0.0780(4) Å, displaced from the mean plane through the four equatorial atoms pointing towards the carbyne carbon atom, whereas in **3** this deformation was much more enhanced, the W atom being displaced by 0.3535(3) Å. The W≡C bond

Table 3. Selected bond lengths [Å] and angles [°] for complex **2b**

W(1)−C(1)	1.848(5)	W(1)−N(1)	2.200(5)
W(1)−P(2)	2.533(1)	W(1)−P(1)	2.538(1)
S(1)−C(13)	1.627(7)	N(1)−C(13)	1.158(8)
C(1)−C(2)	1.427(7)	C(2)−C(3)	1.354(8)
C(3)−C(4)	1.510(11)	C(3)−C(10)	1.516(9)
C(4)−C(5)	1.515(11)	C(9)−C(10)	1.519(10)
C(5)−C(6)	1.538(11)	C(8)−C(9)	1.514(13)
C(6)−C(7)	1.523(14)	C(7)−C(8)	1.515(13)
P(1)−C(22)	1.826(6)	P(1)−C(14)	1.841(6)
P(1)−C(16)	1.834(6)	P(2)−C(28)	1.831(6)
P(2)−C(34)	1.836(6)	P(2)−C(15)	1.840(6)
O(1)−C(11)	1.141(8)	O(2)−C(12)	1.148(8)
C(1)−W(1)−N(1)	173.6(2)	C(13)−N(1)−W(1)	168.8(5)
C(1)−W(1)−C(11)	87.6(2)	C(1)−W(1)−C(12)	91.2(2)
C(11)−W(1)−C(12)	87.4(3)	C(11)−W(1)−N(1)	88.0(2)
C(12)−W(1)−N(1)	93.2(2)	C(1)−W(1)−P(2)	97.3(2)
C(11)−W(1)−P(2)	175.0(2)	C(12)−W(1)−P(2)	93.6(2)
N(1)−W(1)−P(2)	87.0(1)	C(1)−W(1)−P(1)	92.4(2)
C(11)−W(1)−P(1)	98.8(2)	C(12)−W(1)−P(1)	173.0(2)
N(1)−W(1)−P(1)	83.7(1)	P(2)−W(1)−P(1)	79.99(5)
C(2)−C(1)−W(1)	171.5(4)	C(3)−C(2)−C(1)	127.0(6)
C(2)−C(3)−C(4)	120.7(6)	C(2)−C(3)−C(10)	119.8(7)
C(4)−C(3)−C(10)	119.5(6)	N(1)−C(13)−S(1)	176.4(6)
C(3)−C(4)−C(5)	113.7(7)	C(4)−C(5)−C(6)	116.8(7)
C(5)−C(6)−C(7)	115.9(7)	C(8)−C(7)−C(6)	116.5(8)
C(7)−C(8)−C(9)	116.5(8)	C(10)−C(9)−C(8)	114.7(7)
C(3)−C(10)−C(9)	117.7(7)	O(2)−C(12)−W(1)	177.9(6)
O(1)−C(11)−W(1)	176.9(6)		

Table 4. Selected bond lengths [Å] and angles [°] for complex **3**

W(1)−C(2)	1.821(5)	W(1)−P(3)	2.473(2)
W(1)−P(2)	2.485(2)	W(1)−P(1)	2.488(2)
W(1)−Cl(1)	2.572(1)	C(2)−C(3)	1.446(7)
C(3)−C(4)	1.346(8)	W(1)−C(1)	2.009(6)
P(1)−C(19)	1.835(6)	P(3)−C(12)	1.856(6)
P(1)−C(13)	1.838(5)	P(3)−C(31)	1.854(6)
P(1)−C(9)	1.865(6)	P(3)−C(37)	1.833(5)
P(2)−C(25)	1.826(5)	P(2)−C(11)	1.841(5)
P(2)−C(10)	1.829(5)	C(9)−C(10)	1.527(8)
C(11)−C(12)	1.541(8)	C(4)−C(5)	1.501(8)
C(4)−C(8)	1.518(8)	C(7)−C(8)	1.466(11)
C(5)−C(6)	1.486(9)	C(6)−C(7)	1.405(12)
C(2)−W(1)−C(1)	87.9(2)	C(2)−W(1)−P(3)	97.6(2)
C(1)−W(1)−P(3)	96.3(2)	C(2)−W(1)−P(2)	102.0(1)
C(1)−W(1)−P(2)	169.7(2)	P(3)−W(1)−P(2)	79.95(6)
C(2)−W(1)−P(1)	100.9(2)	C(1)−W(1)−P(1)	100.6(2)
P(3)−W(1)−P(1)	155.18(5)	P(2)−W(1)−P(1)	80.22(6)
C(2)−W(1)−Cl(1)	177.3(1)	C(1)−W(1)−Cl(1)	90.3(2)
P(3)−W(1)−Cl(1)	80.53(5)	P(2)−W(1)−Cl(1)	79.65(5)
P(1)−W(1)−Cl(1)	81.36(5)	C(3)−C(2)−W(1)	172.9(4)
C(4)−C(3)−C(2)	128.7(6)	O(1)−C(1)−W(1)	178.0(5)
C(3)−C(4)−C(5)	127.1(5)	C(7)−C(8)−C(4)	105.0(7)
C(3)−C(4)−C(8)	125.4(6)	C(6)−C(7)−C(8)	110.4(7)
C(5)−C(4)−C(8)	107.6(6)	C(7)−C(6)−C(5)	109.2(8)
C(6)−C(5)−C(4)	105.5(6)		

lengths were 1.848(5) Å in **2b** and 1.821(5) Å in **3**, comparable to those found in analogous alkenyl−carbyne complexes.[1] As expected, a remarkable alkenylcarbyne *trans* influence can be envisaged: (a) The value of the W−N bond length in **2b**, 2.200(5) Å, is longer than the average (2.148 Å) found for 12 hexacoordinate tungsten complexes with terminal N-bonded thiocyanate ligands, and (b) The W−Cl bond length in **3**, 2.572(1) Å, is much longer than the average (2.388 Å) found for 80 hexacoordinate tungsten complexes with terminal chloride ligands. (From the Cambridge Crystallographic Data Base). It is noteworthy that the W−P bond lengths in **2b** with the dppe ligand, 2.533(1) and 2.538(1) Å, are significantly longer than those found in **3** with the triphos ligand, 2.488(2), 2.485(2), and 2.473(2) Å.

Electrochemical Studies

The electrochemical behaviour of the alkenylcarbyne complexes **2a**−**2d**, **3** and, for comparative purposes, of the related compounds **2e**,[2] **2f**,[1a] **2g**,[1b] and **4**,[1a] in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]/NCMe (or THF), was studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), at a Pt (or vitreous C) disk or a Pt-gauze electrode, respectively.

Table 5. Cyclic voltammetric data for the alkenylcarbyne complexes **2a**−**d**, **2e**−**g** (Type D: Scheme 1), **3** and **4** (*n* = 1; Type A: Scheme 1)

Compound	X	*n*	$^{I}E^{ox}_{p/2}$ ($^{I}E^{ox}_{1/2}$)[a]	$^{II}E^{ox}_{p}$ ($^{II}E^{ox}_{1/2}$)[a]	E_p^{red}
2a	SCN	1	1.04	1.20[b]	−1.93
2b	SCN	4	1.06	1.23[b]	−1.98
2c	OCN	1	0.85	(1.02)[b]	−2.17
2d	OCN	4	0.85	(1.01)[b]	−2.19
2e[c]	F	4	0.92	1.34	−1.57 −1.93
2f[c]	Cl	1	0.82	1.33[b]	−2.22[d]
2g[c]	$S_2P(OEt)_2$	1	0.69	−	−1.61[e] −2.07
3		1	(0.32)	0.59	−
4[c]		1	1.78	−	−1.08

[a] Potentials (peak potential E_p or half-peak potential $E_{p/2}{}^{ox}$ for the irreversible processes, or, in brackets, half-wave potential $E^{ox}_{1/2}$ for the reversible ones) in Volt ± 0.02 vs. SCE measured in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]/NCMe at a scan rate of 0.2 V s^{-1}, at a Pt disc (d = 0.5 mm) electrode, unless stated otherwise. [b] With a decreasing current intensity, relatively to the first anodic wave, upon increasing scan rate. [c] Included for comparison (electrochemical behavior investigated in this study): **2e**,[2] **2f**,[1a] **2g**,[1b] **4**.[1a] − [d] In THF. − [e] Broad and with a relatively low current-intensity.

Complexes **2** and **4** underwent, by CV (Table 5), one irreversible anodic wave (I) ($^{I}E^{ox}_{p/2}$ in the range 0.7−1.1 V vs. SCE for **2**, or 1.78 V for **4**), $^{I}E^{ox}_{p/2}$ which was usually followed, at a higher potential (ca. 1.0−1.3 V for **2**), by a second one (II) which was, however, not detected for **4**, conceivably being buried under the solvent/electrolyte discharge. An irreversible cathodic wave was also detected at E^{red}_{p} in the range −1.6 to −2.2 V (**2**) or −1.08 V (**4**).

For the triphos complex **3**, with just a single CO ligand, the first anodic wave (which corresponds to a single-electron reversible oxidation) was observed at the lowest oxidation potential ($^{I}E^{ox}_{1/2}$ = 0.32 V) when compared with those of **2** (dicarbonyl complexes) or **4** (tricarbonyl compound), in agreement with the known[14] strong π-electron acceptance of the CO ligand(s) with resulting enhancement of the oxidation potential of the corresponding complexes. In fact, the oxidation potential of the first anodic wave clearly reflects the net π-acceptor minus σ-donor character of the ligands, as measured by the electrochemical P$_L$ ligand parameter[14] (the stronger that character, the higher the P$_L$). This is shown by the linear plot of $^{I}E^{ox}_{p/2}$ vs. P$_L$ (Figure 3), for the series of complexes with a common alkenylcarbyne (n = 1), namely the neutral complexes [Type **D**; X = SCN (**2a**), OCN (**2c**), Cl (**2f**) or CN] and the cationic complexes **4** (Type **A**) and **1a** in which P$_L$ refers to the variable ligand (X or L) coordinated to the common metal centre. The $^{I}E^{ox}_{p/2}$ values for the cyano- and the acetonitrile complexes were previously reported[3] and are included for comparative purposes.

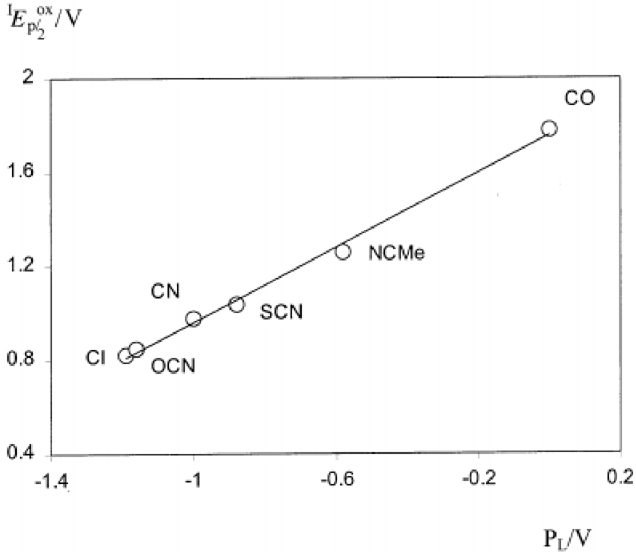


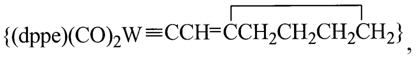
Figure 3. Plot of $^{I}E^{ox}_{p/2}$ for complexes **D** [n = 1; X = SCN (**2a**), OCN (**2c**), Cl (**2f**), or CN[3]], **A** [n = 1 (**4**)], and **1a**[3], vs. the electrochemical P$_L$ ligand (X or L)[14] parameter. $^{I}E^{ox}_{p/2}$ = 0.80 P$_L$ + 1.76 (correlation coefficient r = 0.998)

A lowering of the net σ-electron-donor minus π-electron-acceptor ability of the X or L ligand (or, in other words, an increase of its net π-electron-acceptor minus σ-electron-donor character) results in stabilisation of the HOMO of the complex and therefore in an anodic shift of the oxidation potential. Hence, the values of the oxidation potential of complexes **2** with the anionic X ligand follow the order Cl$^-$ < OCN$^-$ < CN$^-$ < SCN$^-$ (with corresponding P$_L$ ligand values of −1.19, −1.16, −1.00 or −0.88 V[14]) and are significantly lower than that, $^{I}E^{ox}_{p/2}$ = 1.26 V,[3] of the acetonitrile complex, and much less anodic than that, $^{I}E^{ox}_{p/2}$ = 1.78 V, of the carbonyl analogue **4**, and are also in close agreement with the increasingly higher P$_L$ values for ligating NCMe and CO (−0.58 and 0.0 V, respectively[14]). The tricarbonyl complex **4** with an alkenylcarbyne ligand exhibited a much higher oxidation potential than that of the related tetracarbonyl [W(CO)$_4$(dppe)] ($E^{ox}_{1/2}$ = 1.02 V),[3] indicating that the ligating alkenylcarbyne behaves as a much stronger net π-electron-acceptor minus σ-electron-donor than carbonyl. This is also the reason why the other alkenylcarbyne complexes with the strong electron-donating SCN$^-$ ligand were still oxidized at a potential higher than that of [W(CO)$_4$(dppe)]. The carbyne ligands in *trans*-[ReX(≡CCH$_2$R)(dppe)$_2$][BF$_4$] (X = F or Cl; R = alkyl, aryl or ester) have also been shown[4] to behave as more efficient π-electron acceptors than CO.

The above linear plot corresponds to the expression [Equation (1)] proposed by C. J. Pickett et al.[14] that relates the oxidation potential of the members of a series of 18-electron octahedral complexes $[M_sL]$ (with a common $\{M_s\}$ site) with P_L for the variable L ligand. E_s is a measure of the electron richness of the metal site, and is expressed by the oxidation potential of the carbonyl complex $[M_s(CO)]$ (the higher E_s, the lower the electron richness is), and β is a measure of the polarisability of the metal site.

$$E^{ox}[M_sL] = E_s + \beta \cdot P_L(L) \qquad (1)$$

Therefore, from the intercept and the slope of the plot of Figure 3, one can estimate these parameters for the common metal site of our study, $\{M_s\}$ =



$\{(dppe)(CO)_2W{\equiv}CCH{=}\overline{CCH_2CH_2CH_2CH_2}\}$,

as E_s = 1.76 V and β = 0.80. This is the first time such parameters have been estimated for a metal site with a carbyne ligand and it is noteworthy to mention that the electron richness of this centre is rather low, even lower than that (E_s = 1.50 V) of $\{M(CO)_5\}$ (M = Cr, Mo or W),[14,15] on account of the very strong π-electron acceptor character of the alkenylcarbyne ligand and of the two carbonyls.

Moreover, the polarisability is also low [e.g., for $\{M(CO)_5\}$ (M = Cr, Mo, or W), β = 1.0−0.9[14,16]], indicating a high capacity of the alkenylcarbyne ligand to "buffer" changes in the energy of the HOMO of the complex upon replacement of the *trans* ligand, conceivably as a result of extensive delocalization of the HOMO along the carbyne ligand. Such a propensity, exhibited by strong π-electron-acceptor ligands is known for other cases such as the rhenium carbonyl centre $\{Re(CO)(dppe)_2\}^+$ with a much lower β (0.62)[17] than that of the related chloride site $\{ReCl(dppe)_2\}$ (β = 3.4).[18]

This study also provided an opportunity to investigate the electronic coordination properties of a S-bonded ligand. In spite of the relevance of S-bonded ligands in coordination chemistry, the P_L of these ligands have virtually never been determined. From the above plot, it was possible to estimate the P_L value for the ligand $S_2P(OEt)_2^-$ as −1.34 V. Hence, this ligand behaves as a slightly stronger net electron donor than Cl^- and NCO^- (P_L = −1.19 or −1.16 V, respectively),[14] and is a much more effective electron releaser than NCS^- (P_L = −0.88 V[14]).

The anodic processes of the alkenyl−carbyne complexes of this study are commonly multi-electronic on the time scale of CPE and involve anodically induced proton loss. This has also been observed[3] for the related complexes **D** (X = CN; *n* = 1 or 4) (Scheme 1), **1a** and **1b**. Hence, CPE of, for example, **2f** at the first anodic wave (I) consumes ca. 3 Faradays/mol and generates ca. 2 mol H^+/mol complex measured by potentiometric acid−base titration of the electrolysed solution, whereas a total of ca. 4 Faradays/mol and ca. 4 mol H^+/mol complex was measured upon exhaustive CPE at the peak potential of the second anodic wave (II).

As a result of the oxidation of the complex, the Brönsted acidity of the alkenylcarbyne ligand is enhanced and proton loss occurs not only from the W≡C−CH= group but also from the carbocyclic moiety. Although we could postulate the formation of, for example, vinylidene or allenylidene species, we unfortunately did not succeed in the attempted isolation and full characterisation of the products derived from CPE.

The aminocarbyne (CNH_2) and the isocyanide (CNH) ligands at *trans*-$[ReCl(CNH_n)(dppe)_2][BF_4]_{n-1}$ (*n* = 2 or 1)[6] and *trans*-$[FeH(CNH)(dppe)_2][BF_4]$,[19] as well as some aminocarbenes in complexes of Pd^{II} or Pt^{II} [20] are also anodically activated toward proton extrusion, but the less acidic carbynes CCH_2R (R = alkyl, aryl or ester) in *trans*-$[ReX({\equiv}C{-}CH_2R)(dppe)_2][BF_4]$ (X = F or Cl)[4] do not undergo such a reaction upon single-electron oxidation of their complexes; this oxidation is fully reversible on the time scale of the CV.

The proton loss is also in agreement with the detection, by CV (cathodic sweep) of the electrolysed solution, of an irreversible and broad cathodic wave, usually at ca. −0.5 V, assigned to H^+ reduction. This cathodic wave was also observed in the cyclic voltammetric study of the complexes, upon reverse of the anodic scan (run at a sufficiently low scan rate) following the oxidation waves. When the Pt electrode was replaced with a vitreous carbon one, that cathodic wave underwent an extensive cathodic shift (e.g., to ca. −1.2 V for **2g**) in agreement with the expected overpotential required for H^+ reduction at vitreous carbon.

The involvement of more than one electron with coupled H^+ extrusion in the anodic CV processes, at sufficiently low scan rates, was also corroborated by the enhancement of their current functions $i_p^{ox}\ C^{-1}\ v^{-1/2}$ (i_p^{ox}, anodic peak current; C, concentration; *v*, scan rate) upon (i) a decrease of the scan rate (e.g., by a factor of ca. 2−2.5 for **2a**, **2b** or **2f**, from $v = 10\ V\ s^{-1}$ to $0.050\ V\ s^{-1}$) and (ii) addition of pyridine. (e.g., by a factor of ca. 2, for a fivefold molar excess of base, for **2f** at $v = 0.2\ V\ s^{-1}$). In the absence of base and at sufficiently high scan rates, the extent of deprotonation is lowered due to the restricted duration of the assay, and the first anodic wave tends to that of a single-electron process, for example, the current function of **2f** approaches that of the one-electron oxidation of *trans*-$[ReCl(N_2)(dppe)_2]$ at scan rates above ca. 5 Vs^{-1}.

Concluding Remarks

Our studies on the chemistry of α,β-unsaturated carbyne Fischer-type tungsten complexes[1−3] were extended (Scheme 1) by the work reported here on novel mononuclear complexes of type **D** (X = NCS, NCO; *n* = 1,4) (**2a−d**) (Scheme 2) and the analogous monocarbonyl derivative **3** (Scheme 3) containing the tridentate phosphane $PPh(CH_2CH_2PPh_2)_2$ (triphos). These complexes are further examples of the synthetic potential of the acetonitrile precursor complexes **1** for the preparation of the relatively scarcely known unsaturated carbyne complexes. Special features of these complexes are the following: (a) They have a conjugated π-system of C≡N and C=C bonds, bridged by a metal carbyne $M\equiv C$ moiety. In recent years, there has been an increasing interest in metal complexes with extended π-conjugated systems, since they can be used as components of molecular materials with enhanced electrical conductivities and nonlinear (NLO) properties.[21] (b) As shown by the X-ray crystal structure determinations, the bond lengths W−Cl and W−NCS in complexes **2a** and **3**, respectively, are longer than the average values; this indicates that the alkenylcarbyne group has a *trans* influence. (c) Such an influence conceivably results from the extensive π-electron-acceptor ability of these carbyne ligands, as shown by electrochemical studies which also indicate, for the first time, that such ligands have a remarkable lowering effect on both the electron richness and polarisability of the metal sites which they belong to. These features confirm the above proposed extended π-electron delocalisation along the alkenylcarbyne−metal−*trans*-ligand framework. (d) The alkenylcarbyne ligand is susceptible to anodically-induced deprotonation; the potential synthetic use of this towards the formation of novel multiple metal−carbon bonded species should be further explored.

Experimental Section

General: The reactions were carried out under dry nitrogen by Schlenk techniques. All solvents were dried by standard methods and were distilled under nitrogen before use. The precursor complexes **1a**,**b** and **2f** as well as **2e**, **2g**, and **4** were prepared by literature methods.[1a,1b,2] NaOCN, KSCN, $[NBu_4]SCN$, triphos $[PhP(CH_2CH_2PPh_2)_2]$ (Aldrich) were used as received. − Infrared spectra were recorded on a Perkin−Elmer 1720-XFT spectrometer. − Mass spectra (FAB) were recorded on a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. − The conductivities were measured at room temp, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductivimeter. − The C, H, and N analyses were carried out with a Perkin−Elmer 240-B microanalyzer. − ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were run on a Bruker AC200 spectrometer at 200 MHz (^{1}H), 81 MHz (^{31}P) or 50.3 MHz (^{13}C) and a Bruker AC300 spectrometer at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.5 MHz (^{13}C). The spectral references were tetramethylsilane (TMS) for ^{1}H and ^{13}C, and 85% H_3PO_4 for ^{31}P-NMR measurements. All spectra were recorded with $CDCl_3$ as solvent. − Selected IR and ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectroscopic data are collected in Table 1 and 2.

Synthesis of 2a (X = SCN; *n* = 1), 2b (X = SCN; *n* = 4), 2c (X = OCN; *n* = 1), 2d (X = OCN; *n* = 4): An equiv. of KSCN (0.019 g) or NaOCN (0.013 g) was added to an orange solution of **1a** (0.172 g) or **1b** (0.180 g) (0.2 mmol) in 40 mL of methanol. The mixture was stirred at room temperature for a few hours. The reactions were followed by IR spectroscopy. The resulting solution was evaporated to dryness when no more starting material was detected. The residue was extracted with CH_2Cl_2 and filtered. Removal of the solvent in vacuo gave the desired compounds **2a−d** as yellow solid in very high yield. **2a**,**b** were prepared similarly from $[Bu_4N]SCN$ in CH_2Cl_2. Yield: **2a**, 0.139 g, 88%; **2b**, 0.167 g, 90%; **2c**, 0.142 g, 92%; **2d**, 0.147 g, 90%.

2a: IR [KBr, ν(SCN); ν(CO)]: 2057 (vs); 1989 (vs), 1920 (vs). − ^{1}H NMR ($CDCl_3$): δ = 1.48 (m, 4 H, 2 CH_2), 1.96 (m, 2 H, CH_2), 1.99 (m, 2 H, CH_2), 2.60 [m, 2 H, $P(CH_aH_b)_2P$], 2.80 [m, 2 H, $P(CH_aH_b)_2P$], 7.37−7.73 (m, 20 H, 2 PPh_2). − ^{13}C NMR ($CDCl_3$): δ = 25.6 (s, CH_2), 26.2 (s, CH_2), 27.6 [m, $P(CH_2)_2P$], 31.5 (s, CH_2), 34.3 (s, CH_2), 128.3−135.5 (m, $C_β$, 2 PPh_2). − $C_{36}H_{33}NO_2P_2SW$: calcd. C 54.8, H 4.2, N 1.8; found C 55.2, H 4.2, N 1.6.

2b: IR [KBr, ν(SCN); ν(CO)]: 2056 (vs); 1984 (vs), 1911 (vs). − ^{1}H NMR ($CDCl_3$): δ = 1.40 (m, 6 H, 3 CH_2), 1.47 (m, 2 H, CH_2), 1.70 (m, 2 H, CH_2), 1.80 (m, 2 H, CH_2), 2.32 (m, 2 H, CH_2), 2.60 [m, 2 H, $P(CH_aH_b)_2P$], 2.80 [m, 2 H, $P(CH_aH_b)_2P$], 7.18−7.73 (m, 20 H, 2 PPh_2). − ^{13}C NMR ($CDCl_3$): δ = 25.5 (s, CH_2), 26.7 (s, CH_2), 26.8 (s, CH_2), 26.9 (s, CH_2), 27.0 (s, CH_2), 27.6 [m, $P(CH_2)_2P$], 31.6 (s, CH_2), 35.7 (s, CH_2), 128.3−132.5 (m, 2 PPh_2). − MS (FAB, *m/z*) [M^+ − 2 CO] = 775, [M^+ − SCN] = 773. − $C_{39}H_{39}NO_2P_2SW$: calcd. C 56.3, H 4.7, N 1.7; found C 55.8, H 4.6, N 1.5.

2c: IR [KBr, ν(OCN); ν(CO)]: 2209 (vs); 1986 (s), 1914 (s). − ^{1}H NMR ($CDCl_3$): δ = 1.47 (m, 4 H, 2 CH_2), 1.97 (m, 2 H, CH_2), 2.00 (m, 2 H, CH_2), 2.60 [m, 2 H, $P(CH_aH_b)_2P$], 2.80 [m, 2 H, $P(CH_aH_b)_2P$], 7.36−7.74 (m, 20 H, 2 PPh_2). − ^{13}C NMR ($CDCl_3$): δ = 25.6 (s, CH_2), 26.1 (s, CH_2), 27.3 [m, $P(CH_2)_2P$], 31.8 (s, CH_2), 34.1 (s, CH_2), 128.2−135.6 (m, $C_β$, OCN, 2 PPh_2). − $C_{36}H_{33}NO_3P_2W$: calcd. C 55.9, H 4.3, N 1.8; found C 55.5, H 4.5, N 2.0.

2d: IR [KBr, ν(OCN); ν(CO)]: 2211 (vs); 1987 (s), 1916 (s). − ^{1}H NMR ($CDCl_3$): δ = 1.41 (m, 6 H, 3 CH_2), 1.48 (m, 2 H, CH_2), 1.71 (m, 2 H, CH_2), 1.78 (m, 2 H, CH_2), 2.34 (m, 2 H, CH_2), 2.60 [m, 2 H, $P(CH_aH_b)_2P$], 2.80 [m, 2 H, $P(CH_aH_b)_2P$], 7.33−7.72 (m, 20 H, 2 PPh_2). − ^{13}C NMR ($CDCl_3$): δ = 25.6 (s, CH_2), 26.8 (s, CH_2), 26.9 (s, CH_2), 27.0 (s, 2 CH_2), 27.4 [m, $P(CH_2)_2P$], 31.5 (s, CH_2), 35.8 (s, CH_2), 128.3−135.4 (m, OCN, 2 PPh_2). − $C_{39}H_{39}NO_3P_2W$: calcd. C 57.4, H 4.8, N 1.7; found C 57.5, H 4.5, N 1.8.

Synthesis of 3: A yellow solution of **2f** (0.383 g, 0.5 mmol) and an equiv. amount of $PhP(CH_2CH_2PPh_2)_2$ (0.267 g) in 50 mL of toluene was stirred under reflux for 24 h. The resulting orange solution was evaporated to dryness and the residue was washed with diethyl ether (3 × 10 mL) to remove the dppe. Drying in vacuo gave the desired compound **3** as an orange solid in good yield (0.339 g, 75%). − IR [KBr, ν(CO)]: 1874 (s). − ^{1}H NMR ($CDCl_3$): δ = 1.39 (m, 4 H, 2 CH_2), 1.84 (br, 2 H, CH_2), 1.97 (br, 2 H, CH_2), 2.14 (m, 2 H, PCH_2), 2.55 (m, 4 H, 2 PCH_2), 3.39 (m, 2 H, PCH_2), 7.14−7.78 (m, 25 H, Ph, 2 PPh_2). − ^{13}C NMR ($CDCl_3$): δ = 26.4 (m, PCH_2), 27.0 (s, CH_2), 27.6 (s, CH_2), 31.8 (s, CH_2), 34.4 (m, PCH_2), 34.5 (s, CH_2), 128.3−140.4 (m, $C_β$, Ph, 2 PPh_2). − MS (FAB, *m/z*) [M^+ − CO] = 847, [M^+ − CO − Cl − H] = 810, [M^+ − C_5H_8] = 807, [M^+ − Cl − C_5H_{10}] = 770, [M^+ − CO − C_7H_9] = 754, [M^+ − CO − Cl − C_6H_8] = 731. − $C_{42}H_{42}ClOP_3W$: calcd. C 57.7, H 4.8; found C 58.0, H 4.8.

Crystal Structure Determination of 2b and 3: The intensity data were collected at room temp on a Philips PW 1100 (**2b**) and on a Siemens AED (**3**) single-crystal diffractometer with graphite-monochromated Mo-$K_α$ radiation and the θ/2θ scan technique. Final unit cell parameters were obtained from a least-squares refinement of 24 (**2b**) and 28 (**3**) reflections. Crystallographic and experimental details for both structures are summarised in Table 6. Data were corrected for Lorentz and polarisation effects in the usual manner. A correction for absorption was made for both complexes [maximum and minimum value for the transmission coefficient was 1.000 and 0.5754 (**2b**) and 1.000 and 0.6493 (**3**)].[22]

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with

Table 6. Experimental data for the X-ray diffraction studies of complexes **2b** and **3**

Empirical formula	$C_{39}H_{39}NO_2P_2SW$	$C_{42}H_{42}ClOP_3W$
Formula mass	831.6	875.0
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit-cell dimensions	a = 10.784(3)Å	a = 11.174(4)Å
	b = 18.611(5)Å	b = 17.800(5)Å
	c = 18.425(4)Å	c = 19.148(5)Å
	β = 91.61(2)°	β = 96.07(6)°
Volume	3696(2) Å^3	3787(2) Å^3
Z	4	4
Density (calculated)	1.494 Mg/m^3	1.535 Mg/m^3
Absorption coefficient, μ	3.301 mm^{-1}	3.280 mm^{-1}
F(000)	1664	1752
Crystal size	0.18 × 0.27 × 0.22 mm	0.21 × 0.34 × 0.35 mm
θ range (deg)	3.07−30.02	3.05−28.05
Index ranges	$-15 \leq h \leq 15$	$-14 \leq h \leq 12$
	$0 \leq k \leq 26$	$-21 \leq k \leq 23$
	$0 \leq l \leq 25$	$-25 \leq l \leq 16$
Reflections collected	11062	9408
Independent reflections	10771 (R_{int} = 0.0555)	9157 (R_{int} = 0.0364)
Obs. refl [$I > 2\sigma(I)$]	7039	4981
Refinement method	Based on F^2	Based on F^2
Data/restr./param.	10771/0/422	9157/0/445
Goodness-of-fit on F^2	1.820	0.887
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0410, $wR2$ = 0.1009	$R1$ = 0.0366, $wR2$ = 0.0916
R indices (all data)[a]	$R1$ = 0.1018, $wR2$ = 0.1500	$R1$ = 0.0822, $wR2$ = 0.1041
Largest diff. peak and hole	2.521 and −2.284 eÅ^{-3}	1.336 and −1.812 eÅ^{-3}

[a] $R1 = \Sigma|F_o - F_c|/|\Sigma(F_o)$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and were refined riding on the corresponding carbon atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2F_o^2 + (0.0730\,P)^2 + 0.5625\,P]$ (**2b**) and $w = 1/[\sigma^2F_o^2 + (0.0627\,P)^2]$ (**3**) where $P = (F_o^2 + 2\,F_c^2)/3$ was used. All calculations were carried out on the DIGITAL AlphaStation 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica del CNR," Parma, with the SHELX-97 systems of crystallographic computer programs.[23]

Electrochemical Measurements: The electrochemical experiments were carried out either on an EG&G PAR 273 A potentiostat/galvanostat connected to a 386-SX personal computer through a GPIB interface, or on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer. Cyclic voltammetry (CV) was undertaken in a two-compartment three-electrode cell, at a platinum- or vitreous carbon disc (d = 0.5 mm) working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed. Controlled-potential electrolyses (CPE) were carried out in a three-electrode H-type cell with a platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. The oxidation potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]/NCMe (or THF), in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the SCE by using the $[\text{Fe}(\eta^5\text{-}C_5H_5)_2]^{0/+}$ couple ($E_{1/2}^{\text{ox}}$ = 0.42 or 0.545 V vs SCE, in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]/NCMe or THF, respectively). The use, as reference electrode, of the SCE or other electrode in aqueous medium, was avoided due to the sensitivity of the systems to water. The CPE experiments were monitored regularly by CV, thus assuring that no significant potential drift occurred along the electrolyses.

The acid−base titrations of the electrochemically oxidised solutions were carried out as indicated before,[20] with a solution of NaOH in CH_3OH which was standardised by titration against benzoic acid in the organic solvent (thymol blue was used as the indicator). The results presented were corrected for background effects by performing, in each case, the titration of the blank solution of 0.2 mol dm^{-3} [NBu$_4$][BF$_4$] which was electrolysed under identical conditions to those used for the corresponding complex solution.

Supplementary Material: The supplementary material for both structures includes the lists of atomic coordinates for the non-H atoms, calculated coordinates for the hydrogen atoms, and anisotropic thermal parameters. The details of the crystal structure investigations are deposited at the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-130866 (**2b**) and CCDC-130867 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (0)1223/336 033, E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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