

Mono and Dinuclear Tungsten Alkenyl-Carbyne Complexes Bridged by Cyanide and Diisocyanide Ligands: Synthesis, Electrochemical- and ^{183}W -NMR Studies

Lei Zhang,^[a,b] M. Pilar Gamasa,^[a] José Gimeno,^{*,[a]} Rodrigo J. Carbajo,^[a]
Fernando López-Ortiz,^[a,c] M. Fátima C. Guedes da Silva,^[b,d] and
Armando J. L. Pombeiro^{*,[b]}

Keywords: Alkenylcarbynes / Dinuclear tungsten complexes / Electrochemistry / Tungsten NMR

Neutral *trans*-cyanide alkenylcarbyne complexes **2a** and **2b** have been prepared by reaction of the complex **1a** and **1b** with NaCN or $[\text{Bu}_4\text{N}]\text{CN}$. The reaction of complexes **2a** and **2b** with an equimolar amount of the acetonitrile complexes **1a** and **1b** in CH_2Cl_2 leads to the cationic cyanide-bridged bis(alkenylcarbyne) di-tungsten complexes **3a–d**. Diisocyanide-bridged bis(alkenylcarbyne) di-tungsten complexes **4a** and **4b** have been synthesized by the reaction of complexes **1a** and **1b** with 0.5 equivalents of the diisocyanide 1,4-(CN) $_2$ C $_6$ H $_4$. IR as well as ^1H -, $^{31}\text{P}\{^1\text{H}\}$ -, $^{13}\text{C}\{^1\text{H}\}$ -, and ^{183}W -NMR data are reported. The spectroscopic data show that in the dinuclear complexes **3a–d**, the bridging CN group and the alkenylcarbyne units are located in *trans* positions, while in the dinuclear complexes **4a** and **4b**, the isocyanide groups of the bridging ligand 1,4-(CN) $_2$ C $_6$ H $_4$ and the two alkenylcarbyne moieties are *cis*. The ^{183}W chemical shifts of complexes **2a**, **2b**, **3a–d**, **4a**, and **4b** were obtained through two-dimensional indirect ^{31}P , ^{183}W NMR recording techniques. A downfield shifting of ^{183}W resonances of the

cyanide-bridged dinuclear complexes **3a–d** with respect to the mononuclear ones, **2a** and **2b**, was observed. The $\delta^{183}\text{W}$ of isocyanide bridging dinuclear complexes **4a** and **4b** appear at higher field than those of the corresponding mononuclear cyanide **2a** and **2b** in accordance with the higher π -acceptor electron properties of the isocyanide ligand. The electrochemical behaviour of all the complexes has been investigated by cyclic voltammetry and controlled potential electrolysis in aprotic media and at a Pt (or vitreous C) electrode. Complexes **1**, **2**, or **3** undergo multi-electron irreversible oxidation processes involving anodically induced proton dissociation from the alkenylcarbyne ligands, and irreversible cathodic processes are also observed for all the complexes. The order of the redox potentials reflects that of the net electron π -acceptor/ σ -donor character of the ligands and the ligating alkenylcarbynes are shown to behave as remarkably strong π -electron acceptors (even stronger than CO).

Introduction

Among the extensively studied chemistry of complexes with multiple metal–carbon bonds, that concerned with Fischer-type carbyne complexes of group 6 metals has remained a topic of interest during the last years.^{[1][2]} However, it is now apparent that this chemistry is not as well developed as that of metal carbene derivatives. In particular, only a few carbyne complexes bearing α,β -unsaturated substituents have been described to date,^[3] although the corre-

sponding Fischer-type carbene derivatives have proven to be excellent substrates in modern organic synthesis. Even more rare derivatives are dinuclear complexes containing unsaturated carbyne groups.^[4] Most of them are dimetallic species bearing a di-carbyne group acting as a bridging ligand: $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{C}-\text{CPh}=\text{CPh}-\text{C}\equiv\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$,^[5] $\{[\text{Br}(\text{CO})_4\text{M}\equiv\text{C}-(p\text{-C}_6\text{H}_4)-\text{C}\equiv\text{M}(\text{CO})_4\text{Br}]\}$ ($\text{M} = \text{Cr}, \text{W}$),^[6] $\{[\text{Tp}'(\text{CO})_2\text{M}\equiv\text{C}-\text{CR}=\text{CR}-\text{C}\equiv\text{M}(\text{CO})_2\text{Tp}']\}$ ($\text{M} = \text{Mo}; \text{R} = \text{H}, \text{M} = \text{W}; \text{R} = \text{H}, \text{Me}, \text{CH}_2\text{Ph}$), $\{[\text{Tp}'(\text{CO})_2\text{M}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{M}(\text{CO})_2\text{Tp}']\}$ ($\text{M} = \text{Mo}, \text{W}$).^[3c] Here we report the synthesis of ditungsten bis(alkenylcarbyne) complexes **A** and **B** along with the mononuclear complexes **C** (Scheme 1). Complexes of type **A** and **B** belong to a new type of α,β -unsaturated carbyne dimetallic derivatives in which the metal atoms are linked by a cyanide and diisocyanide bridging group.^[7]

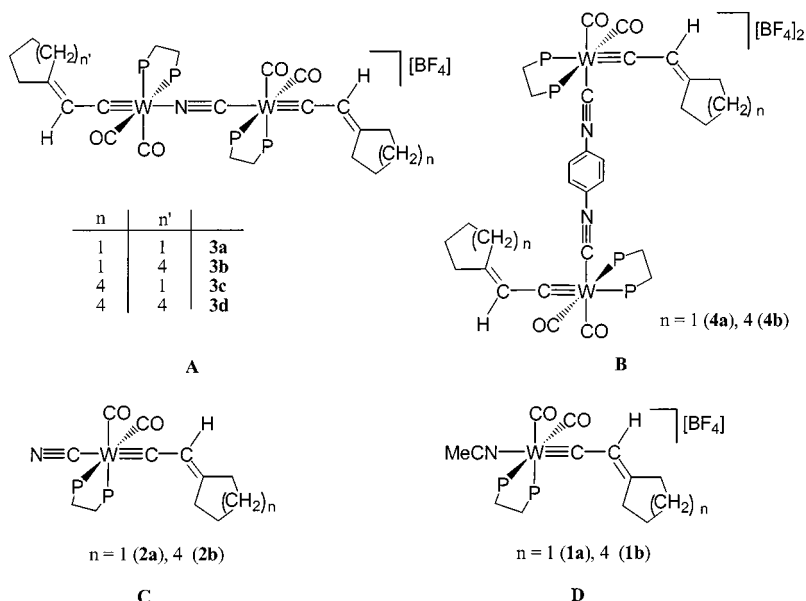
We have recently described^[3b] the utility of the labile acetonitrile carbyne complexes **D** as excellent precursor of alkenylcarbyne and alkenylketenyl derivatives containing dithio ligands. In this work we report on an extension of this synthetic methodology which has led to the synthesis of dinuclear complexes of type **A** and **B**, obtained by the reaction of complexes **D** with the cyanide derivatives **C** and the diisocyanide ligand $\text{C}\equiv\text{N}-(1,4\text{-C}_6\text{H}_4)-\text{N}\equiv\text{C}$, respec-

^[a] Instituto Universitario de Química Organometálica “Enrique Moles” (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain
Fax: (internat.) +34-98/510-3446
E-mail: jgh@sauro.chem.uniovi.es

^[b] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,
Av. Rovisco Pais, P-1049-001 Lisbon, Portugal
Fax: (internat.) +351-1/8414455
E-mail: pombeiro@alfa.ist.utl.pt

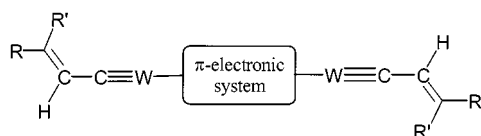
^[c] Current address: Facultad de Ciencias Experimentales, Área de Química Orgánica,
Universidad de Almería, E-04120 Almería, Spain

^[d] Universidade Lusófona de Humanidades e Tecnologias,
Av. Campo Grande 376, P-1749-024 Lisbon, Portugal



Scheme 1. Alkenylcarbyne Fischer-type tungsten complexes

tively. Since the electrochemical investigation of complexes with multiple metal–carbon bonds is still a rather undeveloped field of research,^[8–17] and has not been previously reported for alkenylcarbyne compounds, we have also studied the electrochemical behaviour of our novel alkenylcarbyne complexes. ¹⁸³W-NMR data of all the complexes are also reported.

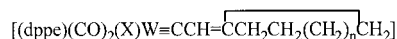
Scheme 2. Two terminal unsaturated carbyne tungsten moieties linked by bridging ligands with π -electronic delocalized systems

Results and Discussion

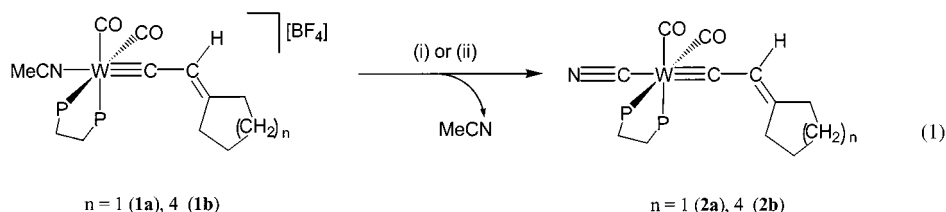
Mononuclear Cyanide Alkenylcarbyne Complexes **2a** and **2b**

The addition of NaCN to an orange solution of complexes **1a** and **1b** in methanol at room temperature led to the substitution of the acetonitrile ligand by the cyanide anion to afford the neutral alkenylcarbyne complexes **2a** and **2b** (90–95% yield) isolated as air stable orange solids (Equation 1). Complexes **2a** and **2b** are also formed by the treatment of **1a** and **1b** with [NBu₄]CN in CH₂Cl₂.

IR spectra (CH₂Cl₂) show the typical pattern of *cis*-dicarbonyl complexes, of two $\nu(\text{CO})$ absorptions at 1999 and 1931 (**2a**), and 1998 and 1930 (**2b**) cm^{−1}. As expected for the transformation of cationic to neutral complexes, a lowering in absorption frequencies (ca. 12 cm^{−1}) is observed. The presence of the terminal linear CN ligand is confirmed by the IR spectra (CH₂Cl₂ solution or KBr pellet) which show a very weak $\nu(\text{CN})$ absorption at 2112 cm^{−1}.^{[18][19]} The phosphorus resonances appear in the ³¹P-NMR spectra (Table 1) as singlet signals, indicating the chemical equivalence of the phosphorus atoms of dppe, and are therefore in accordance with the *trans* carbyne–cyanide arrangement. The $J(\text{W-P})$ values (ca. 225.5 Hz) are similar to those found in analogous complexes



(X = Cl, Br, I) which also show a similar *trans* arrangement of phosphorus nuclei to the carbonyl ligands.^[3a] The ¹H-NMR shows a broad signal for the alkenyl proton ($=\text{C}-\text{CH}=\text{}$) at $\delta = 4.98$ (**2a**) and 4.66 (**2b**). The carbyne carbon resonances of these complexes appear in the ¹³C-NMR spectra as triplet signals at $\delta = 283.4$ [$^2J(\text{P-C})$ ca. 10 Hz] (Table 2). These signals appear at a lower field with respect to those shown by the corresponding halide carbyne complexes [$\delta = 266.9\text{--}269.8$, $^2J(\text{P-C})$ ca. 10 Hz]^[3a] and at

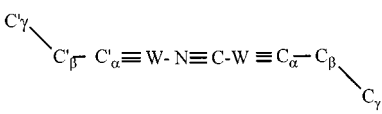


(i) NaCN, MeOH, rt, 2h. (ii) [NBu₄]CN, CH₂Cl₂, rt, 2h.

Table 1. Selected IR^[a] and ³¹P{¹H}- and ¹H-NMR^[b] data for complexes **2a**, **2b**, and **3a–d**

	IR ν(CO)	ν(C≡N)	³¹ P{ ¹ H} ^[c] 2 P, 2 P'	¹ H CH _β	CH _β '
2a	1999 (vs), 1931 (vs)	2112 (vw)	39.8 s (225.7)	4.98 s,br	
2b	1998 (vs), 1930 (vs)	2112 (vw)	39.7 s (225.4)	4.66 s,br	
3a	2003 (vs), 1937 (vs)	2113 (vw), 2099 (vw)	39.5 s (229.0), 41.0 s (232.5)	4.67 s,br	4.58 s,br
3b	2004 (vs), 1938 (vs)	2113 (vw), 2100 (vw)	39.5 s (230.5), 41.0 s (233.0)	4.67 s,br	4.24 s,br
3c	2004 (vs), 1937 (vs)	2112 (vw), 2098 (vw)	39.4 s (228.7), 40.9 s (232.6)	4.31 s,br	4.58 s,br
3d	2003 (vs), 1937 (vs)	2112 (vw), 2098 (vw)	39.4 s (227.8), 41.0 s (234.0)	4.31 s,br	4.24 s,br

^[a] Spectra recorded in CH₂Cl₂, ν(cm⁻¹). Abbreviations: s, strong; vs, very strong; vw, very weak. – ^[b] Spectra recorded in CDCl₃, δ in ppm, *J* in Hz. Abbreviations: s, singlet, br, broad. – ^[c] ¹J(W–P).

Table 2. Selected ¹³C{¹H}-NMR data for the complexes **2a**, **2b**, and **3a–d**^[a]


	C _α	C _α '	C _γ	C _γ '	C≡N	2 <i>cis</i> CO, 2 <i>cis</i> CO'
2a	283.4 t (10.1)		166.0 t (3.2) ^[b]		140.2 t (10.7)	212.4 <i>vr.</i> dd (30.8, 7.0)
2b	283.4 t (10.2)		164.8 s		140.3 t (10.7)	212.6 <i>vr.</i> dd (31.4, 7.0)
3a	286.7 m	289.8 m	169.9 s	168.0 s	161.6 m	212.5 m
3b	286.7 t (9.5)	289.8 t (9.6)	169.7 s	166.1 s	161.9 m	211.4 <i>vr.</i> dd (29.9, 7.1)
3c	286.7 t (9.4)	289.5 t (9.6)	169.7 s	167.3 s	162.0 m	211.5 <i>vr.</i> dd (30.0, 7.1) 213.2 <i>vr.</i> dd (37.2, 7.2)
3d	286.8 m	289.7 m	169.2 s	166.3 s	162.1 m	211.6 <i>vr.</i> dd (30.1, 7.0) 213.2 <i>vr.</i> dd (36.5, 7.0)

^[a] Spectra recorded in CDCl₃, δ in ppm, *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet; *vr.*, *virtual*. Within parenthesis ²*J*(P–C). – ^[b] ⁴*J*(P–C).

a higher field (ca. 8.5 ppm) than those of the cationic precursor complexes **1a** and **1b**. The resonances of the C_β atom of the alkenylcarbyne chain are assigned and distinguished by DEPT from the C_γ and the carbon atom of the cyanide group. The resonances of the *cis*-dicarbonyl ligands appear as doublet signals in the range of δ = 212.4–212.6 (Table 2) and are in accordance with the reported data for the similar alkenylcarbyne halide complexes.^[3a]

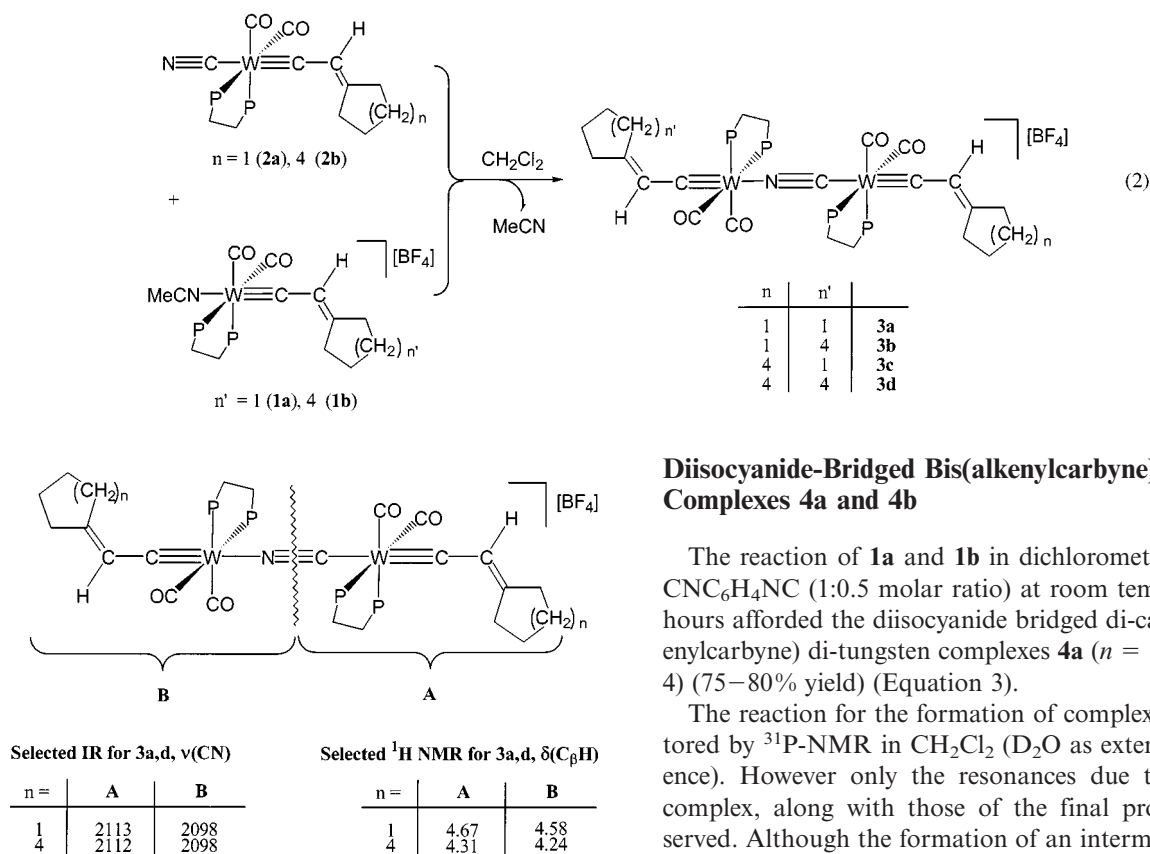
Cyanide Bridged Bis(alkenylcarbyne) Dinuclear Complexes **3a–d**

The reaction of complexes **2a** and **2b** with an equivalent of **1a** and **1b** in dichloromethane at room temperature for 1 hour led to the displacement of the acetonitrile ligand to give the cationic bis(alkenylcarbyne) di-tungsten complexes **3a–d** (82–85% yield) in which the metal atoms are bridged by the cyanide group (Equation 2).

Complexes **3a** and **3d** have been also prepared in similar yields from the treatment of **1a** and **1b** in methanol with NaCN in a 2:1 molar ratio. The reaction probably proceeds through the formation of complexes **2a** and **b** as intermediates.

IR and NMR spectroscopic data show the molecular asymmetry of these dinuclear complexes even for **3a** (*n* = *n*' = 1) and **3d** (*n* = *n*' = 4) containing two identical metal carbyne moieties. Thus, IR spectra (CH₂Cl₂) show (Table 1) two weak ν(C≡N) absorptions^{[18][19]} at 2112–2113 and 2098–2100 cm⁻¹ and two very strong ν(CO) absorptions at 2003–2004 and 1937–1938 cm⁻¹ which apparently indicate an overlapping of the absorptions expected for the two unsymmetrical *cis*-dicarbonyl pairs of each tungsten moiety. Since the ν(C≡N) absorptions at higher frequency appear at a similar energy to those of complexes **2a** and **b**, they may be assigned to the ν(N≡C–W) stretching (side A in Figure 1) while those at lower energy are assigned to the corresponding ν(W–N≡C) (side B in Figure 1).

NMR data of **3a–d** are in accordance with the linear –C≡W–(μ–N≡C)–W≡C– arrangement. Thus, the ³¹P-NMR spectra (Table 1) show two singlets at δ = 39.4–39.5 [*J*(W–P) = 227.8–230.5 Hz] and 40.9–41.0 [*J*(W–P) = 232.5–234.0 Hz], which are expected for each equivalent pair of phosphorus nuclei of dppe *trans* to carbonyl groups in sides A and B (Figure 1). As discussed before, since the higher-field signals are at the same chemical shifts as those of **2a** and **2b** (0.3 ppm higher), they are assigned to the two equivalent phosphorus atoms at side A, while those at

Figure 1. Selected IR and ^1H -NMR data for complexes **3a** and **3d**

lower-field are assigned to the phosphorus atoms of side **B**. We were not able to assign the proton and carbon resonances (Tables 1 and 2) for each moiety **A** and **B** using the conventional methods due to the similar values of chemical shifts. However, the spectroscopic characterisations have been performed through 2D ^1H , ^{183}W - and ^{31}P , ^{183}W -HMQC experiments, as will be discussed below (^{183}W -NMR studies). The alkenyl proton resonances appear in the ^1H -NMR spectra (Table 1) as two different broad singlets.

^{13}C -NMR spectra (Table 2) show two carbyne carbon resonances at $\delta = 286.7\text{--}289.8$ [$J(\text{P-C}) = 9.4\text{--}9.6$ Hz]. For complexes **3b** and **3c**, bearing two different carbyne groups at each side of the bridge, the signals appear as two triplets, while for **3a** and **3d** these resonances are not well defined and appear as two multiplets. The assignments of these resonances for each moiety have been done through 2D ^1H , ^{13}C -HMBC correlation experiments, on the basis of the previously known proton assignments. The carbon resonances of the cyanide group are shifted to lower field (> 20 ppm) (Table 2) appearing very close to those of the C_γ atom of the alkenylcarbyne chain, indicating that a significant electron donation has occurred in the formation of the dinuclear species through the coordination of the $[\text{W}]\text{--CN}$ moiety of complexes **2a** and **2b**. ^{13}C -NMR spectra also show carbonyl resonances which appear as virtual doublet-of-doublet signals at $\delta = 211.4\text{--}213.2$ [$^2J(\text{P-C}) = 7.0\text{--}7.2$, $29.9\text{--}37.3$ Hz] (Table 2) as expected for each inequivalent *cis*-dicarbonyl pair.

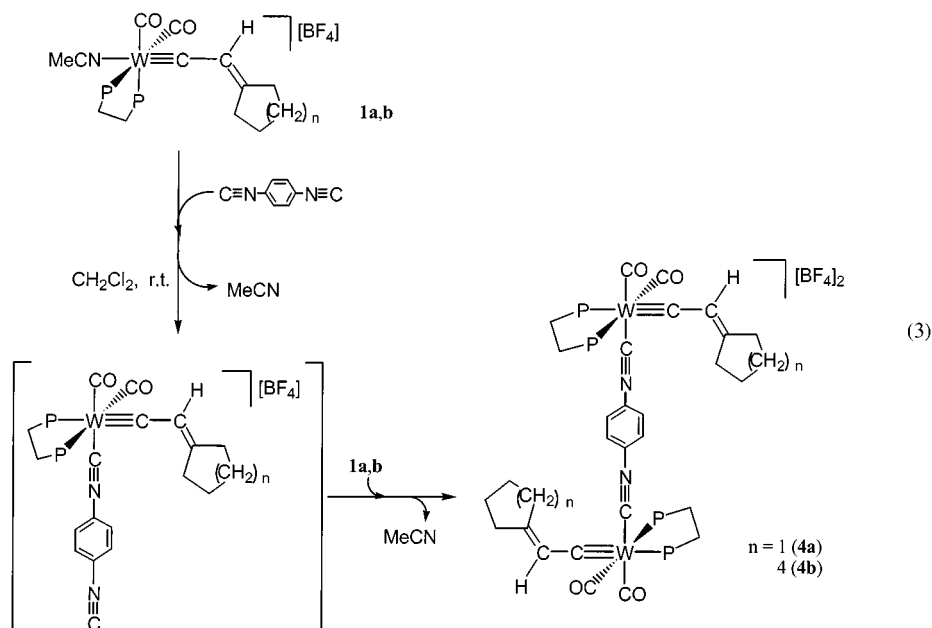
Diisocyanide-Bridged Bis(alkenylcarbyne) Dinuclear Complexes **4a** and **4b**

The reaction of **1a** and **1b** in dichloromethane with 1,4- $\text{CNC}_6\text{H}_4\text{NC}$ (1:0.5 molar ratio) at room temperature for 2 hours afforded the diisocyanide bridged di-cationic bis(alkenylcarbyne) di-tungsten complexes **4a** ($n = 1$) and **4b** ($n = 4$) (75–80% yield) (Equation 3).

The reaction for the formation of complex **4a** was monitored by ^{31}P -NMR in CH_2Cl_2 (D_2O as external lock reference). However only the resonances due to the starting complex, along with those of the final product, are observed. Although the formation of an intermediate mononuclear complex is plausible, apparently the subsequent coordination of the uncoordinated isocyanide group is more favoured than the formation of the intermediate. All attempts to prepare the mononuclear complexes by using a 1:1 molar ratio failed, giving instead mixtures of the dinuclear complexes **4a** and **4b** and the mononuclear ones, even if a large excess of the ligand was used.

Elemental analyses, conductivity, and spectroscopic data support the dinuclear nature of the complexes and the proposed symmetric structure. The IR spectra of **4a** and **4b** (CH_2Cl_2) show two very strong and broad $\nu(\text{CO})$ absorptions at 2066–2088 and 1960–1961 cm^{-1} , typical of a *cis* dicarbonyl arrangement for each tungsten centre. The spectra also show one $\nu(\text{C}\equiv\text{N})$ absorption at 2130 and 2132 cm^{-1} , for **4a** and **4b**, respectively (Table 3).

The NMR spectra indicate that the two isocyanide groups occupy the *cis* positions with respect to the carbyne ligand of the corresponding metal centre. Thus, ^{31}P -NMR spectra of **4a** and **4b** display (Table 3) two singlet resonances at $\delta = 21.6$ and 40.0, and $\delta = 21.9$ and 40.1, respectively, indicating the chemical unequivalence of the phosphorus atoms of dppe. The $J(\text{W-P})$ values allow the assignment of the coordination sites. Thus, the lower-field signals with relatively large values [$J(\text{W-P}) = 229.6$ and 231.6 Hz] are typical of a mutually *trans* P–CO arrangement, while those of the higher-field signals [$J(\text{W-P}) = 83.9\text{--}85.4$ Hz] are characteristic of a phosphorus atom *trans* to carbyne ligands.^[3a] This reflects the high *trans*-influence of the carbyne ligand,^[3a,20] and it is also in accord with previous reported data for similar derivatives. The carbyne carbon resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Table 4) which ap-

Table 3. Selected IR^[a] and ³¹P{¹H}- and ¹H-NMR^[b] data for complexes **4a**, and **4b**

	IR ν(CO)	ν(C≡N)	2 P <i>trans</i> to carbyne	³¹ P{ ¹ H} ^[c] 2 P <i>trans</i> to carbonyl	¹ H CH _β
4a	2008 (vs), 1961 (s)	2132 (m)	21.6 s (85.4)	40.0 s (231.6)	6.00 s,br
4b	2006 (vs), 1960 (s)	2130 (m)	21.9 s (83.9)	40.1 s (229.6)	5.92 s,br

^[a] Spectra recorded in CH₂Cl₂, ν (cm⁻¹). Abbreviations: s, strong; vs, very strong; m, medium. — ^[b] Spectra recorded in CDCl₃, δ in ppm, *J* in Hz. Abbreviations: s, singlet, br, broad. — ^[c] within parenthesis *J*(W-P).

pear as a doublet of doublets at ca. δ = 298 [²*J*(P-C) ca. 22, 10 Hz] are also consistent with the *trans* position of the carbyne groups with respect to one of the phosphorus atom of dppe. The chemical unequivalence of the carbonyl groups is also shown by the corresponding carbon resonances. Thus, those of carbonyl groups *trans* to the phosphorus atom of dppe appear as a double doublet signal at δ = 209.3 [²*J*(P-C) = 7.3–8.6, 24.0–24.5 Hz] while those of the *cis* carbonyl ligands appear as an apparent triplet signal at δ = 207.5–207.9 [²*J*(P-C) = 7.4–7.5 Hz] (Table 4). Furthermore, ¹³C{¹H}-NMR spectra also show resonances of the equivalent isocyanide groups at δ = 161.6 (**4a**) and 161.9 (**4b**) as apparent triplets [²*J*(P-C) = 7.5–8.4 Hz] along with that of the C_γ atom of the alkenylcarbyne chain observed as a singlet at δ = 175.0 (**4a**) or 174.5 (**4b**).

¹⁸³W-NMR Studies

¹⁸³W-NMR data of complexes **2a**, **2b**, **3a–d**, **4a**, and **4b** are collected in Table 5. ¹⁸³W data were acquired by indirect detection through ¹H and/or ³¹P, using standard HMQC pulse sequence.^{[21][22]} For transition metal nuclei the chemical shift is dominated by the paramagnetic contribution to the total shielding, which can be approximated by Equation 4, where *r* represents the distance to the valence d electrons from the metal nucleus, Δ*E* is the average electronic excitation energy, and Δ*Q_N* is the angular imbalance of charge. The angular imbalance of charge can be considered as constant for complexes having the same d-electron configuration and symmetry. In this way we can rationalise the chemical shifts variations of the complexes studied accord-

Table 4. Selected ¹³C{¹H}-NMR data for complexes **4a** and **4b**^[a]

	C _α	C _γ	(W-CN) ₂	2 CO <i>cis</i> to P	2 CO <i>trans</i> to P
4a	298.4 dd (22.0, 10.0)	175.0 s	161.6 <i>vr.</i> t (8.4)	207.5 <i>vr.</i> t (7.4)	209.3 dd (24.0, 8.6)
4b	298.3 dd (23.2, 9.0)	174.5 s	161.9 <i>vr.</i> t (8.4)	207.9 <i>vr.</i> t (7.5)	209.3 dd (24.5, 7.3)

^[a] Spectra recorded in CDCl₃, δ in ppm, *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet; *vr.*, *virtual*. Within parentheses, ²*J*(P-C).

ing to the fluctuations of the r and ΔE terms, showing an upfield shift of the metal nucleus when r or ΔE increase, and consequently a deshielding when one of the terms becomes smaller.

$$\sigma_p \approx -\langle r^{-3} \rangle (\Delta E)^{-1} \Sigma Q_N \quad (4)$$

Table 5. ^{183}W -NMR data for complexes **2**–**4**

	$\delta^{183}\text{W}$		$\delta^{183}\text{W}$	
		A		B
2a	–2116	3a	–2094	–1819
2b	–2100	3b	–2096	–1804
4a	–2127	3c	–2078	–1821
4b	–2108	3d	–2078	–1805

The ^{183}W -NMR spectra of **2a** and **2b** ($\delta = -2116$, -2100 , respectively) show that the substitution of the acetonitrile ligand of the starting material **1a** and **1b** ($\delta = -1786$, -1775 , respectively)^[21] by the cyanide ligand produces a shielding of the tungsten nuclei by 330–325 ppm. This upfield shift effect is in agreement with the higher π -acceptor ability of CN^- compared to CH_3CN , which implies an increase in the ΔE term of Equation 4. The 16 ppm deshielding of **2b** with respect to **2a** is of the same order of the ^{183}W chemical shift difference between found in the starting carbyne complexes (**1a** and **1b**). This fact can be, and is explained, by the electronic and steric effects induced by the change in of the carbocyclic moiety size.^[21]

The assignment of $\delta^{183}\text{W}$ for each moiety **A** and **B** of dinuclear complexes **3a–d** (Figure 1) is in accordance with the corresponding chemical shifts of precursor complexes **1a** and **1b**, and **2a** and **2b**. Thus, the $\delta^{183}\text{W}$ signals at higher field, which can be compared to those of cyanide complexes **2a** and **2b**, are assigned to the **A** moiety, while those at lower field, which resemble appear at analogous chemical shifts of the acetonitrile complexes **1a** and **1b**, are assigned to moiety **B**. When moving from the mononuclear complexes **2a** and **2b** to the dinuclear ones **3a–d**, a downfield shift of 20–22 ppm in the $\delta^{183}\text{W}$ of the **A** substructure is observed. The bidentate coordination of the CN^- group, acting as a bridging ligand, produces a reduction in its π -acceptor ability and consequently a decrease of the ΔE term. As observed before, an increase in the size of the carbocyclic moiety in either the **A** or **B** part of complexes **3a–d** leads to a deshielding of the metal by 15–18 ppm. It is worth mentioning that in complexes **3b** and **3c** the larger carbocyclic ring produces the expected deshielding of the tungsten nucleus bonded to the corresponding carbyne, but also a 2 ppm upfield shift to the signal of the other metal. Although $^5J(^{183}\text{W}-^1\text{H})^{23}$ are observed within each moiety **A** and **B**, there are no cross peaks between the tungsten atom of the **A** moiety with the proton and phosphorus nuclei of **B** (and vice versa). Hereby, this small shift can be assigned to field or solvent effects.

As expected, the $\delta^{183}\text{W}$ of complexes **4a** and **4b** appear at higher field than those of the corresponding **2a** and **2b** (8 and 11 ppm, respectively) in accordance with the higher

π -acceptor ability of diisocyanide ligand 1,4-(CN) $_2\text{C}_6\text{H}_4$ with respect to the cyanide group. The ^{183}W chemical shift of complex **4b** bearing two eight-membered rings is deshielded by 19 ppm with respect to **4a**, as is also shown in the spectra of complexes **2a**, **2b**, and **3a–d** (see above).

In addition, the ^{183}W -NMR spectra allow the assignment of the ^1H and ^{13}C resonances in compounds **3a–d**. Thus, the assignment of the alkenyl proton resonance in each moiety (H_β and $\text{H}_{\beta'}$) was done through their correlations with the metal nuclei in the ^1H , ^{183}W HMQC spectra. On the basis of these assignments the rest of the ^1H and ^{13}C resonances were identified through the conventional ^1H , ^{13}C -HMQC and -HMBC experiments.

Electrochemical Studies

The electrochemical behaviour of the alkenylcarbyne complexes has been investigated by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in aprotic medium (see Experimental Section).

With the exception of the dicationic complexes **4** (for which no anodic wave was detected, their oxidation conceivably occurring only at a potential above that of the onset of the solvent/electrolyte discharge), all the compounds exhibit irreversible anodic and cathodic waves by CV (Table 6). The oxidation peak potential of the first (I) anodic wave (E_{p}^{ox}) for the cyanide complexes **2** (ca. 1.1 V vs. SCE) is lower than those shown by the other complexes (ca. 1.3–1.4 V, for **1** and **3**) in agreement with the known^[24] stronger net electron σ -donor minus π -acceptor ability of cyanide compared with a nitrile or an isocyanide ligand.

Table 6. Cyclic voltammetric data for complexes **1–4**^[a]

Compound	E_{p}^{ox}	E_{p}^{ox}	$E_{\text{p}}^{\text{red}}$	$E_{\text{p}}^{\text{red}}$
1a	1.34	1.58	–1.58	–
1b	1.28	1.59	–1.65	–
2a	1.07	1.34	–1.89	–
2b	1.09	1.42	–1.88	–
3a	1.30	1.38	–1.58	–1.89
3b ^[b]	1.38	1.50	–1.65	–1.90
3c ^[b]	1.26	1.37	–1.70	–1.94
3d ^[b]	1.28	1.43	–1.73	–1.96
4a	–	–	–1.25	–1.48
4b ^[c]	–	–	–1.20	–1.43
$[\text{W}(\text{CO})_4(\text{dppe})]$ ^[d]	1.02 ^[e]	–	–	–

^[a] Potentials in Volt ± 0.02 vs. SCE measured in 0.2 mol dm^{-3} $[\text{NBu}_4][\text{BF}_4]/\text{MeCN}$ (CH_2Cl_2 for compounds **3a**, **4a**, and $[\text{W}(\text{CO})_4(\text{dppe})]$) at a scan rate of 0.2 V s^{-1} and at a Pt disc ($d = 0.5$ mm) electrode, unless stated otherwise. – ^[b] In vitreous C; at a Pt electrode, only one broad wave is observed at ca. 1.4 V. – ^[c] In vitreous C. – ^[d] Included for comparative purposes. – ^[e] Reversible wave ($\Delta E_{1/2}^{\text{ox}}$ value given).

Moreover, the values of oxidation potential for all the complexes are higher than that for $[\text{W}(\text{CO})_4(\text{dppe})]$ ($E_{1/2}^{\text{ox}} = 1.02$ V) which was also measured for comparative purposes, indicating that the alkenylcarbyne ligands are behaving as even stronger net electron π -acceptors than CO, thus compensating for the stronger net electron donor ability of the nitrile, isocyanide, or cyanide ligand compared

with CO, which should result in a lowering of the oxidation potential of our complexes relative to that of $[\text{W}(\text{CO})_4(\text{dppe})]$. This is consistent with the reported^[9] behaviour of the carbyne ligands in *trans*- $[\text{ReX}(\equiv\text{CCH}_2\text{R})(\text{dppe})_2][\text{BF}_4]$ ($\text{X} = \text{F}$ or Cl ; $\text{R} = \text{alkyl}$, aryl, or ester).

For the cyanide-bridged dinuclear complexes **3**, two close and extensively overlapped anodic waves are observed. Since these complexes can be viewed as the assembling of the tungsten moieties **A** (attached to a formal isocyanide ligand) and **B** (attached to a formal nitrile ligand) (Figure 1) it is expected that the tungsten atom of moiety **A** undergoes an oxidation process at a more anodic potential with respect to that of moiety **B**. Moreover, E_p^{ox} values for these complexes are close to those of the acetonitrile precursors **1**. This is in accord with the ^{183}W chemical shifts for parts **A** and **B** of complexes **3** (see above).

In the cyclic voltammograms of complexes **1**, **2**, and **3**, the first anodic wave (I) is followed, at a slightly higher potential, by a second one (II), also irreversible and broad, that partially overlaps with the former wave. Although this precluded an accurate discrimination of the respective numbers of electrons, the overall involvement, by CPE, of multi-electron anodic processes with electron-induced proton liberation from the alkenylcarbyne ligand is evident.

In fact, exhaustive anodic CPE of those complexes, usually in acetonitrile, corresponds to an overall consumption (waves I + II) of ca. 3 (complexes **1** or **2**) or ca. 4 (complexes **3**) faradays/mol. The evolution of H^+ is indicated by the detection, by CV (cathodic sweep) of the electrolysed solution, at a Pt electrode, of an irreversible and broad cathodic wave at ca. -0.5 V, assigned to H^+ reduction. This wave shifts to a much lower potential upon replacement of the Pt by a vitreous carbon electrode, in accord with the expected large overpotential required for H^+ reduction at the latter electrode. The proton emission was also measured by acid-base titration of the electrochemically oxidised complex solutions: ca. 1 H^+ /molecule for complexes **2**, ca. 3 H^+ /molecule for complexes **1**, or ca. 4 H^+ /molecule for complexes **3**. The higher numbers of protons for **1** and **3** relative to **2** are in accord with the expected stronger acidity of the carbyne ligand in the former complexes, as a result of the charge and the absence of the stabilising strong electron-donor mono-hapto cyanide ligand. Moreover, the highest number of protons lost for compounds **3** may also reflect their biscarbyne (dinuclear) character.

Proton dissociation can also occur during the time scale of CV, at a sufficiently low scan rate, since its cathodic wave (with the above features) is detected as well upon scan reversal following the anodic scan of a solution of an alkenylcarbyne complex.

Consistent with an anodic multi-electron process, at a sufficiently high time scale, involving electron-induced proton loss followed by further oxidation of the product(s), the following observations by CV are possible: the anodic current-functions $i_p^{\text{ox}} C^{-1} \nu^{-1/2}$ (i_p^{ox} – anodic peak current, C – concentration, ν – scan rate) increase (i) with a decrease of the scan rate (e.g. by a factor of ca. 2 from $\nu =$

10 V s^{-1} , when it corresponds roughly to a single-electron process, to 50 mV s^{-1} for complexes **1**) and (ii) with addition of a base such as pyridine, which enhances the deprotonation step.

The proton liberation at the anodic process, now reported for the first time for alkenylcarbyne ligands, indicates a promotion of their acidic character as a result of oxidation of the complexes, and parallels the anodically induced deprotonation observed for the aminocarbyne (CNH_2) and isocyanide (CNH) ligands in *trans*- $[\text{ReCl}(\text{CNH})_n(\text{dppe})_2][\text{BF}_4]_{n-1}$ ($n = 2$ or 1)^[10] and *trans*- $[\text{FeH}(\text{CNH})(\text{dppe})_2][\text{BF}_4]$,^[25] as well as for some aminocarbene complexes^[11a] of Pd^{II} or Pt^{II} . However, the behaviour of the alkenylcarbyne ligands of this study contrasts with the stability, toward anodically-induced deprotonation, of the carbyne ligands $\equiv\text{CCH}_2\text{R}$ in the complexes *trans*- $[\text{ReX}(\equiv\text{CCH}_2\text{R})(\text{dppe})_2][\text{BF}_4]$,^[9] which undergo a reversible single-electron oxidation by CV. This difference conceivably results from the higher acidity of the alkenyl proton ($\equiv\text{C}-\text{CH}=\text{}$) of our complexes compared to the alkyl protons ($\equiv\text{C}-\text{CH}_2\text{R}$) in the Re compounds, and/or the occurrence of anodically induced *ortho*-deprotonation of the ring. Hence, the anodic conversion of a ligating alkenylcarbyne into e.g., an allenylidene or a vinylidene ligand is plausible, but unfortunately we did not succeed in the identification of the products of the CPE or of the attempted chemical oxidations by oxidising agents such as the triarylammonium (Magic Blue) salt $[\text{N}(4\text{-BrC}_6\text{H}_4)_3][\text{SbCl}_6]$.

The alkenylcarbyne complexes of this study display, by CV, a single-electron irreversible cathodic wave (as shown by CPE) (Table 6), which for the dinuclear compounds (**3** and **4**), is followed by a second one at a lower potential, which involves a two-electron process for **4** (as measured by CPE). The observation of the two distinct cathodic waves for complexes **4** with two identical metal centres could suggest an interaction through a delocalized LUMO along the bridged aromatic diisocyanide, but the complexity of the cathodic processes prevents such an interpretation.

Conclusions

In this work, novel types of dinuclear **A** and **B** and mononuclear **C** alkenylcarbyne Fischer-type tungsten complexes are reported (Scheme 1). Complexes of type **A** and **B** belong to a new type of α,β unsaturated carbyne dimetallic derivatives, in which the metal atoms are linked by a cyanide and diisocyanide bridging group. These novel dinuclear complexes display a π -conjugated system consisting of two terminal unsaturated carbyne tungsten moieties linked by bridging ligands with π -electronic delocalized systems (Scheme 2). There is currently much research on this type of derivatives because they disclose appropriate molecular arrangements, with potential utility as precursors of mixed valence complexes and materials with enhanced electrical conductivities and nonlinear optical (NLO) properties.^[26] Our study also allowed the investigation, for the first time, of the electrochemical behaviour of alkenylcarbyne com-

plexes, revealing that (i) the alkenylcarbyne ligands are activated, by oxidation of their complexes, towards heterolytic C–H bond cleavage (a behaviour which is of potential synthetic interest for the generation of other unsaturated multiple metal-carbon bonded species) and that (ii) the alkenylcarbyne ligands behave as even stronger π -electron acceptors than CO.

Experimental Section

Synthesis and Characterization of Alkenylcarbyne Complexes: The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The precursor complexes **1a**, and **b** were prepared by the literature methods.^[3a] NaCN, [Bu₄N]CN, and 1,4-(CN)₂C₆H₄ (Aldrich Chemical Co.) were used as received. – Infra-red spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. – Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. – The conductivities were measured at room temperature, 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. – NMR spectra were run on Bruker AC300 and AMX400 spectrometers. The parameters used for the indirect detection experiments ¹H, ¹⁸³W 2D HMQC and ³¹P, ¹⁸³W {¹H} 2D HMQC have been previously described.^[3a,21] The spectral reference used for ¹⁸³W was Na₂WO₄. – Selected IR and ¹H-, ¹³C{¹H}-, ³¹P{¹H}-, and ¹⁸³W-NMR spectroscopic data for the novel carbyne tungsten complexes are collected in Tables 1–5.

Preparation of Mononuclear Cyanide Alkenylcarbyne Complexes 2a and 2b. – **General Procedure:** A small excess of NaCN solid was added to an orange solution of **1a** or **1b** (0.2 mmol) in 20 mL of methanol. The mixture was stirred at room temperature for 2 h. The resulting solution was filtered off and the filtrate was evaporated to dryness. The residue was extracted with CH₂Cl₂ and the filtrate was dried under vacuum to give an orange solid. Yield: **2a**, 90%; **2b**, 95%.

The complexes **2a** and **2b** were also prepared following the procedure below: An orange solution of **1a** or **1b** (0.2 mmol) and 1 equiv. of [NBu₄]CN in 10 mL of CH₂Cl₂ was stirred at room temperature for 2 h. After evaporation of the solvent to dryness the residue was extracted with toluene and filtered off on Alox. Removal of the solvent and washing the resulting solid with diethyl ether (2 × 10 mL) and hexane (2 × 10 mL) and drying in vacuo gave an orange solid. Yields ca. 70%.

Spectral and Analytical Data for 2a: IR [KBr, ν (CN); ν (CO)] $\tilde{\nu}$ = 2111 (vw); 1987 (vs), 1917 (vs). – ¹H NMR (δ , CDCl₃) 1.48 (m, 4 H, 2 CH₂), 1.94 (m, 4 H, 2 CH₂), 2.60 [m, 2 H, P(CH₂H₆)₂P], 2.85 [m, 2 H, P(CH₂H₆)₂P], 7.36–7.75 (m, 20 H, 2 PPh₂). – ¹³C{¹H} NMR (δ , CDCl₃) 25.5 (s, CH₂), 26.1 (s, CH₂), 28.5 [m, P(CH₂)₂P], 31.8 (s, CH₂), 34.7 (s, CH₂), 128.2–136.3 (m, C _{β} , 2 PPh₂). – C₃₆H₃₃NO₂P₂W: calcd C 57.1, H 4.4, N 1.8; found: C 57.5, H 4.2, N 1.9.

Spectral and Analytical Data for 2b: IR [KBr, ν (CN); ν (CO)] $\tilde{\nu}$ = 2112(vw); 1984 (vs), 1916 (vs). – ¹H NMR (δ , CDCl₃) 1.40 (m, 4 H, 2 CH₂), 1.44 (m, 2 H, CH₂), 1.53 (m, 2 H, CH₂), 1.70 (m, 2 H, CH₂), 1.82 (m, 2 H, CH₂), 2.31 (m, 2 H, CH₂), 2.58 [m, 2 H, P(CH₂H₆)₂P], 2.88 [m, 2 H, P(CH₂H₆)₂P], 7.36–7.88 (m, 20 H, 2 PPh₂). – ¹³C{¹H} NMR (δ , CDCl₃) 25.5 (s, CH₂), 26.7 (s, CH₂), 26.9 (s, CH₂), 26.96 (s, CH₂), 27.02 (s, CH₂), 28.6 [m, P(CH₂)₂P],

31.9 (s, CH₂), 36.3 (s, CH₂), 128.3–136.2 (m, 2 PPh₂), 135.7 (s, C _{β}). – MS (FAB, m/z) [M⁺ – CN] = 773, [M⁺ – CO] = 771, [M⁺ – CN – CO] = 745, [M⁺ – 2 CO] = 743. – C₃₉H₃₉NO₂P₂W: calcd. C 58.6, H 4.9, N 1.8; found: C 58.2, H 4.7, N 1.3.

Preparation of Cyanide-Bridged Bis(alkenylcarbyne) Ditungsten Complexes (3a–d): General Procedure: A mixture of complexes **2a** (0.2 mmol) and **1a** (0.2 mmol) in 20 mL of dichloromethane was stirred at room temperature for 1 h. The resulting orange-red solution was evaporated to dryness and the residue was washed with hexane (3 × 5 mL) to give an orange solid (**3a**). The complexes **3b–d** were prepared similarly. The complexes **3a** and **3d** were also prepared directly from the reaction of 2 equiv. of **1a** and **1b** with [Bu₄N]CN in dichloromethane, or with NaCN in methanol, in the similar yields. Yield: 82–85%. – Conductivity (acetone, 20°C, Ω^{-1} cm² mol^{–1}): **3a**, 123; **3b**, 120; **3c**, 115; **3d**, 118.

Spectral and Analytical Data for 3a: ¹H NMR (δ , CDCl₃) 1.40 (m, 8 H, 4 CH₂), 1.69 (m, 4 H, 2 CH₂), 1.85 (m, 4 H, 2 CH₂), 2.3–3.0 [m, 8 H, 2 P(CH₂)₂P], 7.18–7.70 (m, 40 H, 4 PPh₂). – ¹³C{¹H} NMR (δ , CDCl₃) 25.2 (s, CH₂), 25.3 (s, CH₂), 25.9 (s, 2 CH₂), 28.0 [m, 2 P(CH₂)₂P], 31.4 (s, CH₂), 31.7 (s, CH₂), 34.4 (s, CH₂), 34.9 (s, CH₂), 128.2–136.4 (m, C _{β} , C _{β'} , 4 PPh₂). – C₇₁H₆₆BF₄NO₄P₄W₂: calcd. C 54.1, H 4.2, N 0.9; found: C 53.4, H 4.4, N 0.7.

Spectral and Analytical Data for 3b: IR [KBr, ν (CN); ν (CO); ν (BF₄)] $\tilde{\nu}$ = 2110 (vw), 2099 (vw, sh); 1994 (vs, br), 1925 (vs, br); 1059 (m, br). – ¹H NMR (δ , CDCl₃) 1.30 (m, 12 H, 6 CH₂), 1.41 (m, 6 H, 3 CH₂), 1.69 (m, 2 H, CH₂), 2.10 (m, 2 H, CH₂), 2.3–2.9 [m, 8 H, 2 P(CH₂)₂P], 7.18–7.70 (m, 40 H, 4 PPh₂). – ¹³C{¹H} NMR (δ , CDCl₃) 25.15 (s, CH₂), 25.23 (s, CH₂), 25.8 (s, CH₂), 26.4 (s, CH₂), 26.6 (s, CH₂), 26.7 (s, CH₂), 27.0–29.0 [m, CH₂, 2 P(CH₂)₂P], 31.4 (s, CH₂), 31.7 (s, CH₂), 34.8 (s, CH₂), 35.5 (s, CH₂), 128.3–136.4 (m, C _{β} , C _{β'} , 4 PPh₂). – C₇₄H₇₂BF₄NO₄P₄W₂: calcd. C 54.9, H 4.5, N 0.9; found: C 53.7, H 4.5, N 0.7.

Spectral and Analytical Data for 3c: IR [KBr, ν (CN); ν (CO); ν (BF₄)] $\tilde{\nu}$ = 2109 (vw, sh), 2098 (vw); 1993 (vs, br), 1924 (vs, br); 1056 (s, br). – ¹H NMR (δ , CDCl₃) 1.38 (m, 10 H, 5 CH₂), 1.69 (m, 4 H, 2 CH₂), 1.82 (m, 4 H, 2 CH₂), 2.07 (m, 4 H, 2 CH₂), 2.40–3.0 [m, 8 H, 2 P(CH₂)₂P], 7.17–7.87 (m, 40 H, 4 PPh₂). – ¹³C{¹H} NMR (δ , CDCl₃) 25.1 (s, CH₂), 25.8 (s, CH₂), 26.3 (s, CH₂), 26.6 (s, CH₂), 26.7 (s, CH₂), 26.8 (s, CH₂), 27.0 (s, CH₂), 28.0 [m, 2 P(CH₂)₂P], 31.2 (s, CH₂), 31.7 (s, CH₂), 34.2 (s, CH₂), 35.8 (s, CH₂), 127.9–136.6 (m, C _{β} , C _{β'} , 4 PPh₂). – C₇₄H₇₂BF₄NO₄P₄W₂: calcd. C 54.9, H 4.5, N 0.9; found: C 54.0, H 4.8, N 0.7.

Spectral and Analytical Data for 3d: ¹H NMR (δ , CDCl₃) 1.39 (m, 16 H, 8 CH₂), 1.68 (m, 4 H, 2 CH₂), 1.81 (m, 4 H, 2 CH₂), 2.09 (m, 4 H, 2 CH₂), 2.3–3.0 [m, 8 H, 2 P(CH₂)₂P], 7.17–7.68 (m, 40 H, 4 PPh₂). – ¹³C{¹H} NMR (δ , CDCl₃) 25.3 (s, CH₂), 25.4 (s, CH₂), 26.6–27.1 (m, 8 CH₂), 28.2 [m, 2 P(CH₂)₂P], 31.8 (s, CH₂), 31.9 (s, CH₂), 35.6 (s, CH₂), 36.1 (s, CH₂), 128.2–135.6 (m, C _{β} , C _{β'} , 4 PPh₂). – C₇₇H₇₈BF₄NO₄P₄W₂: calcd. C 55.7, H 4.7, N 0.8; found: C 54.3, H 4.9, N 0.8.

Preparation of Diisocyanide-Bridged Bis(alkenylcarbyne) Ditungsten Complexes 4a and 4b: General Procedure: A mixture of complex **1a** or **1b** (0.2 mmol) and 0.5 equiv. of 1,4-phenylenediisocyanide (0.1 mmol) in 20 mL of dichloromethane was stirred at room temperature for 2 h. The resulting orange-red solution was evaporated to dryness and the residue was washed with diethyl ether (2 × 5 mL) and hexane (3 × 5 mL) to give an orange-red solid **4a** and **4b**. Yield: 75–80%. Conductivity (acetone, 20°C, Ω^{-1} cm² mol^{–1}): **4a**, 200; **4b**, 195.

Spectral and Analytical Data for 4a: IR [KBr, $\nu(\text{CN})$; $\nu(\text{CO})$; $\nu(\text{BF}_4)$]: $\tilde{\nu} = 2133$ (m); 2000 (vs), 1947 (s); 1061 (s, br). — ^1H NMR (δ , CDCl_3) 1.76 (m, 8 H, 4 CH_2), 2.36 (m, 4 H, 2 CH_2), 2.56 (m, 4 H, 2 CH_2), 2.7–3.4 [m, 8 H, 2 $\text{P}(\text{CH}_2)_2\text{P}$], 6.42–7.78 [m, 44 H, $(\text{CN})_2\text{C}_6\text{H}_4$, 4 PPh_2]. — $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3) 25.4 (s, 2 CH_2), 25.5 (m, 2 $\text{PC}_6\text{H}_5\text{C}_6\text{H}_5\text{P}$), 26.0 (s, 2 CH_2), 27.3 (m, 2 $\text{PC}_6\text{H}_5\text{C}_6\text{H}_5\text{P}$), 33.2 (s, 2 CH_2), 35.6 (s, 2 CH_2), 125.7–133.5 [m, C_β , C_β' , $(\text{CN})_2\text{C}_6\text{H}_4$, 4 PPh_2]. — $\text{C}_{78}\text{H}_{70}\text{B}_2\text{F}_8\text{N}_2\text{O}_4\text{P}_4\text{W}_2$: calcd. C 53.1, H 4.0, N 1.6; found: C 52.8, H 4.1, N 1.5.

Spectral and Analytical Data for 4b: IR [KBr, $\nu(\text{CN})$; $\nu(\text{CO})$; $\nu(\text{BF}_4)$]: $\tilde{\nu} = 2128$ (m); 1997 (vs), 1944 (s); 1055 (s, br). — ^1H NMR (δ , CDCl_3) 1.50 (m, 12 H, 6 CH_2), 1.76 (m, 4 H, 2 CH_2), 1.82 (m, 4 H, 2 CH_2), 2.20 (m, 4 H, 2 CH_2), 2.63 (m, 4 H, 2 CH_2), 2.8–3.2 [m, 8 H, 2 $\text{P}(\text{CH}_2)_2\text{P}$], 6.36–7.79 [m, 44 H, $(\text{CN})_2\text{C}_6\text{H}_4$, 4 PPh_2]. — $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3) 25.6 (m, 2 $\text{PC}_6\text{H}_5\text{C}_6\text{H}_5\text{P}$), 25.5 (s, 2 CH_2), 26.5 (s, 2 CH_2), 26.7 (s, 2 CH_2), 27.2 (s, 2 CH_2), 27.5 (m, 2 $\text{PC}_6\text{H}_5\text{C}_6\text{H}_5\text{P}$), 27.8 (s, 2 CH_2), 33.0 (s, 2 CH_2), 37.1 (s, 2 CH_2), 125.7–133.6 [m, $(\text{CN})_2\text{C}_6\text{H}_4$, 4 PPh_2], 136.4 [d, $^3\text{J}(\text{C}-\text{P}) = 16.7$ Hz, C_β , C_β']. — MS (FAB, m/z) 0.5 [$\text{M}^+ - 2 \times (\text{BF}_4) - (\text{CN})_2\text{C}_6\text{H}_4$] = 773. — $\text{C}_{84}\text{H}_{82}\text{B}_2\text{F}_8\text{N}_2\text{O}_4\text{P}_4\text{W}_2$: calcd. C 54.6, H 4.5, N 1.5; found: C 53.8, H 4.3, N 1.8.

Electrochemical Measurements: The electrochemical experiments were performed on an EG & G PARC 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A) or on an EG & G PARC 173 potentiostat/galvanostat and an EG & G PARC 175 Universal programmer. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum- or vitreous carbon-disc working electrode ($d = 0.5$ or 1 mm, respectively), probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum auxiliary electrode was employed. Controlled potential electrolyses were carried out in a two-compartment three electrode cell with 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 electrochemical experiments were performed in an inert atmosphere (N_2) at room temperature. The potentials were measured in 0.2 mol dm^{-3} [NBu_4][BF_4]/MeCN or CH_2Cl_2 , and are quoted relative to the saturated calomel electrode (SCE) by using as internal reference the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ couple ($E_{\text{ox}} = 0.45$ or 0.53 V vs. SCE).

The acid-base potentiometric titrations of the electrochemically oxidised solutions were carried out by using a solution of NaOH in MeOH that was standardised by titration against benzoic acid in MeCN or CH_2Cl_2 . The results have been corrected for background effects by also performing, in each case, the titration of a blank electrolyte solution which has been electrolysed under identical conditions to those used for the corresponding complex solution.

Acknowledgments

This work was supported by the Dirección General de Investigación Científica y Técnica (Project PB96-0558) and the EU (Human Capital Mobility Programme, Project ERBCHRXCT 940501). L. Z. is grateful to the Spanish Ministerio de Asuntos Exteriores (Agencia Española de Cooperación Internacional) for a doctoral grant and the Fundação para a Ciência e a Tecnologia, PRAXIS XXI Programme (Portugal) for a post-doctoral grant (for doing the detailed electrochemical studies). R. J. C. thanks the Spanish Ministerio de Educación y Cultura for a predoctoral fellowship.

- [1] For recent reviews on metal carbyne complexes see: [1a] P. F. Engel, M. Pfeiffer, *Chem. Rev.* **1995**, 95, 2281. — [1b] *Transition Metal Carbyne Complexes*; NATO ASI Series, Kluwer Academic Publishers, Dordrecht, **1993**.
- [2] For applications of metal carbyne complexes in organic synthesis see: L. McElwee-White, *Synlett* **1996**, 806.
- [3] For recent developments see: [3a] L. Zhang, M. P. Gamasa, J. Gimeno, R. J. Carbajo, F. López-Ortiz, M. Lanfranchi, A. Tiripicchio, *Organometallics* **1996**, 15, 4274. — [3b] L. Zhang, M. P. Gamasa, J. Gimeno, A. Galindo, C. Mealli, M. Lanfranchi, A. Tiripicchio, *Organometallics* **1997**, 16, 4099 and references therein. — [3c] B. E. Woodworth, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1997**, 119, 828 and references therein. — [3d] D. E. Main, L. McElwee-White, *J. Am. Chem. Soc.* **1997**, 119, 4551. — [3e] L. Weber, G. Dembeck, R. Boese, D. Bläser, *Chem. Ber./Rec* **1997**, 130, 1305. — [3f] B. E. Woodworth, D. S. Frohnappfel, P. S. White, J. L. Templeton, *Organometallics* **1998**, 17, 1655.
- [4] A few examples containing saturated di-carbyne bridging units are also known: [4a] $[\text{Tp}'(\text{CO})_2\text{M}=\text{C}-\text{CH}(\text{R})-\text{CH}(\text{R})-\text{C}\equiv\text{M}(\text{CO})_2\text{Tp}']$ ($\text{M} = \text{Mo}$, $\text{R} = \text{H}$; $\text{M} = \text{W}$, $\text{R} = \text{Me}$, CH_2Ph , CHMe_2) (ref. 3c). — [4b] $[\text{Tp}'(\text{CO})_2\text{M}=\text{C}-\text{C}\equiv\text{W}(\text{CO})_2(\text{PhC}\equiv\text{CPh})\text{Tp}']$ ($\text{M} = \text{Mo}$, W) B. E. Woodworth, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1998**, 120, 9028. — [4c] $[\text{Cp}\{\text{P}(\text{OMe})_3\}_2\text{Mo}\equiv\text{C}-\text{C}(\text{H})\text{tBu}-\text{C}(\text{H})\text{tBu}-\text{C}\equiv\text{Mo}\{\text{P}(\text{OMe})_3\}_2\text{Cp}]$ R. G. Beevor, M. J. Freeman, M. Green, C. E. Morton, A. G. Orpen, *J. Chem. Soc., Chem. Commun.* **1985**, 68.
- [5] N. A. Ustynyuk, V. N. Vinogradova, V. G. Andrianov, Y. T. Struchkov, *J. Organomet. Chem.* **1984**, 268, 73.
- [6] [6a] E. O. Fischer, W. Röhl, N. H. T. Huy, K. Ackermann, *Chem. Ber.* **1982**, 115, 2951. — [6b] N. O. Dao, H. Fevrier, M. Jouan, E. O. Fischer, W. Röhl, *J. Organomet. Chem.* **1984**, 275, 191.
- [7] To the best of our knowledge only the following analogous complexes of this type are known: [7a] $[\text{W}_2(\mu\text{-Cl})_2(\mu\text{-Ph}_2\text{AsCH}_2\text{-AsPh}_2)(\equiv\text{CPh})_2]$: E. O. Fischer, A. Ruhs, *Chem. Ber.* **1978**, 111, 2774. — [7b] $[\text{M}(\equiv\text{C}-\text{NEt}_2)(\text{CO})_3(\mu\text{-L})_2]$ ($\text{M} = \text{Mo}$, W , $\text{L} = \text{Br}$, I , SPh , NCO , etc.): E. O. Fischer, D. Wittmann, D. Himmelreich, R. Cai, K. Ackermann, D. Neugebauer, *Chem. Ber.* **1982**, 115, 3152.
- [8] A. J. L. Pombeiro, J. A. McCleverty, *Molecular Electrochemistry of Inorganic, Bioinorganic, and Organometallic Compounds*, NATO ASI Series; Kluwer Academic Publishers, Dordrecht, The Netherlands, **1993**.
- [9] S. S. P. R. Almeida, A. J. L. Pombeiro, *Organometallics*, **1997**, 16, 4469.
- [10] M. A. N. D. A. Lemos, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Inorg. Chim. Acta*, **1994**, 226, 9.
- [11] [11a] R. Bertani, M. Mozzon, R. A. Michelin, F. Benetollo, G. Bombieri, T. J. Castilho, A. J. L. Pombeiro, *Inorg. Chim. Acta*, **1991**, 189, 175. — [11b] G. Facchin, M. Mozzon, R. A. Michelin, M. T. A. Ribeiro, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, **1992**, 2827. — [11c] R. Bertani, M. Mozzon, R. A. Michelin, T. J. Castilho, A. J. L. Pombeiro, *J. Organomet. Chem.*, **1992**, 431, 117. — [11d] Y. Wang, A. J. L. Pombeiro, R. A. Michelin, M. Mozzon, R. Bertani, *Bull. Pol. Acad. Sci.*, **1994**, 42, 307. — [11e] U. Belluco, R. Bertani, R. A. Michelin, M. Mozzon, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, Y. Wang, *Inorg. Chim. Acta*, **1995**, 235, 397.
- [12] N. G. Connelly, in: *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds* (Eds.: A. J. L. Pombeiro, J. A. McCleverty), NATO ASI Series; Kluwer Academic Publishers, Dordrecht, The Netherlands, **1993**.
- [13] M. K. Lloyd, J. A. McCleverty, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, **1973**, 1743.
- [14] [14a] E. O. Fischer, M. Schluge, J. O. Besenhard, *Angew. Chem. Int. Ed. Engl.*, **1976**, 15, 683. — [14b] E. O. Fischer, F. J. Gammel, J. O. Besenhard, A. Frank, D. Neugebauer, *J. Organomet. Chem.*, **1980**, 191, 261. — [14c] E. O. Fischer, D. Wittmann, D. Himmelreich, D. Neugebauer, *Angew. Chem. Int. Ed. Engl.*, **1982**, 21, 444.
- [15] [15a] I. Kovacic, O. Gevert, H. Werner, M. Schimittel, R. Sollner, *Inorg. Chim. Acta*, **1998**, 275–276, 435. — [15b] R. D. Rieke, H. Kojima, K. Ofele, *Angew. Chem., Int. Ed. Engl.*, **1980**, 19, 538.
- [16] [16a] P. J. Krusic, U. Klabunde, C. P. Casey, T. F. Block, *J. Am. Chem. Soc.*, **1976**, 98, 2015. — [16b] C. P. Casey, L. D. Albin, M. C. Seaman, D. H. Evans, *Organomet. Chem.*, **1978**, 155, C37.

- [17] [17a] J. –P. Battioni, D. Lexa, D. Mansuy, J.-M. Savéant, *J. Am. Chem. Soc.*, **1983**, *105*, 207. – [17b] M. Lange, D. Mansuy, *Tetrahedron Lett.*, **1981**, *22*, 2561.
- [18] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley-Interscience Publication: New York, **1986**, p.283.
- [19] D. F. Shriver, S. A. Shriver, S. E. Anderson, *Inorg. Chem.* **1965**, *4*, 725.
- [20] E. M. Shustorovich, M. A. Poraikoshits, Yu. A. Buslaev, *Coord. Chem. Rev.* **1975**, *17*, 1.
- [21] R. J. Carbajo, L. Zhang, F. López-Ortiz, *Magn. Reson. Chem.* **1998**, *36*, 807.
- [22] F. López-Ortiz, R. J. Carbajo, *Current Org. Chem.* **1998**, *2*, 97.
- [23] $^7J(^{183}\text{W}-^1\text{H})$ have been described in the literature: A. Macchioni, P. S. Pregosin, P. F. Engel, S. Mecking, M. Pfeffer, J.-C. Daran, J. Vaissermann, *Organometallics* **1995**, *14*, 1637.
- [24] J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, **1980**, 2032.
- [25] S. S. P. R. Almeida, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, **1999**, 467.
- [26] [26a] D. W. Bruce, D. O'Hare *Inorganic Materials*, Wiley, New York, **1992**. – [26b] M. H. Chisholm, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 673.

Received July 7, 1999
[199251]