Synthesis and Characterization of Tungsten Alkenyl−Carbyne Complexes $[(dppe)(CO)_2LW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (L = CO, MeCN, PMe_3) and $[(dppe)(CO)_2XW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2]$ (X = Cl, Br, I). X-ray Crystal Structure of $[(dppe)(CO)_2ClW{\equiv}CCH{=}CCH_2CH_2CH_2CH_2]$ and ^{183}W NMR Studies

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Alkenyl−vinylidene complexes *mer*-$[(dppe)(CO)_3W{=}C{=}CHC{=}CH(CH_2)_nCH_2CH_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane; $n = 1$ (**1a**), $n = 3$ (**1c**), $n = 4$ (**1d**)) have been prepared by reaction of the complex *fac*-$[(dppe)(CO)_3W(Me_2CO)]$ with 1-ethynylcyclopentanol, 1-ethynylcycloheptanol, and 1-ethynylcyclooctanol. Protonation at the C_δ of the alkenyl−vinylidene moiety with $HBF_4{\cdot}OEt_2$ in diethyl ether or THF leads to the formation of cationic alkenyl−carbyne complexes *mer*-$[(dppe)(CO)_3W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ ($n = 1$ (**2a**), $n = 3$ (**2c**), $n = 4$ (**2d**)). When the protonation is carried out in CH_2Cl_2, isomeric carbyne complexes *mer*-$[(dppe)(CO)_3W{\equiv}CCH_2C{=}CH(CH_2)_nCH_2CH_2][BF_4]$ (**2a′**, **2c′**, **2d′**) are also generated. The alkenyl−carbyne complexes undergo carbonyl substitution by donor ligands to give dicarbonyl derivatives of the following types: (a) cationic complexes *trans*-$[(dppe)(CO)_2LW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (L = CH_3CN, $n = 1$ (**3a**), $n = 4$ (**3d**); L = PMe_3, $n = 1$ (**4a**), $n = 4$ (**4d**)) and (b) neutral complexes *trans*-$[(dppe)(CO)_2XW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2]$ (X = Cl, $n = 1$ (**5a**), $n = 2$ (**5b**), $n = 3$ (**5c**), $n = 4$ (**5d**); X = Br, $n = 1$ (**6a**), $n = 4$ (**6d**); X = I, $n = 1$ (**7a**), $n = 3$ (**7c**), $n = 4$ (**7d**)). The structure of complex **5a** was determined by X-ray diffraction methods. The W atom displays a distorted octahedral coordination with the Cl atom [W−Cl = 2.540(1) Å] *trans* to the alkenyl−carbyne group [W≡C = 1.830(3) Å]. IR and ^1H, ^{31}P, ^{13}C, and ^{183}W NMR data are reported. The sequence for the *trans* influence in the order alkenyl−carbyne > alkenyl−vinylidene > CO could be found from the corresponding $^1J(^{31}P{-}^{183}W)$ values. The low values for the alkenyl−carbyne groups are among the lowest ever reported, indicating a high *trans* influence of the carbyne group. ^{183}W chemical shifts of compounds **1a**−**7a** were obtained through two-dimensional indirect ^{31}P, ^{183}W recording techniques. A down field shifting of ^{183}W resonances with decreasing π-acceptor ability of the ligands in complexes **2a**−**7a** was observed.

Introduction

Transition metal carbene complexes, and particularly Fischer type unsaturated carbene complexes, have been extensively used in organic synthesis due to the wide range of synthetic applications.[1,2] In contrast, the utility of carbyne metal complexes for similar purposes is comparatively much less exploited. Although the chemistry of metal-carbon triple bonds has been explored

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(1) See for instance: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988. (c) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Elmsford, NY, 1991; Vol. 5.

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considerably during the past decade,[3] the reactivity of Fischer type (low-valent) alkylidyne complexes toward unsaturated organic substrates such as alkenes or alkynes[3d,4] has been little investigated.[5] Only a few coupling reactions of alkylidyne ligands with alkynes and alkenes leading to carbon−carbon bond formation have been reported,[6] although the active species are mostly transient carbene complexes formed by protonation of the carbyne precursors.[7]

Reactivity studies with functionalized carbyne complexes are much more scarce. Recently McElwee-White and co-workers have studied[8] the reactivity of acyl-substituted and other related functionalized carbyne complexes which undergo chemical transformations under photooxidative and thermal conditions to give cyclopentenones, cyclohexenones, and oxymetallacycles depending on the carbyne substituents. This behavior demonstrates that appropriate substitutions in the alkylidyne group may induce substantial modifications in the chemistry of the metal carbyne system. Therefore, it is apparent that the utility of functionalized metal carbyne complexes for organic transformations has yet to be investigated. Taking into account that among the α,β unsaturated carbene complexes the alkenyl derivatives are some of the most efficient synthons for synthetic applications, we believed that the synthesis of analogous carbyne complexes would be desirable because of the potential interest in synthesis.

Up to now, as far as we are aware, only cyclopentenyl carbyne group 6 metal Fischer type complexes $[M\{\equiv C\overline{C{=}CH(CH_2)_2CH_2}\}(CO)_4X]$ (M = Cr, W; X = halide) have been described. They have been prepared by the classical method from the corresponding carbene derivatives using boron halide as the Lewis acid.[9] This synthetic strategy has limited the scope of the applicability to other metallic substrates and has probably determined that the number of unsaturated carbyne derivatives remains still very scarce.

It is well-established that the vinylidene functionality undergoes nucleophilic and electrophilic attacks in a number of transition metal complexes.[10] While nucleophiles add to the C_α atom (e.g., methanol or hydride) to give methoxycarbene and alkenyl complexes, respectively, electrophiles can be added to the C_β to form carbyne derivatives.

$$[M]{=}C{=}CR_2 + E^+ \rightarrow [M]^+{\equiv}CCR_2(E)$$

This latter approach provides a very simple entry to the synthesis of alkyl and arylcarbyne complexes which has been used to prepare a series of rhenium,[11] molybdenum,[12] iridium,[13] and tungsten[14] complexes. Similarly an allenylidene group may also undergo electrophilic additions to give alkenyl−carbyne derivatives.

$$[M]{=}C{=}C{=}CR_2 + E^+ \rightarrow [M]^+{\equiv}CC(E){=}CR_2$$

Although this methodology seems to be a good entry to alkenyl-substituted carbyne complexes, it has only been applied for the synthesis of $[Mn(\equiv CCH{=}CR_2)(\eta^5\text{-}C_5H_5)(CO)_2]X$ (R = Bu^t, X = CF_3COO; R = Ph, X = Cl, CF_3COO, BF_4) which are obtained from the protonation of allenylidene complexes $[Mn({=}C{=}C{=}CR_2)(\eta^5\text{-}C_5H_5)(CO)_2]$.[15a] In addition analogous manganese[15b,c] and rhodium[16] derivatives $[Mn\{\equiv CC(Me){=}C(Me)(OMe)\}(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$, $[Mn\{\equiv CC(Me){=}CRR'\}(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]^+$, and $[Rh\{\equiv CC(H){=}CMe_2\}Cl(PPr^i_3)]$ have also been prepared[17] using proton and methyl additions to functionalized vinylidene derivatives.

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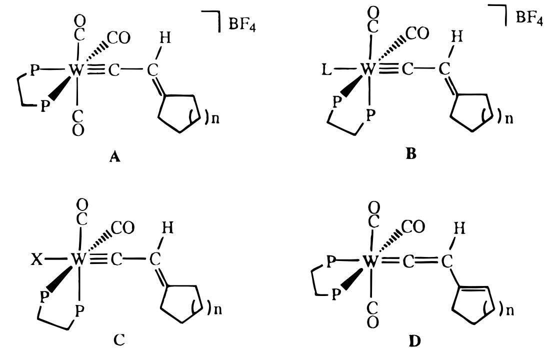
Table 1. IR[a] and ^{1}H and ^{31}P{^{1}H} NMR[b] Data for the Tricarbonyl Vinylidene Complexes *mer*-[(dppe)(CO)$_3$W=C=CHC=CH(CH$_2$)$_n$CH$_2$CH$_2$] (*n* = 1 (1a), 3 (1c), 4 (1d))

		^{31}P{^{1}H}		^{1}H		
	IR ν(CO)	P *trans* to vinylidene[c]	P *trans* to CO[c]	C$_\beta$H[d]	C$_\delta$H[e]	others
1a	2002 (m), 1924 (m), 1891 (vs)	35.9 d (1.4,[f] 158.5)	46.2 d (1.4,[f] 241.9)	4.97 dd (4.8, 2.5)	5.14 br	1.85 m (CH$_2$), 2.42 m (2 CH$_2$), 2.57 m, 2.63 m (P(CH$_2$)$_2$P), 7.30−7.62 m (Ph)
1c	2001 (m), 1923 (m), 1890 (vs)	37.6 s (160.2)	47.0 s (243.3)	4.96 dd (4.8, 2.6)	5.31 t (6.5)	1.37 m (CH$_2$), 1.46 m (CH$_2$), 1.94 m (2 CH$_2$, P(CH$_2$)$_2$P), 2.52 m (CH$_2$), (6.62−7.42 m (Ph)
1d	2001 (m), 1924 (m), 1890 (vs)	36.6 d (2.5,[f] 159.9)	46.3 d (2.5,[f] 242.7)	4.66 dd (5.1, 2.4)	5.07 t (8.1)	1.45 m (3 CH$_2$), 1.60 m (CH$_2$), 2.11 m (CH$_2$), 2.41 t (5.9,[f] CH$_2$), 2.54 m, 2.63 m (P(CH$_2$)$_2$P), 7.30−7.62 m (Ph)

[a] Spectra recorded in THF, ν (cm^{-1}). Abbreviations: m, medium; s, strong; vs, very strong. [b] Spectra recorded in CDCl$_3$ (**1a**,**d**) or C$_6$D$_6$ (**1c**). δ in ppm, *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. [c] *J*(P−W). [d] ^4J(H−P). [e] *J*(H−H). [f] *J*(P−P).

Chart 1

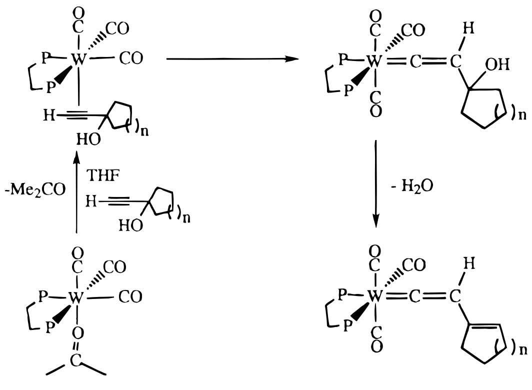


As part of our ongoing studies into the chemistry of functionalized vinylidene complexes,[18] we sought to exploit this methodology to investigate the preparation of alkenyl−vinylidene tungsten(0) complexes. The synthesis of these derivatives would provide appropriate synthons of novel alkenyl−carbyne derivatives through electrophilic additions.

Here we report the synthesis and characterization of novel cationic alkenyl-carbyne tungsten complexes (**A**, Chart 1) and their carbonyl-substituted derivatives (**B**) (L = PMe$_3$, MeCN), (**C**) (X = Cl, Br, I) and the preparation of the alkenyl−vinylidene complexes (**D**), which are the precursors of the alkenyl−carbyne derivatives (**A**). ^{183}W NMR data for the first member of each series of compounds (*n* = 1, complexes **1a**−**7a**) and the first X-ray crystal structure of an alkenyl−carbyne tungsten complex, namely *trans*-[(dppe)(CO)$_2$ClW≡CCH=C(CH$_2$)$_3$CH$_2$] (**5a**), are also reported.

Results and Discussion

Alkenyl−Vinylidene Complexes. A THF solution of *fac*-[W(CO)$_3$(dppe)(Me$_2$CO)] (dppe = 1,2-bis(diphenylphosphino)ethane) reacts with 1-ethynylcyclopentanol, 1-ethynylcycloheptanol, and 1-ethynylcyclooctanol at room temperature to give a green solution from which alkenyl−vinylidene complexes **1a**, **1c**, and **1d** are isolated in good yields as green air-sensitive solids (slow decomposition is observed over 0 °C) (eq 1). Although we have not investigated the nature of the intermediates, the reactions probably proceed, as it is well-known from other transition metal complexes,[10] through π-coordination of the alkynols followed by a rearrangement to give hydroxy vinylidene species (concomitant *fac* → *mer* tricarbonyl isomerization occurs). Subsequent dehydration processes proceed in a regioselective manner (isomeric allenylidene species are not detected), leading to the alkenyl−vinylidene complexes **1a**, **1c**, and **1d**. Similar transformations have been reported from isoelectronic d^6 ruthenium (II) complexes.[18,19] However, the reaction with 1-ethynylcyclohexanol (*n* = 2) leads to a mixture of the corresponding alkenyl−vinylidene complex **1b** (characterized by IR and ^{31}P NMR; see Experimental Section) and other unidentified species. Attempts to isolate the vinylidene complex **1b** with analytical purity were unsuccessful.



(1)

n= 1 (**1a**), 2 (**1b**), 3 (**1c**), 4 (**1d**)

The reactions can be monitored by IR in the carbonyl region and are allowed to proceed until total disappearance of the absorptions corresponding to the starting *fac*-tricarbonyl complex. IR and NMR spectra of **1a, 1c**, and **1d** (Tables 1 and 2) are in accordance with this formulation. The vinylidene ligands are identified by the characteristic low-field ^{13}C NMR chemical shifts of the C$_\alpha$ (in the range 338.8−342.2 ppm; dd ^2J(C−P$_{trans}$) and ^2J(C−P$_{cis}$) = *ca.* 16 and 8 Hz, respectively). The formation of the *mer*-tricarbonyl isomers is supported by the ^{31}P NMR spectra since two doublet signals (AB system) appeared in the ranges of δ 35.9−37.6 and 46.2−47.0 ppm and confirmed by the different ^2J(C−P) values for the vinylidene α-carbon atom. IR spectra (THF) displaying a typical pattern of three ν(CO)

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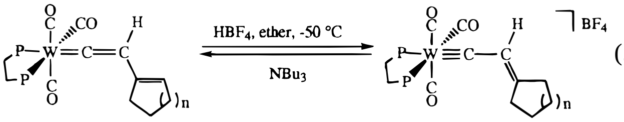
Table 2. Selected $^{13}C\{^1H\}$ NMR[a] Data for the Tricarbonyl Vinylidene Complexes *mer*-[(dppe)(CO)$_3$W=C=CHC=CH(CH$_2$)$_n$CH$_2$CH$_2$] (n = 1 (1a), 3 (1c), 4 (1d))

	$^{13}C\{^1H\}$					
	C_α[b]	C_β[c]	C_δ	CO *cis* to P[b]	CO *trans* to P[b]	others
1a	338.8 dd (15.9, 7.9)	114.4 d (12.2)	118.1 s	202.4 dd (6.4, 4.5)	211.5 dd (21.4, 8.7)	23.6 s, 32.2s , 33.8 s (3 CH$_2$), 28.1 m, 30.3 m (P(CH$_2$)$_2$P), 127.6−136.3 m (C_γ, Ph)
1c	342.2 dd (17.4, 7.9)	124.5 d (11.6)	120.9 s	204.1 dd (6.6, 4.3)	213.6 dd (21.6, 8.6)	27.8 s, 29.0 s, 29.6 s, 33.2 s, 34.0 s (5 CH$_2$), 31.0 m (P(CH$_2$)$_2$P), 128.4−138.1 m (C_γ, Ph)
1d	339.2 dd (15.5, 7.3)	120.8 d (11.9)	117.4 s	202.6 dd (7.0, 4.0)	212.1 dd (21.0, 8.9)	26.2 s, 26.5 s, 26.9 s, 27.1 s, 29.0 s, 31.2 s (6 CH$_2$), 28.5 m (P(CH$_2$)$_2$P), 128.5−136.2 m (C_γ, Ph)

[a] Spectra recorded in CDCl$_3$ (**1a**,**d**) or C$_6$D$_6$ (**1c**), δ in ppm, J in Hz. Abbreviations: s, singlet; d, doublet; m, multiplet. [b] ^2J(C−P). [c] ^3J(C−P).

stretching absorptions are consistent with the *mer*-tricarbonyl fragment. Different J(P−W) coupling constants are observed for the phosphorus resonances showing unusually small values (*ca.* 160 Hz) for the high-field signals in each complex. This is consistent with the strong *trans* influence of the vinylidene ligands and with the larger J(P−W) coupling constants (*ca.* 242 Hz) expected for phosphorus nuclei *trans* to the carbonyl ligands.[20] The alkenyl−vinylidene moiety is assessed by ^{13}C and ^{1}H NMR. Significantly, the spectra exhibit the characteristic proton and carbon resonances of the =CH− vinylidene and −C=CH- alkenyl groups (Tables 1 and 2).

(a) Cationic Tricarbonyl Carbyne Complexes. Addition of a slight excess of HBF$_4$ to a saturated green solution in diethylether of neutral vinylidene complexes **1a**, **1c**, and **1d** at −50 °C leads to the precipitation of yellow solids identified as the corresponding cationic alkenyl−carbyne complexes **2a**, **2c**, and **2d** which are isolated as the tetrafluoroborate salts (eq 2). The cationic carbyne complexes are acidic and readily undergo deprotonation when a solution in THF is treated with NBu$_3$ to regenerate the precursor vinylidene complexes.

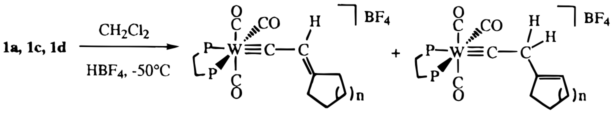


(2)

n= 1 (**2a**), 3 (**2c**), 4 (**2d**)

IR spectra (CH$_2$Cl$_2$) of **2a**, **2c**, and **2d** show two ν(CO) absorptions with an intensity pattern consistent with retention of the original *mer* geometry of the carbonyl groups. Significantly, the CO stretching bands appear (Table 3) at higher frequencies (about 70 cm^{-1}) than those of the precursor vinylidene complexes, reflecting the cationic character of the new complexes as well as the stronger π−electron attracting properties of the carbyne groups. ^{13}C and ^{31}P NMR spectra (Table 3) are also consistent with this geometry, showing, as with the precursor vinylidene complexes, the expected coupled signals for the carbyne carbon nucleus (δ *ca.* 303 ppm, dd, ^2J(C−P) = 19.2, 8.3 Hz) and phosphorus nuclei of dppe (δ *ca.* 23 and 39 ppm). In particular the phosphorus resonances exhibit the expected different J(P−W) values (*ca.* 98 and 240 Hz, respectively). The coupling constants of the low-field signals (240 Hz) are typical of the phosphines *trans* to a carbonyl group with values which can be compared to those of the corresponding vinylidene complexes (*ca.* 242 Hz). However, J(P−W) values of the high-field signals (97.6−98.5 Hz), assigned to the phosphorus nucleus *trans* to the carbyne, are smaller than those of the vinylidene complexes (*ca.* 160 Hz), reflecting the higher *trans* influence associated with a carbyne ligand.[21]

The formation of the alkenyl−carbyne species **2a**, **2c**, and **2d** is dependent on the solvent. Thus, when the protonation of the vinylidene complexes **1a**, **1c**, and **1d** is carried out in CH$_2$Cl$_2$ under similar reaction conditions, a mixture of the carbyne complexes **2a**, **2c**, and **2d** and their corresponding isomers **2a′**, **2c′**, and **2d′** is obtained (eq 3). The yellow crystalline solids isolated from these reactions were characterized as a *ca.* 1:1 mixture of the alkenyl−carbyne and the corresponding propenyl−carbyne isomers.



(3)

n=1 (**2a**), 3 (**2c**), 4 (**2d**) n=1 (**2a′**), 3 (**2c′**), 4 (**2d′**)

Additional signals to those assigned to complexes **2a**, **2c**, and **2d** can be observed in the ^{1}H, ^{13}C, and ^{31}P NMR spectra, allowing the appropriate assignments to the isomer complexes **2a′**, **2c′**, and **2d′** (Table 3). Their carbyne and phosphorus resonances exhibit coupling patterns identical with those shown by alkenyl−carbyne isomers, indicating that the *mer*-carbonyl geometry is maintained. However, the chemical shifts of the carbyne carbon nucleus are shifted to lower field ($\Delta\delta$: *ca.* 17 ppm) while those of the phosphorus *trans* to the carbyne group are shifted to higher field ($\Delta\delta$: *ca.* 1 ppm) with smaller values of J(P−W) (*ca.* 6 Hz). This seems to indicate that the propenyl−carbyne is a moiety with a slightly stronger *trans* influence than the alkenyl−carbyne.

Although we have not studied the interconversion processes of both isomers, we have found that alkenyl−carbyne complexes are exclusively isolated when mixtures of the isomers are recrystallized from THF. Likewise, selective formation of **2a**, **2c**, and **2d** also takes place when the protonation of vinylidene complexes **1a**, **1c**, and **1d** is performed in THF.

Stirring at room temperature a CH$_3$CN solution of *mer*-tricarbonyl carbyne complexes **2a** and **2d** leads to the substitution of one carbonyl ligand with concomitant isomerization, to form *trans* acetonitrile carbyne dicar-

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(20) (a) Pregosin, P. S., Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Pregosin, P. S., Ed.; Springer-Verlag: Berlin, 1979. (b) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis. Organic Compounds and Metal Complexes*; Verkade, J. G.; Quin, L. D., Eds.; VCH Publishers: Weinheim, Germany, 1987.

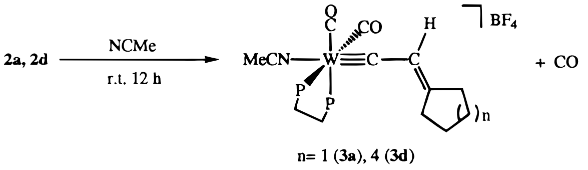
(21) Shustorovich, E. M.; Poraikoshits, M. A.; Buslaev, Yu. A. *Coord. Chem. Rev.* **1975**, *17*, 1.

Table 3. IR^a and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR^b Data for the Cationic Tricarbonyl Carbyne Complexes

	IR		^1H		$^{13}C\{^1H\}$					
	ν(CO)	$^{31}P\{^1H\}^c$	C_β-H, C_δ-H	others	$C_\alpha{}^d$	$C_\beta{}^e$	C_γ	CO *cis* to P^d	CO *trans* to P^d	others
2a	2073 w, 1999 vs	23.1 s (97.6), 39.1 s (240.0)	5.96 br, $C_\beta H$	1.73 m (2 CH_2), 2.31m (CH_2), 2.51 br (CH_2), 3.12m ($P(CH_2)_2P$), 7.41−7.66m (Ph)	303.0 dd (19.2, 8.3)	*f*	181.6s	199.6t (7.4)	204.8 dd, (21.6, 8.4)	25.2 s, 25.8 s, 33.6 s, 36.2 s (4 CH_2), 27.2 m ($P(CH_2)_2P$), 128.4−132.6 m (C_β, Ph)
2a′	2083 w, 1999 vs	22.1 s (92.3), 39.1 s (241.0)	3.40 br, $C_\beta H_2$, 5.64 br, $C_\delta H$	1.83 m (CH_2), 2.31 m (CH_2), 3.12 m (CH_2, $P(CH_2)_2P$), 7.28−7.74 m (Ph)	318.9 dd (20.1, 8.3)	55.9 d (14.5)	*f*	199.4 t (7.3)	204.0 m	23.2 s, 32.5 s, 35.4 s (3 CH_2), 27.2 m ($P(CH_2)_2P$), 127.8−134.0 m (C_γ, C_δ, Ph)
2c	2073 w, 2000 vs	23.2 s (98.5), 39.0 s (240.2)	5.82 br, $C_\beta H$	1.49 m (2 CH_2), 1.60 m (2 CH_2), 2.27 t (5.8,^{g} CH_2), 2.65 t (5.8,^{g} CH_2), 3.12 m ($P(CH_2)_2P$), 7.30−7.66 m (Ph)	303.0 m	136.2 d (15.8)	178.0 s	199.8 t (7.5)	204.6 m	26.8 s, 27.2 s, 28.9 s, 29.5 s, 34.3 s, 38.4 s (6 CH_2), 27.0 m ($P(CH_2)_2P$), 128.2−132.9 m (Ph)
2c′	2083 w, 1999 vs	22.2 s (91.6), 39.2 s (240.6)	3.14 br, $C_\beta H_2$, 5.68 t (6.2),^{g} $C_\delta H$	1.47 m (2 CH_2), 2.07 m (CH_2), 2.20 m (CH_2), 2.95 m (CH_2), 3.10 m ($P(CH_2)_2P$), 7.28−7.66 m (Ph)	320.2 m	64.6 d (13.7)	*f*	199.4 t (7.8)	204.6 m	26.4 s, 26.6 s, 28.4 s, 31.7 s, 33.9 s (5 CH_2), 27.0 m ($P(CH_2)_2P$), 128.7−136.3 m (C_γ, C_δ, Ph)
2d	2072 w, 2000 vs	23.3 s (98.4), 39.0 s (239.7)	5.88 br, $C_\beta H$	1.40 m (3 CH_2), 1.73 m (2 CH_2), 2.20 t (5.1,^{g} CH_2), 2.58 t (5.1,^{g} CH_2), 3.05 m ($P(CH_2)_2P$), 7.39−7.61 m (Ph)	302.6 dd (19.2, 8.7)	136.1 d (15.9)	181.2 s	199.9 t (7.4)	205.0 dd (21.8, 8.4)	25.4 s, 26.6 s, 26.8 s, 27.0 s, 28.0 s 33.5 s, 37.3 s (7 CH_2), 27.0 m ($P(CH_2)_2P$), 129.0−136.1 m (Ph)
2d′	2083 w, 2000 vs	22.2 s (91.6), 39.1 s (240.2)	3.15 br, $C_\beta H_2$, 5.52 t (8.1),^{g} $C_\delta H$	1.40 m (2 CH_2), 2.06 m (2 CH_2), 2.20 m (CH_2), 2.92 m (CH_2), 3.05 m ($P(CH_2)_2P$), 7.27−7.68 m (Ph)	320.6 dd (19.6, 5.4)	61.4 d (14.1)	*f*	199.4 t (7.5)	203.6 dd (21.8, 8.7)	25.8 s, 26.1 s, 25.5 s, 27.8 s, 29.4 s 29.6 s (6 CH_2), 27.0 m ($P(CH_2)_2P$), 128.2−136.1 m (C_γ, C_δ, Ph)

[a] Spectra reported in CH_2Cl_2, ν (cm^{-1}). Abbreviations: w, weak; vs, very strong. [b] Spectra recorded in $CDCl_3$, δ in ppm, J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. [c] J(P−W). [d] ^2J(C−P). [e] ^3J(C−P). [f] Overlapped by aromatic signals. [g] J(H−H).

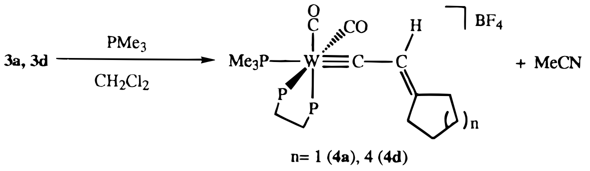
bonyl complexes *trans*-$[(dppe)(CO)_2(MeCN)W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ **3a** ($n = 1$) and **3d** ($n = 4$) (eq 4) which have both phosphorus atoms of dppe and



(4)

the two carbonyls *cis* to the carbyne ligand. The transformation of the *mer*-tricarbonyl to the *cis*-dicarbonyl complexes can be monitored in solution by IR spectroscopy which shows the typical pattern of two strong ν(CO) stretching frequencies (2011, 1943 cm^{-1} (**3a**); 2010, 1943 cm^{-1} (**3d**)). Total conversion is accomplished after *ca.* 12 h.

The presence of the coordinated MeCN ligand is confirmed by the IR (KBr) spectra which show the typical ν(C≡N) absorption (2310, 2278 cm^{-1}) and by the proton methyl resonances in the ^1H NMR spectra (δ 1.50 ppm) (Table 4). Substitution of the acetonitrile ligand in complexes **3a**, **3d** by PMe_3 is readily achieved yielding *trans*-$[(dppe)(CO)_2(Me_3P)W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2]$-$[BF_4]$ **4a** ($n = 1$), **4d** ($n = 4$) (eq 5) which were identified



(5)

by ^{31}P NMR spectra (Table 4). Resonances at δ 39.7 (**4a**) (2P, d, ^2J(P−P) = 22.8 Hz) and 39.1 (**4d**) (2P, d, ^2J(P−P) = 24 Hz) ppm are assigned to the two equivalent dppe phosphorus nuclei, and those at δ −55.6 (**4a**) (1P, t, ^2J(P−P) = 22.8 Hz) and −56.4 (**4d**) (1P, t, ^2J(P−P) = 24 Hz) ppm are assigned to the PMe_3 ligand.

Small values of J(P−W) coupling constants of 89 Hz associated with the PMe_3 ligands are in accordance with the *trans* influence of the carbyne ligands in these complexes. ^{13}C and ^1H NMR spectra display the expected resonances for the alkenyl groups (Table 4), indicating that the functionalization of the carbyne moiety does not change during the substitution processes. Significantly, carbyne carbon chemical shifts appear at a higher field (*ca.* 6 and 10 ppm) with respect to the tricarbonyl precursor complexes. This is fairly consistent with the substitution of carbonyl groups by the poorer π-acceptor ligands PMe_3 and MeCN. Larger shifting to higher fields are observed in the neutral carbyne derivatives (*vide infra*).

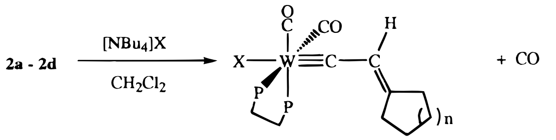
(b) Neutral Carbyne Complexes. Substitution of one carbonyl group in *mer*-$[(dppe)(CO)_3W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (**2a**, **2c**, and **2d**) or the acetonitrile ligand in *trans*-$[(dppe)(CO)_2(MeCN)W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (**3a**, **3d**) can be easily achieved by addition of $[NBu_4]X$ (X = Cl, Br, I) to CH_2Cl_2 solutions of the cationic carbyne complexes affording neutral *cis*-dicarbonyl halide complexes $[(dppe)(CO)_2XW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2]$ in good yields

Table 4. Selected IR[a] and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR[b] Data for the Dicarbonyl Carbyne Complexes[c]

	IR		^1H		$^{13}C\{^1H\}$		
	$\nu(CO)$	$^{31}P\{^1H\}$[d]	$C_\beta H$	CH_3	C_α[e]	C_γ	CO[e]
3a	2011, 1943	47.1 s (233.2)	5.34 br	1.50 s	292.0 t (8.9)	169.2 s	213.5 dd (33.7, 7.1)
3d	2010, 1943	47.0 s (233.1)	5.03 br	1.50 s	291.7 t (9.2)	168.0 s	213.5 dd (33.5, 7.1)
4a	1999, 1934	−55.6 t (22.8,[f] 89.6) , 39.7 d (22.8,[f] 228.3)	5.23 br	0.46 d, (9.5)[g]	296.9 m	171.1 d (1.5)[h]	212.9 m
4d	1998, 1932	−56.4 t (24.0,[f] 91.6), 39.1 d (24.0,[f] 227.3)	5.10 br	0.54 d (9.4)[g]	296.9 m	171.8 s	213.3 m
5a	1999, 1929	39.1 s (228.1)	4.78 br		269.8 t (9.9)	162.7 s	214.0 dd (44.5, 7.0)
5b	2000, 1930	39.3 s (228.4)	4.66 br		269.4 t (9.9)	156.8 s	213.7 dd (44.4, 6.7)
5c	2000, 1930	39.1 s (228.1)	4.62 br		269.8 t (10.0)	159.8 s	213.9 dd (44.4, 6.7)
5d	1999, 1929	39.1 s (227.8)	4.54 br		269.6 t (10.0)	161.1 s	214.0 dd (44.4, 6.8)
6a	1999, 1929	36.5 s (228.8)	4.95 br		269.0 t (9.7)	162.9 s	212.8 dd (42.8, 6.9)
6d	1999, 1930	36.4 s (228.7)	4.54 br		268.8 t (10.1)	161.5 s	212.9 dd (42.7, 6.7)
7a	1999, 1932	30.6 s (228.7)	4.91 br		267.3 t (9.8)	163.4 s	210.8 dd (40.1, 7.0)
7c	1999, 1932	30.4 s (228.6)	4.56 br		267.1 t (9.0)	160.6 s	210.8 dd (40.1, 7.2)
7d	1998, 1931	30.4 s (228.5)	4.56 br		266.9 t (10.2)	162.2 s	211.0 dd (40.1, 6.9)

[a] Spectra recorded in CH_2Cl_2, ν (cm^{-1}). All absorption are very strong. [b] Spectra recorded in $CDCl_3$, unless ^1H NMR of **4a** (CD_2Cl_2), δ in ppm, J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [c] For additional data see Experimental Section. [d] $J(P-W)$. [e] $^2J(C-P)$. [f] $^2J(P-P)$. [g] $^2J(H-P)$. [h] $^4J(C-P)$.

(eq 6). Complex **5b** ($n = 2$; X = Cl) is obtained directly in low yield (25%) by treatment of the mixture containing the alkenyl–vinylidene complex *mer*-[(dppe)-$(CO)_3W{=}C{=}CHC{=}CH(CH_2)_3CH_2$] (*vide supra*) with HBF_4 followed by the addition of $[NBu_4]Cl$ and after chromatography workup.



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Complex	**5a**	**5b**	**5c**	**5d**	**6a**	**6d**	**7a**	**7c**	**7d**
X	Cl	Cl	Cl	Cl	Br	Br	I	I	I
n	1	2	3	4	1	4	1	3	4

IR spectra (CH_2Cl_2) (Table 4) show the typical two $\nu(CO)$ carbonyl stretching absorptions in the range of 1929–2000 cm^{-1} for *cis*-dicarbonyl complexes, indicating that the substitution takes place with isomerization of the original geometry in the precursor *mer*-tricarbonyl species. As expected from the transformation of cationic to neutral complexes, a lowering in the absorption frequencies (average 74 cm^{-1}) is observed. The phosphorus resonances appear in the ^{31}P NMR spectra (Table 4) as singlet signals, indicating the chemical equivalence of the phosphorus atoms of dppe and therefore in accordance with this *trans* carbyne halide arrangement. $J(P-W)$ values (*ca.* 228.5 Hz) are similar to those found (*vide supra*) for resonances of phosphorus nuclei *trans* to carbonyl ligands. Single signals are also observed at low temperatures (*ca.*170 K). However, the X-ray crystal structure determination of **5a** (*vide infra*) shows that the orientation of the carbyne alkenyl moiety is such that the phosphorus atoms of dppe are chemically inequivalent in the solid state since the cyclopentane ring is closer to one of them (see Figure 1).

The carbyne carbon ^{13}C resonances of the halide carbyne complexes *trans*-[$(dppe)(CO)_2XW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2$] appear as triplet signals in the range of δ 266.9–269.8 ($^2J(P-P)$ *ca.* 10 Hz) (Table 4), which are close to the signal (δ 276.3 ppm) reported for *trans*-[$(dppe)(CO)_2ClW{\equiv}CCH_2Ph$][14] and at higher field (*ca.* 35 ppm) than those of the corresponding cationic carbyne complexes. ^1H and ^{13}C NMR spectra also exhibit ethylene (PCH_2CH_2P), alkenyl (=CH–), and methylene (–CH_2–) signals of dppe and the cyclic alkenyl–carbyne chain in accord with the proposed structure of the complexes. In addition, the structure of complex **5a** has been determined by X-ray diffraction methods.

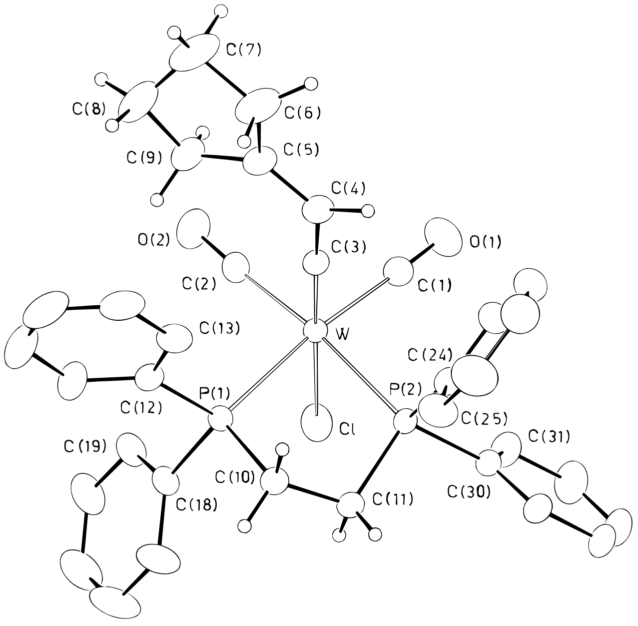


Figure 1. ORTEP view of the molecular structure of the complex [$(dppe)(CO)_2ClW{\equiv}CCH{=}CCH_2CH_2CH_2CH_2$] (**5a**) with the atom numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

The structure of complex **5a** is shown in Figure 1 together with the atom numbering scheme; selected bond distances and angles are given in Table 5. The W atom displays a distorted octahedral coordination with the two apical positions occupied by a Cl atom [W–Cl = 2.540(1) Å] and by a C atom from the alkenyl-carbyne group [W–C = 1.830(3) Å], two *cis*-equatorial sites being occupied by CO group [W–C(1) = 2.034(4) and W–C(2) = 2.014(3) Å] and the other two by P atoms from the chelating dppe ligand [W–P(1) = 2.539(1) and W–P(2) = 2.524(1) Å]. The W atom deviates slightly [0.0748(3) Å] from the mean plane through the four equatorial

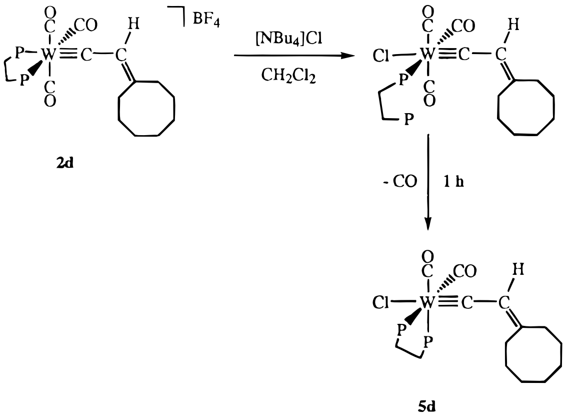
Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 5a

W−Cl	2.540(1)	W−C(3)	1.830(3)
W−P(1)	2.539(1)	W−P(2)	2.524(1)
W−C(1)	2.034(4)	W−C(2)	2.013(3)
P(1)−C(10)	1.846(3)	P(2)−C(11)	1.846(4)
P(1)−C(12)	1.834(3)	P(2)−C(24)	1.824(3)
P(1)−C(18)	1.825(3)	P(2)−C(30)	1.825(3)
O(1)−C(1)	1.121(5)	O(2)−C(2)	1.135(4)
C(3)−C(4)	1.432(4)	C(5)−C(6)	1.511(5)
C(4)−C(5)	1.359(5)	C(5)−C(9)	1.487(5)
C(6)−C(7)	1.500(7)	C(7)−C(8)	1.531(7)
C(8)−C(9)	1.532(7)	C(10)−C(11)	1.524(4)
C(2)−W−C(3)	89.3(1)	W−C(1)−O(1)	178.0(3)
C(1)−W−C(3)	90.3(1)	W−C(2)−O(2)	176.5(3)
C(1)−W−C(2)	89.8(1)	W−C(3)−C(4)	178.9(2)
P(2)−W−C(3)	94.3(1)	C(3)−C(4)−C(5)	123.3(3)
P(2)−W−C(1)	94.7(1)	C(4)−C(5)−C(9)	125.4(3)
P(1)−W−C(3)	94.1(1)	C(4)−C(5)−C(6)	124.9(3)
P(1)−W−C(2)	95.5(1)	C(6)−C(5)−C(9)	109.7(3)
P(1)−W−P(2)	79.7(0)	C(5)−C(6)−C(7)	104.7(3)
Cl−W−C(2)	90.3(1)	C(6)−C(7)−C(8)	103.4(4)
Cl−W−C(1)	88.2(1)	C(7)−C(8)−C(9)	104.6(4)
Cl−W−P(2)	86.2(0)	C(5)−C(9)−C(8)	104.1(3)
Cl−W−P(1)	87.5(0)		

atoms toward the C(3) atom. To the best of our knowledge, there are no examples of structurally characterized tungsten complexes in which an alkenyl−carbyne group is present. The length of the W−C triple bond is comparable to those found in the related complexes [(η^5-C_5H_5)(CO)$_2$W≡C(Tol)], 1.82(2) Å,[22] and [(η^5-C_5H_5)(CO)$_2$W≡C(2-C_4H_3S)], 1.828(10) Å,[7b] in which the W atoms shows a three-legged piano-stool coordination. Of note is the remarkable carbyne *trans* influence, the value of the W−Cl bond length being much longer than the average one found in about 80 hexacoordinate tungsten complexes [2.388 Å, from Cambridge Crystallographic Data Base].

The pentaatomic ring displays a twist conformation with the C(7) and C(8) atoms out of the mean plane through the WC(3)C(4)C(5)C(6)C(9)H(4) fragment by −0.314(7) and 0.242(6) Å, respectively. This plane forms angles of 21.0(2) and 74.0(1)° with the W−C(2) and W−C(1) lines, respectively.

In order to study the mechanism of the isomerization involved in the formation of these complexes, we have monitored by ^{31}P NMR the reaction of *mer*-[(dppe)(CO)$_3$W≡CCH=$\overline{C(CH_2)_6CH_2}$][BF$_4$] (**2d**) with [NBu$_4$]Cl in CH_2Cl_2. The first reaction step is apparently very fast since after 5 min the signals of the starting *mer*-tricarbonyl complex at δ 23.3 and 39.0 ppm are no longer observed. Instead new signals appear: a singlet at δ 39.3, assigned to the final carbyne dicarbonyl complex **5d**, and two doublets at δ 15.5 and −11.9 ppm (^3J(P−P) = 39 Hz), a typical pattern for a monodentate coordination of dppe. After *ca.* 60 min the spectrum only shows the singlet signal of **5d** at 39.3 ppm. We believe that the substitution proceeds through the dissociation of the phosphorus atom *trans* to the carbyne group and concomitant coordination of the entering chloride ligand to give a not isolated intermediate species, *mer*-[{κ(*P*)-Ph$_2$P(CH$_2$)$_2$PPh$_2$}(CO)$_3$ClW≡CCH=$\overline{C(CH_2)_6CH_2}$] in which the phosphine is acting as a monodentate ligand (eq 7). Subsequent replacement of



(7)

one carbonyl group by the uncoordinated phosphorus atom leads to the final *cis*-dicarbonyl carbyne complex *trans*-[(dppe)(CO)$_2$ClW≡CCH=$\overline{C(CH_2)_6CH_2}$] (**5d**). The formation of the tricarbonyl intermediate species is also confirmed by IR in the ν(CO) stretching region, which shows new absorptions at 2074 and 1997 cm^{-1} along with that corresponding to the dicarbonyl complex **5d**.

(c) ^{183}W NMR studies. ^{183}W NMR data,[23] particularly on organometallic compounds, are scarce because of the low receptivity of this nucleus ($R^C = 6.08 \times 10^{-2}$). To date only one report of ^{183}W NMR spectra of Fischer-type[24] and another one of Schrock-type tungsten carbyne complexes[25] are known in the literature. In both cases direct observation of the transition metal was used, a time consuming method in which applicability is limited by the solubility and/or stability of the sample. In all of the complexes here discussed the tungsten atom is bonded to a bidentate phosphine ligand showing large ^{31}P−^{183}W coupling constants ($^1J(^{31}P-^{183}W)$ = 91.6−243.3 Hz), very suitable to be used in two-dimensional indirect ^{31}P, ^{183}W recording techniques. This methodology is based on the HMQC pulse sequence of Bax *et al.*,[26] with additional proton decoupling throughout all the experiment, and has been successfully exploited in the NMR characterization of low γ nuclei.[27] In this way an increase in the signal to noise (*S*/*N*) ratio by a factor $(\gamma_P/\gamma_W)^{5/2}$, with respect to the direct ^{183}W detection, is predicted. Table 6 collects ^{183}W NMR data for the series of complexes **1a**−**7a** having a five-membered ring in the vinylidene or carbyne moiety. 2D ^{31}P, ^{183}W{^{1}H} HMQC correlations have been used to characterize the ^{183}W chemical shifts which are in the range of −2598/−1739 ppm and therefore spanning 859 ppm. The ^{183}W NMR spectrum of a mixture of the complexes **2a** and **2a′** is shown in Figure 2.

The substitution of one carbonyl ligand in the alkenyl−carbyne complex **2a** by PMe$_3$, CH$_3$CN, or halides

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Table 6. δ^{183}W Chemical Shifts of the Compounds 1a−7a

compound	$\delta(^{183}W)^a$	compound	$\delta(^{183}W)^a$
1a	−2596	**4a**	−2018
2a	−2218	**5a**	−1739
2a′	-2262^b	**6a**	−1786
3a	−1786	**7a**	−1891

[a] Referred to Na_2WO_4. [b] Measured from a sample containing a 40:60 mixture of **2a**:**2a′**.

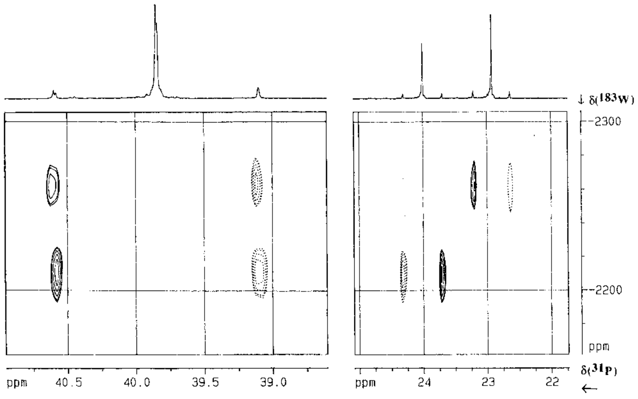

Figure 2. 161.98 MHz ^{31}P, $^{183}W\{^1H\}$ HMQC spectrum of a mixture of **2a** and **2a′** in a ratio of 40:60. The dephasing delay of $^1J(P-W)$ was set to 2.9 ms, and 112 t_1 increments were recorded with an accumulation of 128 scans each. The spectrum was acquired in the TPPI mode without refocusing. Negative cross peaks are represented by dotted lines. All other parameters were as described in the Experimental Section.

to give the complexes **3a**−**7a** leads to a deshielding of the ^{183}W nucleus (Table 6). Complexes **5a**−**7a** exhibit a "normal halogen dependence" with a small $\delta(^{183}W)$ difference between the chloride and bromide complexes and larger shielding effect in the iodide derivative. A similar trend has been observed in W(II) carbonyl complexes.[28] It is worth mentioning the upfield shift of 296 ppm shown by the alkenyl−carbyne complex **5a** (δ −1739 ppm) compared to the resonance of the analogous compound[24] $[(dppf)(CO)_2ClW{\equiv}CC_6H_5]$ (dppf= 1,1'-bis(diphenylphosphino)ferrocene) (δ −1443 ppm). Although it has been claimed that similar electronic effects are expected for dppf and other similar bidentate phosphines,[24] in fact, when the $\delta(^{183}W)$ of $[W(CO)_6]$ (δ −3483 ppm), $[W(CO)_4(dppe)]$ (δ −3291 ppm) and $[W(CO)_4(dppf)]$ (δ −3023 ppm) are compared, it is found that dppf has a deshielding effect 268 ppm larger than dppe. Introducing this correction value for the comparison of the ^{183}W chemical shifts of complexes **5a** (δ −1739 ppm) and $[(dppf)(CO)_2ClW{\equiv}CC_6H_5]$ (δ −1443 ppm), a net high-field shift of only 28 ppm is obtained for the former. Providing that structural effects can be neglected, since similar pseudooctahedron geometry around the tungsten atoms are shown by the X-ray crystal structures of both complexes, the difference in the shielding can be attributed to the substituents in the carbyne moieties.

For heavy nuclei the chemical shift is largely controlled by the paramagnetic contribution[29] (σ^p) to the total shielding constant σ given by the Ramsey equation[30]

$$\sigma = \sigma^p + \sigma^d$$

Assuming that the σ^p term is dominated by the average electronic excitation energy, $\sigma^p \propto (\Delta\epsilon)^{-1}$, then the observed $\delta(^{183}W)$ can be rationalized according to the ligand π-bonding ability. A good π-acceptor ligand is able to stabilize the filled d-orbitals of the metal through back-bonding and consequently $\Delta\epsilon$ will increase to give a high field metal chemical shift. The downfield shifting of ^{183}W resonances observed for complexes **2a**−**7a** (Table 6) as the π-back-donation becomes smaller[31] is in accordance with the well-known π-acceptor ability of the ligands CO > PMe_3 > CH_3CN ≥ halide. On the other hand, it is interesting to note the 378 ppm ^{183}W deshielding of **2a** with respect to **1a** which can be ascribed to the different π-acceptor properties of the alkenyl−carbyne *vs* the alkenyl−vinylidene moieties and the cationic nature of complex **2a**.

Concluding Remarks

Novel alkenyl−vinylidene tungsten(0) complexes *mer*-$[(dppe)(CO)_3W{=}C{=}CHC{=}CH(CH_2)_nCH_2CH_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) have been prepared in good yields. In this work we have developed an efficient route for the synthesis of cationic alkenyl−carbyne complexes *mer*-$[(dppe)(CO)_3W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ from the vinylidene derivatives which undergo regioselective electrophilic addition of protons, in diethyl ether or THF as solvents, at the C_δ of the alkenyl-vinylidene moiety. These alkenyl−carbyne complexes have proven to be good precursors for the high-yield preparation of an extensive series of derivatives: a) cationic derivatives *trans*-$[(dppe)(CO)_2LW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (L = CH_3CN, PMe_3; n = 1, 4) and (b) neutral ones *trans*-$[(dppe)(CO)_2XW{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2]$ (X = Cl, n = 1−4; X = Br, n = 1, 4; X = I, n = 1, 3, 4) which have been prepared by conventional carbonyl substitution reactions. $^{31}P\{^1H\}$ and ^{183}W NMR studies on analogous members of these series allow one to get information on the *trans* influence and the electronic nature of the unsaturated carbyne and carbene moieties. In this regard $^1J(P-W)$ values reveal unusually low values (*ca.* 90 Hz) for the alkenyl−carbyne groups compared to those for alkenyl−vinylidene moieties (*ca.* 160 Hz) and carbonyl ligands (*ca.* 240 Hz), indicating a high *trans* influence of the carbyne group. The coupling constants found in the carbyne complexes are the lowest ever reported along with that shown by a cyclopentadienyl bridged binuclear complex.[27a] This supports the mechanism of the substitution reactions in the tricarbonyl alkenyl−carbyne complexes in which a dissociation of the phosphorus atom of dppe, *trans* to the carbyne

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moiety, is proposed as the first step of the reactions. Even though a clear relationship between oxidation state and ^{183}W chemical shifts in tungsten complexes has not been established,[23] we have found that there is a significant downfield shifting of ^{183}W resonances for the formally W(II) carbyne complexes compared to the analogous W(0) vinylidene derivatives.

In summary, in this work a systematic and simple entry for the preparation of alkenyl−carbyne tungsten complexes is described. Since the analogous α,β unsaturated carbene derivatives are currently one of the most important synthons in organic synthesis, the novel carbyne derivatives provide appropriate substrates for similar reactivity studies.

Experimental Section

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 complex *fac*-[$W(CO)_3(dppe)(Me_2CO)$] was prepared as reported in the literature by a modified method.[32] Tungsten hexacarbonyl (Strem Chemicals), alkynols (Lancaster Chemical Co.), and $HBF_4 \cdot OEt_2$, PMe_3, and [NBu_4]X (X= Cl, Br, I) (Aldrich Chemical Co.) were used as received.

Infrared 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 AC300 instrument was configured with a triple probe (^{1}H, ^{13}C, ^{31}P). The AMX400 instrument was equipped with a third radiofrequency channel. A 5 mm reverse triple probe head was used. The inner coil was doubly tuned for ^{1}H and ^{31}P, and the outer coil was tunable in the frequency range 18−160 MHz. Even though at 9.4 T the frequency of the ^{183}W nucleus lies outside the specifications of the probe, it could be tuned so that a pulse of a reasonable width was obtained. The pulse widths for the 90° pulses and operating frequencies were as follows: 10.4/13.0 μs (^{1}H, 400/300 MHz), 14.5/7.0 μs (^{13}C, 100.6/75.5 MHz), 14.5/10 μs (^{31}P, 161.98/121.5 MHz), and 53 μs (^{183}W, 16.65 MHz). The attenuation levels used in the AMX400 apparatus were 5 dB for the proton channel and 3 dB for the heteronuclei. The spectral references used were tetramethylsilane for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, and Na_2WO_4 for ^{183}W.

Selected spectral parameters in the AMX400 spectrometer were as follows. One-dimensional ^{1}H NMR: 32 K data points; spectral width 4000 Hz. ^{13}C NMR: 64 K data point; spectral width 36 000; exponential multiplication with a line broadening factor of 1 Hz. ^{31}P NMR: 32 K data points; spectral width 3500 Hz; exponential line broadening of 1 Hz. ^{31}P, ^{183}W{^{1}H} 2D HMQC: spectral width, 3500 Hz in F2 and 1000 Hz in F1; 96 increments recorded; final matrix after zero filling, 1024 × 256; evolution delay of ^1J(P−W), 2.2 ms; 80 scans per increment in F1; TPPI mode; qsine multiplication of $\pi/2$ in both dimensions prior to transformation. In each case a first experiment with a large sweep width in F1 was run (up to 50 000 Hz). Subsequently, the spectral window of the tungsten nucleus was reduced to 1000 Hz to ensure that no folding in the F1 dimension occurred and to improve the digital resolution.

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{183}W NMR spectroscopic data for the alkenyl−vinylidene and alkenyl−carbyne complexes are collected in Tables 1−4 and 6.

***fac*-[$W(CO)_3(dppe)(Me_2CO)$].** A mixture of [$W(CO)_6$] (0.25 g, 0.7 mmol) and dppe (0.3 g, 0.7 mmol) in 75 mL of acetone was irradiated by a high-pressure Hg lamp (450 W). The reaction was monitored by IR in the ν(CO) region. The irradiation was discontinued (*ca.* 10 h) when absorptions of $W(CO)_5$(dppe) and $W(CO)_4$(dppe) were no longer observed. The resulting deep yellow solution was transferred *via* stainless steel tubing to a Schlenk flask and the solvent removed under vacuum. The yellow solid residue was triturated and washed with 2 × 10 mL of a 3:1 hexane−diethylether mixture to give a yellow powder of *fac*-[$W(CO)_3(dppe)(Me_2CO)$] which was dried under vacuum. The yield was nearly quantitative, but the solid was contaminated with traces of [$W(CO)_4$(dppe)]. Nevertheless this material was used without further purification for the subsequent syntheses.

***mer*-[(dppe)$(CO)_3W{=}C{=}CHC{=}CH(CH_2)_nCH_2CH_2$] (*n* = 1 (1a), 3 (1c), 4 (1d)). General Procedure.** A mixture of *fac*-[$W(CO)_3(dppe)(Me_2CO)$] (0.50 g, 0.69 mmol) and the corresponding alkynol (1.4 mmol) in 5 mL of tetrahydrofuran (THF) was stirred overnight (*ca.* 10−12 h) at room temperature. The color of the solution changed from deep brown to deep green. After the solvent was removed, the resulting green tar residue was extracted with diethyl ether at −20 °C. Removal of the solvent and washing with hexane at −20 °C gave the desired compounds as green solids. Yield: **1a**, 73%; **1c**, 30%; **1d**, 73%. Mass spectrum and analytical data for **1a**: MS (FAB, *m*/*e*) [M$^+$] = 759, [M$^+$ − CO] = 731. Anal. Calcd for $C_{36}H_{32}O_3P_2W$: C, 57.01; H, 4.25. Found: C, 56.75; H, 4.38. Analytical data for **1c**: Anal. Calcd for $C_{38}H_{36}O_3P_2W$: C, 58.03; H, 4.61. Found: C, 59.17; H, 4.18. Mass spectrum and analytical data for **1d**: MS (FAB, *m*/*e*) [M$^+$] = 801, [M$^+$ - CO] = 773. Anal. Calcd for $C_{39}H_{38}O_3P_2W$: C, 58.52; H, 4.78. Found: C, 58.69; H, 4.56.

***mer*-[(dppe)$(CO)_3W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2$][$BF_4$] (n = 1 (2a), 3 (2c), 4 (2d)). General Procedure.** A green saturated solution (0.5 mmol) of **1a**−**1d** in diethyl ether was cooled to −50 °C, and 60 μL (0.5 mmol) of $HBF_4 \cdot OEt_2$ (80% (w/w) in diethyl ether) was added by syringe. The mixture was stirred at −50 °C for 0.5 h and then allowed to warm to −5 °C, leading to the precipitation of a yellow solid. Removal of the solvent and washing the resulting solid with cold diethyl ether (3 × 10 mL) gave the desired compounds **2a**, **2c**, and **2d** as yellow solids. Yield: **2a**, 86%; **2c**, 80%; **2d**, 84%. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): **2a**, 114; **2c**, 122; **2d**, 109. Spectral and analytical data for **2a**: IR (KBr, ν(BF)) 1059 (s, br). MS (FAB, *m*/*e*) [M$^+$ − BF_4] = 759, [M$^+$ − BF_4 − 2CO] = 731. Anal. Calcd for $C_{36}H_{33}BF_4O_3P_2W$: C, 51.10; H, 3.93. Found: C, 50.80; H, 4.03. Spectral and analytical data for **2c**: IR (KBr, ν(BF)) 1057 (s, br). MS (FAB, *m*/*e*) [M$^+$ − BF_4] = 787, [M$^+$ − BF_4 − 2CO] = 759. Anal. Calcd for $C_{38}H_{37}BF_4O_3P_2W$: C, 52.20; H, 4.26. Found: C, 54.16; H, 4.55. Spectral and analytical data for **2d**: IR (KBr, ν(BF)) 1059 (s, br). MS (FAB, *m*/*e*) [M$^+$ − BF_4] = 801, [M$^+$ − BF_4 − 2CO] = 773. Anal. Calcd for $C_{39}H_{39}BF_4O_3P_2W$: C, 52.73; H, 4.42. Found: C, 52.10; H, 4.37.

***trans*-[(dppe)$(CO)_2$(MeCN)$W{\equiv}CCH{=}CCH_2(CH_2)_n$-$CH_2CH_2$][$BF_4$] (n = 1 (3a), 4 (3d)). General Procedure.** A yellow solution of **2a** or **2d** (0.24 mmol) in 20 mL of acetonitrile was stirred overnight (*ca.* 12 h) at room temperature. Removal of the solvent and washing the residue with diethyl ether gave **3a** and **3d** as yellow solids. Yield: **3a**, 84%; **3d**, 91%. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): **3a**, 110; **3d**, 125. Spectral and analytical data for **3a**: IR (KBr, ν(C≡N), ν(BF)) 2310 (vw), 2278 (vw), 1062 (s, br). ^{1}H NMR (δ, $CDCl_3$) 1.19 (m, 2H, CH_2), 1.50 (m, 4H, 2CH_2), 2.05 (m, 2H, CH_2), 2.55 (m), 3.17 (m, 4H, $P(CH_2)_2P$), 7.32−7.71 (m, 20H, PPh_2). ^{13}C{^{1}H} NMR (δ, $CDCl_3$) 1.9 (s, $NCCH_3$), 25.5 (s, CH_2), 26.1 (s, CH_2), 27.2 (m, $P(CH_2)_2P$), 32.2 (s, CH_2), 34.7 (s, CH_2), 127.8−135.6 (m, C_β, $NCCH_3$, PPh_2). MS (FAB, *m*/*e*) [M$^+$] = 859, [M$^+$ − BF_4 − NCMe] = 731, [M$^+$ − BF_4 − NCMe − 2CO] = 675. Anal.

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Calcd for $C_{37}H_{36}BF_4NO_2P_2W$: C, 51.72; H, 4.22; N, 1.63. Found: C, 51.74; H, 4.43; N, 1.35. Spectral and analytical data for **3d**: IR (KBr, ν(C≡N), ν(BF)) 2313 (vw), 2278 (vw), 1063 (s, br). ^1H NMR (δ, $CDCl_3$) 1.41 (m, 8H, 4 CH_2), 1.73 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 2.43 (m, 2H, CH_2), 2.55 (m), 3.18 (m, 4H, $P(CH_2)_2P$), 7.31−7.71 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 1.7 (s, $NCCH_3$), 25.3 (s, CH_2), 26.7 (br, 4 CH_2), 27.2 (m, $P(CH_2)_2P$), 32.0 (s, CH_2), 35.6 (s, CH_2), 128.6−134.6 (m, C_β, $NCCH_3$, PPh_2). MS (FAB, *m/e*) [$M^+ - BF_4 - NCMe$] = 773. Anal. Calcd for $C_{40}H_{42}BF_4NO_2P_2W$: C, 53.30; H, 4.70; N, 1.55. Found: C, 52.71; H, 4.84; N, 0.87.

***trans*-[(dppe)(CO)$_2$(Me$_3$P)W≡CCH=CCH$_2$(CH$_2$)$_n$CH$_2$CH$_2$][BF$_4$] (n = 1 (4a), 4 (4d)). General Procedure.** 1 equiv amount of PMe_3 was added at room temperature by syringe to a yellow solution of **3a** or **3d** (0.2 mmol) in 10 mL of dichloromethane. The substitution was accomplished in 5 min and could be monitored by IR (ν(CO) stretching range). Removal of the solvent and washing of the residue with diethyl ether gave the desired compounds **4a** and **4d** as yellow solids. Yield: **4a**, 87%; **4d**, 87%. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): **4a**, 128; **4d**, 122. Spectral and analytical data for **4a**: IR (KBr, ν(BF)) 1059 (s, br). ^1H NMR (δ, CD_2Cl_2) 1.34 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 2.72 (m), 3.04 (m, 4H, $P(CH_2)_2P$), 7.30−7.61 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 15.0 (d, *J*(C-P) = 23.2 Hz, $P(CH_3)_3$), 25.2 (s, CH_2), 26.1 (s, CH_2), 26.4 (m, $P(CH_2)_2P$), 32.4 (s, CH_2), 35.2 (s, CH_2), 128.6−135.2 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - BF_4$] = 807, [$M^+ - BF_4 - PMe_3$] = 731. Anal. Calcd for $C_{38}H_{42}BF_4O_2P_3W$: C, 51.04; H, 4.73. Found: C, 51.48; H, 4.19. Spectral and analytical data for **4d**: IR (KBr, ν(BF)) 1058 (s, br). ^1H NMR (δ, $CDCl_3$) 1.51 (m, 8H, 4 CH_2), 1.79 (m, 2H, CH_2), 2.03, (m, 2H, CH_2), 2.54 (m, 2H, CH_2), 2.80 (m), 3.33 (m, 4H, $P(CH_2)_2P$), 7.35−7.84 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 14.9 (d, *J*(C−P) = 23.0 Hz, $P(CH_3)_3$), 25.4 (s, CH_2), 25.9 (s, CH_2), 26.4 (s, CH_2), 26.5 (m, $P(CH_2)_2P$), 27.1 (s, CH_2), 28.0 (s, CH_2), 32.6 (s, CH_2), 35.8 (s, CH_2), 128.1−135.2 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - BF_4$] = 849, [$M^+ - BF_4 - PMe_3$] = 773. Anal. Calcd for $C_{41}H_{48}BF_4O_2P_3W$: C, 52.59; H, 5.17. Found: C, 50.84; H, 5.38.

***trans*-[(dppe)(CO)$_2$ClW≡CCH=CCH$_2$(CH$_2$)$_n$CH$_2$CH$_2$] (*n* = 1 (5a), 3 (5c), 4 (5d)). General Procedure.** A yellow solution of **2a**, **2c**, or **2d** (0.2 mmol) and 1 equiv of $[NBu_4]Cl$ in 10 mL of dichloromethane 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 gave the desired compounds **5a**, **5c**, and **5d** as bright yellow solids. Yield: **5a**, 89%; **5c**, 74%; **5d**, 90%. Spectral and analytical data for **5a**: ^1H NMR (δ, $CDCl_3$) 1.38 (m, 4H, 2 CH_2), 1.85 (m, 2H, CH_2), 1.94 (m, 2H, CH_2), 2.49 (m), 2.78 (m, 4H, $P(CH_2)_2P$), 7.27−7.65 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 25.7 (s, CH_2), 26.2 (s, CH_2), 27.2 (m, $P(CH_2)_2P$), 31.4 (s, CH_2), 34.2 (s, CH_2), 128.2−133.0 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - Cl$] = 731, [$M^+ - 2CO$] = 711. Anal. Calcd for $C_{35}H_{33}ClO_2P_2W$: C, 54.82; H, 4.34. Found: C, 54.06; H, 4.33. Spectral and analytical data for **5c**: ^1H NMR (δ, $CDCl_3$) 1.34 (m, 8H, 4 CH_2), 1.79 (m, 2H, CH_2), 2.23 (m, 2H, CH_2), 2.50 (m), 2.80 (m, 4H, $P(CH_2)_2P$), 7.28−7.66 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 27.1 (s, CH_2), 27.2 (m, $P(CH_2)_2P$), 27.6 (s, CH_2), 29.3 (s, CH_2), 30.0 (s, CH_2), 32.3 (s, CH_2), 37.1 (s, CH_2), 128.2−136.2 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - Cl$] = 760, [$M^+ - 2CO$] = 739. Anal. Calcd for $C_{37}H_{37}ClO_2P_2W$: C, 55.90; H, 4.69. Found: C, 56.20; H, 4.80. Spectral and analytical data for **5d**: ^1H NMR (δ, $CDCl_3$) 1.35 (m, 8H, 4 CH_2), 1.69 (m, 4H, 2 CH_2), 2.30 (m, 2H, CH_2), 2.50 (m), 2.80 (m, 4H, $P(CH_2)_2P$), 7.26−7.66m (20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 25.6 (s, CH_2), 26.8 (s, CH_2), 26.89 (s, CH_2), 26.92 (s, CH_2), 26.97 (s, CH_2), 27.2 (m, $P(CH_2)_2P$), 31.5 (s, CH_2), 35.8 (s, CH_2), 128.2−135.7 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - Cl$] = 773, [$M^+ - 2CO$] = 752. Anal. Calcd for $C_{38}H_{39}ClO_2P_2W$: C, 56.42; H, 4.86. Found: C, 56.47; H, 4.89.

***trans*-[(dppe)(CO)$_2$BrW≡CCH=CCH$_2$(CH$_2$)$_n$CH$_2$CH$_2$] (*n* = 1 (6a), 4 (6d)). General Procedure.** A yellow solution of **2a** or **2d** (0.2 mmol) and 1 equiv of $[NBu_4]Br$ in 10 mL of dichloromethane was heated at reflux for 2 h. The mixture was worked up as described above for isolation of **5a**, **5c**, and **5d** to yield the desired compounds **6a** and **6d** as bright yellow solids. Yield: **6a**, 90%; **6d**, 90%. Spectral and analytical data for **6a**: ^1H NMR (δ, $CDCl_3$) 1.48 (m, 4H, 2 CH_2), 1.91 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 2.54 (m), 2.94 (m, 4H, $P(CH_2)_2P$), 7.32−7.71 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 25.7 (s, CH_2), 26.2 (s, CH_2), 27.1 (m, $P(CH_2)_2P$), 31.6 (s, CH_2), 34.4 (s, CH_2), 128.2−136.2m (C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - Br$] = 731, [$M^+ - 2CO$] = 755. Anal. Calcd for $C_{35}H_{33}BrO_2P_2W$: C, 51.81; H, 4.10. Found: C, 51.60; H, 4.20. Spectral and analytical data for **6d**: ^1H NMR (δ, $CDCl_3$) 1.40 (m, 8H, 4 CH_2), 1.72 (m, 4H, 2 CH_2), 2.34 (m, 2H, CH_2), 2.49 (m), 2.88 (m, 4H, $P(CH_2)_2P$), 7.25−7.65 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 25.6 (s, CH_2), 26.7−27.6 (m, 4 CH_2, $P(CH_2)_2P$), 31.7 (s, CH_2), 36.0 (s, CH_2), 128.2−136.2 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - Br$] = 773, [$M^+ - 2CO$] = 798. Anal. Calcd for $C_{38}H_{39}BrO_2P_2W$: C, 53.48; H, 4.61. Found: C, 53.32; H, 4.82.

***trans*-[(dppe)(CO)$_2$IW≡CCH=CCH$_2$(CH$_2$)$_n$CH$_2$CH$_2$] (*n* = 1 (7a), 3 (7c) 4 (7d)). General Procedure.** A yellow solution of **2a**, **2c**, or **2d** (0.2 mmol) and 1 equiv of $[NBu_4]I$ in 10 mL of dichloromethane was heated at reflux for 5 h. The mixture was worked up as described above for isolation of **5a**, **5c**, and **5d** to yield the desired compounds **7a**, **7c**, and **7d** as bright yellow solids. Yield: **7a**, 86%; **7c**, 71%; **7d**, 89%. Spectral and analytical data for **7a**: ^1H NMR (δ, $CDCl_3$) 1.53 (m, 4H, 2 CH_2), 1.88 (m, 2H, CH_2), 2.01 (m, 2H, CH_2), 2.57 (m), 3.00 (m, 4H, $P(CH_2)_2P$), 7.33−7.71 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 25.7 (s, CH_2), 26.2 (s, CH_2), 27.4 (m, $P(CH_2)_2P$), 32.0 (s, CH_2), 34.8 (s, CH_2), 128.1−136.4 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - 2CO$] = 802, [$M^+ - I$] = 731. Anal. Calcd for $C_{35}H_{33}IO_2P_2W$: C, 48.98; H, 3.88. Found: C, 49.46; H, 3.99. Spectral and analytical data for **7c**: ^1H NMR (δ, $CDCl_3$) 1.37 (m, 8H, 4 CH_2), 1.80 (m, 2H, CH_2), 2.24 (m, 2H, CH_2), 2.50 (m), 2.95 (m, 4H, $P(CH_2)_2P$), 7.24−7.63 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 26.8−32.2 (m, 3 CH_2, $P(CH_2)_2P$), 29.4 (s, CH_2), 32.8 (s, CH_2), 37.6 (s, CH_2), 128.2−136.2 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - 2CO$] = 830, [$M^+ - I$] = 760. Anal. Calcd for $C_{37}H_{37}IO_2P_2W$: C, 50.14; H, 4.21. Found: C, 50.66; H, 4.60. Spectral and analytical data for **7d**: ^1H NMR (δ, $CDCl_3$) 1.48 (m, 8H, 4 CH_2), 1.83 (m, 4H, 2 CH_2), 2.44 (m, 2H, CH_2), 2.58 (m), 3.04 (m, 4H, $P(CH_2)_2P$), 7.34−7.72 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 25.5 (s, CH_2), 26.6−29.7 (m, 4 CH_2, $P(CH_2)_2P$), 31.9 (s, CH_2), 36.3 (s, CH_2), 126.8−136.2 (m, C_β, PPh_2). MS (FAB, *m/e*) [$M^+ - 2CO$] = 844, [$M^+ - I$] = 773. Anal. Calcd for $C_{38}H_{39}IO_2P_2W$: C, 50.69; H, 4.37. Found: C, 51.61; H, 4.63.

***trans*-[(dppe)(CO)$_2$ClW≡CCH=CCH$_2$(CH$_2$)$_2$CH$_2$CH$_2$] (5b).** A mixture of *fac*-[W(CO)$_3$(dppe)(Me$_2$CO)] (0.18 g, 0.25 mmol) and 1-ethynylcyclohexanol (62 mg, 0.5 mmol) in 2 mL of tetrahydrofuran (THF) was stirred for 6 h at room temperature. After the solvent was removed, the resulting green brown tar residue was extracted with diethyl ether at −50 °C. Removal of the solvent and washing of the residue with cold hexane (2 × 5 mL) yielded a pale green solid. It was identified as a mixture of *mer*-[(dppe)(CO)$_3$W=C=CHC=CH(CH$_2$)$_2$CH$_2$CH$_2$] (**1b**) with other unidentified products. **1b**: IR (THF, ν(CO)) 1999 (w), 1922 (m), 1886 (vs). $^{31}P\{^1H\}$ NMR (δ, THF−D_2O): 37.7 (s, *J*(P−W) = 164.5), 46.5 (s, *J*(P−W) = 240.5). The above solid was dissolved in diethyl ether and 21 μL (0.25 mmol) of $HBF_4{\cdot}OEt_2$ (80% (w/w) in diethyl ether) was added by syringe. The mixture was stirred at −50 °C for 0.5 h and then allowed to warm to −5 °C, leading to the precipitation of a yellow solid. Removal of the solvent and washing the resulting solid with cold diethyl ether (5 mL) and hexane (2 × 5 mL) gave a pale yellow solid. A yellow solution of this

Table 7. Experimental Data for the X-ray Diffraction Studies of Complex 5a

formula	$C_{35}H_{33}ClO_2P_2W$
M_r	766.90
cryst system	triclinic
space group	$P\bar{1}$
radiation (λ, Å)	graphite-monochromated (Mo Kα, 0.710 73)
a, Å	10.629(3)
b, Å	15.808(5)
c, Å	10.285(4)
α, deg	107.21(1)
β, deg	95.24(1)
γ, deg	96.64(1)
V, Å^3	1625.3(9)
Z	2
D_{calc}, g cm^{-3}	1.567
$F(000)$	760
cryst size, mm	0.18 × 0.21 × 0.30
μ(Mo Kα), cm^{-1}	37.64
θ range, deg	3−30
reflcns measd	$\pm h, \pm k, l$
unique tot. data	9461
unique obsd data	8219 [$I > 2\sigma(I)$]
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.0259
$R_w = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2}$	0.0299

mixture in 10 mL of dichloromethane and 70 mg (0.25 mmol) of [NBu_4]Cl was stirred at room temperature for 1 h. Evaporation of the solvent to dryness gave a solid residue which was purified by chromatography on alumina using toluene. Removal of the solvent gave the complex **5b** as a bright yellow solid. Yield: 25%. ^{1}H NMR (δ, $CDCl_3$) 1.36 (m, 6H, 3 CH_2), 1.65 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 2.47 (m), 2.81 (m, 4H, $P(CH_2)_2P$), 7.28−7.67 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 26.1 (s, CH_2), 27.1 (m, $P(CH_2)_2P$), 27.4 (s, CH_2), 28.1 (s, CH_2), 30.8 (s, CH_2), 35.8 (s, CH_2), 128.3−135.8 (m, C_β, PPh_2). MS (FAB, *m*/*e*) [$M^+ - 2CO$] = 724, [$M^+ - Cl$] = 745. Anal. Calcd for $C_{36}H_{35}ClO_2P_2W$: C, 55.37; H, 4.52. Found: C, 55.61; H, 4.88.

Crystal Structure Determination of Complex 5a. Selected crystallographic data for the complex **5a** are listed in Table 7. Data were collected at room temperature (22 °C) on a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo Kα radiation. All reflections with θ in the range 3−30° were measured; of 9461 independent reflections, 8219, having $I > 2\sigma(I)$, were considered observed and used in the analysis. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.0 and 0.648).[33]

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were clearly localized in the final ΔF map and refined isotropically. The final cycles of refinement were carried out on the basis of 472 variables; after the last cycles, no parameters shifted by more than 0.7 esd. The highest remaining peak in the final difference map was equivalent to about 1.06 e/Å^3. In the final cycles of refinement a weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 1.248 and 0.0003. Final R and R_w values were 0.0259 and 0.0299, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 34. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELX-86 systems of crystallographic computer programs.[35]

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Supporting Information Available: Fractional atom coordinates (Table SI), hydrogen atom coordinates and isotropic thermal parameters (Table SII), anisotropic thermal parameters (Table SIII), and complete bond distances and angles (Table SIV) (6 pages). Ordering information is given on any current masthead page.

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