Synthesis and Characterization of Tungsten Alkenyl−Carbyne and Alkenyl−Ketenyl Complexes Containing Dithio Ligands. X-ray Crystal Structure and MO Analyses of $[(dppe)\{\kappa^3(S,C,S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}C(CH_2)_3CH_2][BF_4]$

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The reaction of $[(dppe)(CO)_2(MeCN)W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (dppe = 1,2-bis(diphenylphosphino)ethane; $n = 1$ (**1a**), 4 (**1b**)) with S_2CPCy_3 in methanol for 10 min affords $[(dppe)(CO)_2\{\kappa(S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ ($n = 1$ (**2a**), 4 (**2b**)). Similarly, the complexes $[(dppe)(CO)_2\{\kappa(S)\text{-}S_2P(OEt)_2\}W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2]$ ($n = 1$ (**3a**), 4 (**3b**)) have been prepared by the reaction with $[NBu_4][S_2P(OEt)_2]$. When **1a** and **1b** are reacted with S_2CPCy_3 in methanol for 24 h, the complexes $[(dppe)\{\kappa^3(S,C,S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ ($n = 1$ (**4a**), 4 (**4b**)) are formed. Moreover, when **1a** and **1b** are reacted with NaS_2CNR_2 (R = Me, Et), the ketenyl complexes $[(dppe)(CO)\{\kappa^2(S,S)\text{-}S_2CNR_2\}W\{\kappa^2(C,C){=}C{-}(C{=}O)CH{=}CCH_2(CH_2)_nCH_2CH_2\}]$ are formed (R = Me, $n = 1$ (**5a**), 4 (**5b**); R = Et, $n = 1$ (**5c**), 4 (**5d**)) subsequent to the coupling between the carbyne group and carbon monoxide. IR and ^1H, ^{31}P, and ^{13}C NMR data are reported for all of the species. The molecular structure of compound **4a**, determined by X-ray diffraction methods, shows that the S_2CPCy_3 ligand is bound to the metal in a pseudoallylic $\kappa^3(S,C,S)$ fashion. The metal coordination is completed by the W≡C triple bond of the alkenyl−carbyne group and by two additional W−P bonds. Since the metal center in **4a** is formally a deficient 16-electron species and since the synthetic route has clearly indicated that an additional CO ligand is preferentially rejected by the metal, a reasonable interpretation of the bonding has been sought by means of EHMO calculations. Not only has the coexistence between the dithiocarboxylate and the carbyne ligands been elucidated, but also the strength of the W−S bonds is accounted for in comparison with the weaker W−S bonds observed in other saturated W complexes containing a $\kappa^3(S,C,S)$ dithio ligand. Finally, qualitative theoretical considerations are presented for the different behavior of the dithiocarbamate ligand.

Introduction

Since the discovery[1] of the first carbyne complex by E. O. Fischer in 1973, the chemistry of metal−carbon triple bonds has been extensively investigated.[2] Carbyne group 6 low-valent metal complexes (Fischer-type) are genuine examples, and to date, a large number of them have been prepared. Although carbyne complexes of this type are readily accessible through a number of well-established synthetic methodologies,[2a,c,e] only a few complexes bearing unsaturated substituents on the carbyne functionality have been described.[3] We have

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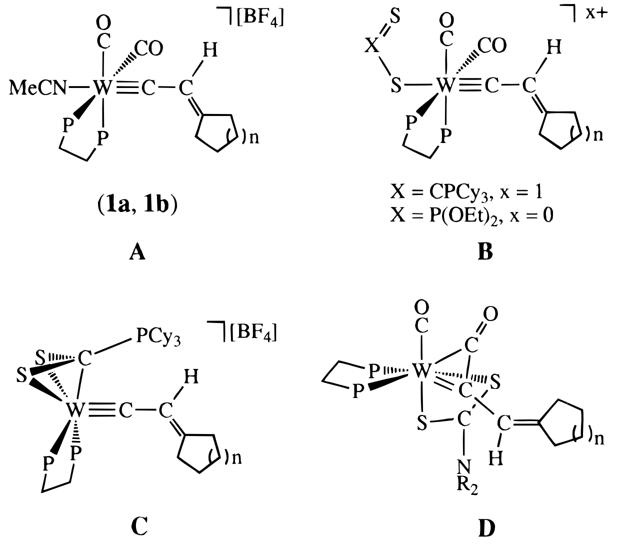
Chart 1



recently reported[4] an efficient route for the synthesis of cationic alkenyl−carbyne complexes of the type $[(dppe)(CO)_2LW{\equiv}CCH{=}\overline{CCH_2(CH_2)_nCH_2CH_2}][BF_4]$ (L = CO, MeCN; dppe = 1,2-bis(diphenylphosphino)ethane; n = 1, 4) (**A**, Chart 1), which have been proven to be good precursors for the preparation of cationic $[(dppe)(CO)_2LW{\equiv}CCH{=}\overline{CCH_2(CH_2)_nCH_2CH_2}][BF_4]$ and neutral $[(dppe)(CO)_2XW{\equiv}CCH{=}\overline{CCH_2(CH_2)_nCH_2CH_2}]$ (X = Cl, Br, I) derivatives. As an extension of the synthetic applications of the precursor complexes (**A**), we have obtained a number of novel tungsten derivatives containing dithio ligands. The series of complexes is as follows: (i) alkenyl−carbyne complexes (**B**) containing monodentate ligands such as $\kappa^1(S)$ diethyldithiophosphate $[S_2P(OEt)_2]^-$ and the zwitterionic tricyclohexylphosphonium dithiocarboxylate S_2CPCy_3, (ii) alkenyl−carbyne complexes (**C**) with the S_2CPCy_3 ligand bonded in a tridentate $\kappa^3(S,C,S)$ coordination mode, and (iii) alkenyl−ketenyl complexes (**D**) which in contrast to the aforementioned complexes (**B**) and (**C**) result from the reactions of complexes **A** with dithiocarbamate ligands $S_2CNR_2^-$ (R = Me, Et) through the coupling of the carbyne group and carbon monoxide (formal insertion of a carbonyl group into the metal−carbon triple bond). The X-ray crystal structure of the complex $[(dppe)\{\kappa^3(S,C,S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}\overline{C(CH_2)_3CH_2}][BF_4]$ (**4a**) is reported to highlight the features of an interesting organometallic species with a formal electron shortage (16 electrons) and in which a η^3-coordinated dithio acid coexists with a triple W≡C bond. In order to elucidate in some detail the electronic nature of **4a**, extended Hückel calculations (EHMO method)[5] have been carried out for a simplified model of the complex, namely $[(PH_3)_2\{\kappa^3(S,C,S)\text{-}S_2CPH_3\}W({\equiv}CCH{=}CH_2)]^+$.

Results and Discussion

Alkenyl−Carbyne Complexes. The addition of an equimolar amount of S_2CPCy_3 to a solution of $[(dppe)(CO)_2(MeCN)W{\equiv}CCH{=}\overline{CCH_2(CH_2)_nCH_2CH_2}][BF_4]$ **(1a** and **1b)** in methanol at room temperature (Scheme 1, eq 1a) in 10 min leads to substitution of the acetonitrile ligand giving the cationic alkenyl−carbyne complexes **2a** and **2b**, isolated as the tetrafluoroborate salts (90% yield). They are orange air-sensitive solids that are not stable over −20 °C. Similarly, the reaction of **1a** and **1b** with $[NBu_4][S_2P(OEt)_2]$ (eq 1b) affords neutral complexes **3a** and **3b** (82−85% yield), isolated as yellow air-stable solids.

The conductance data of acetone solutions show that complexes **2a** and **2b** are 1:1 electrolytes. The IR spectra (CH_2Cl_2) (Table 1) of all of the complexes exhibit the two typical ν(CO) carbonyl stretching absorptions in the range of 2000−1930 cm^{-1} for *cis*-dicarbonyl complexes, indicating the substitution of the acetonitrile ligand.

The presence of the dithio ligands is assessed by the ^{31}P NMR spectra (Table 1). Thus, the phosphorus resonance of S_2CPCy_3 in complexes **2a** and **2b** appears as a singlet signal at 31.7 ppm, as expected for a formal phosphonium character,[6] while the corresponding resonance of the dithiophosphate ligand in complexes **3a** and **3b** appears as a triplet at δ 107.9 ppm (^3J(P−P) = 21.0−20.5 Hz) due to the coupling of the two equivalent phosphorus nuclei of dppe in a *cis* position. The spectra also show the resonances of dppe at δ 42.4 s ppm (**2a,b**) and 38.2−38.1 ppm (d, ^3J(P−P) 21.0−20.5 Hz) (**3a,b**), indicating the chemical equivalence of the phosphorus atoms in accordance with the *trans* carbyne−dithio ligand arrangement.

When complexes **1a** and **1b** are allowed to react in methanol with S_2CPCy_3 for 24 h, a gradual change of color to red is observed along with the precipitation of a red crystalline solid identified as $[(dppe)\{\kappa^3(S,C,S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}\overline{CCH_2(CH_2)_nCH_2CH_2}][BF_4]$ (n = 1 (**4a**) and 4 (**4b**)) (90% yield) (Scheme 1, eq 1c). Alternatively, these complexes can be also obtained in similar yield when solutions of **2a** and **2b** in methanol are stirred at room temperature for 24 h. IR spectra of **4a** and **4b** show no ν(CO) carbonyl stretching absorptions, confirming the total substitution of the carbonyl ligands. The analytical data and mass spectra (FAB) (see Experimental Section) are in accordance with this formulation. The ^{13}C and ^{31}P NMR spectra (Tables 1 and 2) are also consistent with this geometry, indicating

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(2) (a) Fischer, H.; Hofmann, P; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH Publishers: Weinheim, Germany, 1988. (b) Mayr, A. *Comm. Inorg. Chem.* **1990**, *10*, 227. (c) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227. (d) Mayr, A.; Bastos, C. *Prog. Inorg. Chem.* **1992**, *40*, 1. (e) *Transition Metal Carbyne Complexes*; Kluwer Academic Publishers: Dordrecht, Boston, London, 1993. (f) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281.

(3) (a) Alkynyl−carbyne complexes, $[(CO)_4XW{\equiv}CC{\equiv}CPh]$: Fischer, E. O.; Kalder, H. J.; Köhler, F. H. *J. Organomet. Chem.* **1974**, *81*, C23. $[M({\equiv}CC{\equiv}CBu^t)(CO)_2L_2\{OC(O)CF_3\}]$ and $[M({\equiv}CC{\equiv}CBu^t)(CO)_2L_3]$ (M = Mo, W): Hart, I. J.; Hill, A. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2261. (b) Alkenyl−carbyne complexes of group 6 metals of the type $[(CO)_4XM{\equiv}\overline{C{=}CH(CH_2)_2CH_2}]$ (M = Cr, Mo, W): Fischer, E. O.; Wagner, W. R.; Kreissl, F. R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1320. $[(CO)_4XW{\equiv}CCH{=}C(NMe_2)Ph]$: see ref 3a. (c) A trinuclear cluster of tungsten and rhenium containing an alkenyl−carbyne group has also been described: Peng. J. J.; Peng, S. M.; Lee, G. H.; Chi, Y. *Organometallics* **1995**, *14*, 626.

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(6) See for example: Miguel, D.; Riera, V.; Miguel, J. A.; Gómez, M.; Soláns, X. *Organometallics* **1991**, *10*, 1683.

Scheme 1

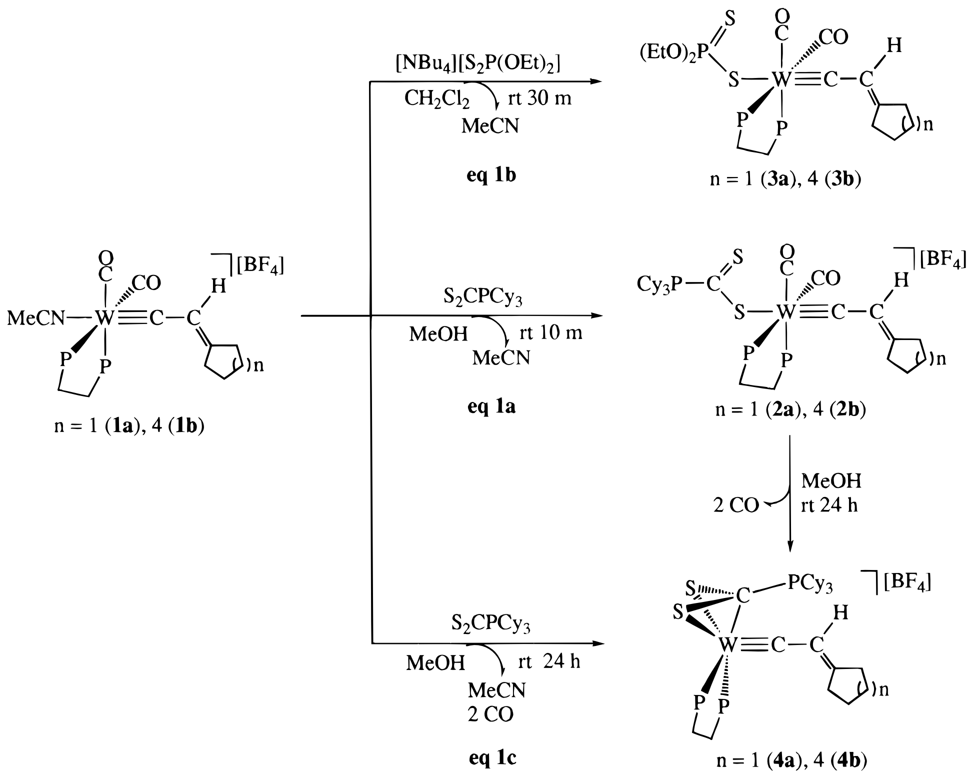

Table 1. IR[a] and $^{31}P\{^1H\}$ and ^{1}H NMR[b] Data for the Alkenyl−Carbyne Complexes

		$^{31}P\{^1H\}$		
	IR ν(CO)	$P(CH_2)_2P$	S_2CPCy_3 or $S_2P(OEt)_2$	^1H $C_\beta H$
2a	2000 s, 1936 vs	42.4 s (230.1)[c]	31.7 s	5.18 s, br
2b	1999 s, 1936 vs	42.4 s (229.4)[c]	31.7 s	4.81 s, br
3a	2001 vs, 1936 vs	38.2 d (21.0[d], 226.9[c])	107.9 t (21.0[d])	4.92 s, br
3b	1999 vs, 1931 vs	38.1 d (20.5[d], 226.8[c])	107.9 t (20.5[d])	4.52 s, br
4a		62.1 d (1.7[e], 294.0[c])	35.2 t (1.7[e])	4.53 s, br
4b		62.2 d (1.5[e], 294.0[c])	35.2 t (1.5[e])	4.46 s, br

[a] Spectra recorded in CH_2Cl_2, ν (cm^{-1}). Abbreviations: s, strong; vs, very strong. [b] Spectra recorded in $CDCl_3$ ($^{31}P\{^1H\}$ NMR spectra of **4a** and **4b** recorded on a Bruker AMX400 spectrometer in CD_2Cl_2), δ in ppm, J in Hertz. Abbreviations: s, singlet; d, doublet; t, triplet; br, broad. [c] J(P−W). [d] ^3J(P−P). [e] J(P−P).

Table 2. $^{13}C\{^1H\}$ NMR Data for the Alkenyl−Carbyne Complexes[a]

	$^{13}C\{^1H\}$				
	C_α[b]	C_β	C_γ	2 *cis* CO[b]	$S_2\mathit{C}PCy_3$[c]
2a	290.9 m	*d*	166.5 s	214.5 dd (33.4, 8.6)	220.9 d (40.6)
2b	290.9 m	*d*	165.2 s	214.7 dd (33.1, 7.8)	220.8 d (40.2)
3a	276.6 m	*d*	164.0 s	213.7 m	
3b	276.7 t (10.4)	134.8 s	162.7 s	213.9 m	
4a	300.5 t (13.4)	*d*	158.4 s		60.6 d (71.5)
4b	300.8 t (13.6)	135.3 s	155.8 s		60.5 d (70.7)

[a] Spectra recorded in $CDCl_3$, δ in ppm, J in Hertz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] ^2J(C−P). [c] J(C−P). [d] Overlapped by the aromatic carbons.

the presence of the alkenyl−carbyne group and the dithio ligand bonded to the metal atom in a κ^3(*S,C,S*) coordination mode. In particular, the carbon resonance of the dithiocarboxylate group in the S_2CPCy_3 ligand appears at a high field (*ca.* δ 60.5 ppm, d, J(C−P) = 70.7−71.5 Hz), and the ^{31}P NMR spectra show a low-field triplet signal at *ca.* δ 35.2 (^3J(P−P) = 1.7−1.5 Hz) typical of a quaternary phosphorus atom bearing a formal positive charge. These values can be compared to those shown by other κ^3(*S,C,S*) phosphonium dithiocarboxylate complexes.[7] The $^{31}P\{^1H\}$ NMR spectra also show resonances due to the dppe ligand (*ca.* δ 62.1 ppm, d, ^3J(P−P) = 1.7−1.5 Hz; J(P−W) = 294.0 Hz), as expected for an AX_2 spin system.

The reactions can be monitored by ^{31}P NMR in $CDCl_3$, which shows a stepwise acetonitrile−carbonyl substitution through the formation of complexes **2a** and **2b** as intermediate species. The first reaction step seems to be very fast, since after 5 min the signal of the starting complex (*e.g.*, **1a**) at δ 47 ppm is no longer observed and two new singlet signals at δ 31.7 and 42.4 ppm appear attributable in complex **2a** (*vide supra*) to the phosphorus atoms of the dithio ligand and dppe, respectively. After *ca.* 1 h, the spectrum also shows two signals at δ 35.2 and 62.1 ppm assigned to the final complex **4a**, which are the only ones observed after *ca.* 24 h of reaction.

X-ray Crystal Structure of 4a. The crystal structure of complex **4a** consists of cationic complexes and of BF_4^- anions. The structure of the cationic complex

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[7] (a) Galindo, A.; Gutiérrez-Puebla, E.; Monge,A.; Pastor, A.; Pizzano, A.; Ruiz, C.; Sánchez, L.; Carmona, E. *Inorg. Chem.* **1993**, *32*, 5569. (b) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Pérez, P.; Sánchez, L. *Inorg. Chem.* **1989**, *28*, 2120. (c) Galindo, A.; Mealli, C.; Cuyás, J.; Miguel, D.; Riera, V.; Pérez-Martínez, J.; Bois, C.; Jeannin, Y. *Organometallics* **1996**, *15*, 2735.

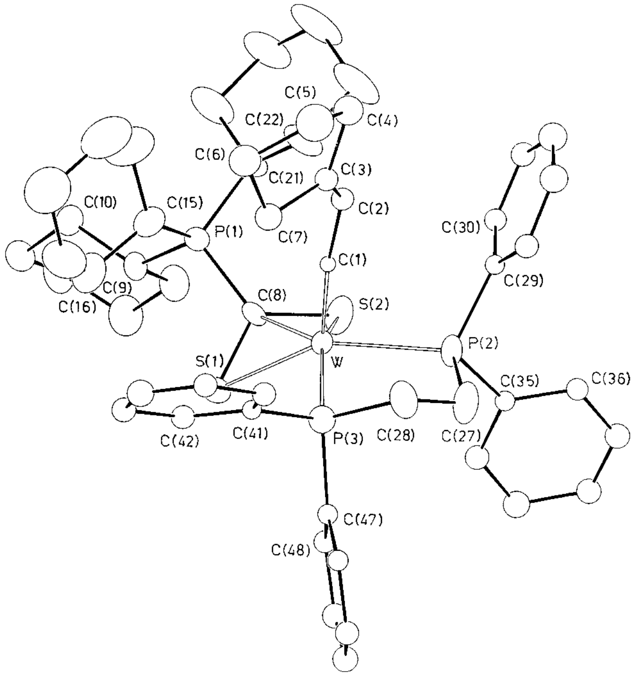

Figure 1. View of the molecular structure of the cationic complex of [(dppe){κ^3(*S,C,S*)-S_2CPCy_3}W≡CCH=$\overline{C(CH_2)_3CH_2}$][BF_4] (**4a**), with the atom-numbering scheme. Only one of the two disordered positions of the alkenyl–carbyne ligand are shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 4a

W–S(1)	2.404(4)	P(3)–C(41)	1.829(11)
W–S(2)	2.401(4)	P(3)–C(47)	1.821(12)
W–P(2)	2.474(4)	C(1A)–C(2A)	1.42(2)
W–P(3)	2.463(4)	C(2A)–C(3A)	1.36(2)
W–C(1A)	1.811(15)	C(3A)–C(4A)	1.52(3)
W–C(1B)	1.808(16)	C(3A)–C(7A)	1.51(3)
W–C(8)	2.142(10)	C(4A)–C(5A)	1.50(5)
S(1)–C(8)	1.747(11)	C(5A)–C(6A)	1.51(5)
S(2)–C(8)	1.766(11)	C(6A)–C(7A)	1.51(4)
P(1)–C(8)	1.823(11)	C(1B)–C(2B)	1.43(2)
P(1)–C(9)	1.820(11)	C(2B)–C(3B)	1.36(3)
P(1)–C(15)	1.824(13)	C(3B)–C(4B)	1.52(4)
P(1)–C(21)	1.862(14)	C(3B)–C(7B)	1.51(3)
P(2)–C(27)	1.867(15)	C(4B)–C(5B)	1.50(5)
P(2)–C(29)	1.831(12)	C(5B)–C(6B)	1.52(6)
P(2)–C(35)	1.814(12)	C(6B)–C(7B)	1.51(4)
P(3)–C(28)	1.825(12)		

C(1B)–W–C(8)	103.9(7)	W–C(1A)–C(2A)	166(1)
C(1A)–W–C(8)	107.6(6)	C(1A)–C(2A)–C(3A)	126(2)
C(1A)–W–C(1B)	18.3(7)	C(2A)–C(3A)–C(7A)	124(2)
P(3)–W–C(8)	139.5(3)	C(2A)–C(3A)–C(4A)	130(2)
P(3)–W–C(1B)	92.4(6)	C(4A)–C(3A)–C(7A)	105(2)
P(3)–W–C(1A)	78.1(6)	C(3A)–C(4A)–C(5A)	102(2)
P(2)–W–C(8)	136.9(3)	C(4A)–C(5A)–C(6A)	108(3)
P(2)–W–C(1B)	85.2(6)	C(5A)–C(6A)–C(7A)	101(3)
P(2)–W–C(1A)	94.0(6)	C(3A)–C(7A)–C(6A)	110(2)
P(2)–W–P(3)	80.4(1)	W–C(1B)–C(2B)	170(2)
S(2)–W–C(8)	45.3(3)	C(1B)–C(2B)–C(3B)	129(2)
S(2)–W–C(1B)	110.9(6)	C(2B)–C(3B)–C(7B)	121(2)
S(2)–W–C(1A)	126.6(6)	C(2B)–C(3B)–C(4B)	125(2)
S(2)–W–P(3)	154.9(1)	C(4B)–C(3B)–C(7B)	112(2)
S(2)–W–P(2)	91.9(1)	C(3B)–C(4B)–C(5B)	98(3)
S(1)–W–C(8)	44.7(3)	C(4B)–C(5B)–C(6B)	107(3)
S(1)–W–C(1B)	125.1(6)	C(5B)–C(6B)–C(7B)	100(3)
S(1)–W–C(1A)	114.7(6)	C(3B)–C(7B)–C(6B)	102(2)
S(1)–W–P(3)	95.7(1)	S(2)–C(8)–P(1)	120.9(6)
S(1)–W–P(2)	149.8(1)	S(1)–C(8)–P(1)	117.1(6)
S(1)–W–S(2)	79.0(1)	S(1)–C(8)–S(2)	120.8(6)

is shown in Figure 1, together with the atom-numbering scheme; selected bond distances and angles are given in Table 3.

The W atom displays a roughly square pyramidal coordination with the triply-bonded C(1) atom from the alkenyl–carbyne group lying at the apical site. Two *cis* basal sites are occupied by the phosphorus atoms of the dppe chelate, while the other two sites are jointly spanned by the S_2C unit of the tricyclohexylphosphonium dithiocarboxylate ligand. The apical alkenyl–carbyne ligand has been found disordered over two positions (A and B) with a separation between the carbynic C(1A) and C(1B) atoms of 0.57 Å. For the sake of clarity, only the ligand in the position A is shown in Figure 1. The structural parameters relative to the carbyne ligand are W–C(1A) = 1.811(15) Å, W–C(1B) = 1.808(16) Å, W–C(1A)–C(2A) = 166(1)°, and W–C(1B)–C(2B) = 170(2)°. The W–C bond lengths are comparable with that found, 1.830(3) Å, in the neutral, 18-electron complex *trans*-[(dppe)(CO)$_2$ClW≡CCH=$\overline{C(CH_2)_3CH_2}$].[4] Remarkably, in the latter, the W–C–C angle is much closer to linearity, *i.e.*, 178.9(2)°. Also, the W–P(2) and W–P(3) bond distances in **4a** appear shorter (2.474(4) and 2.463(4) Å) than those in the above reference complex (2.539(1) and 2.524(1) Å, respectively). The five-membered rings in positions A and B display envelope and twist conformations, respectively.

The coordination of the S_2CPCy_3 ligand is of the pseudoallylic κ^3(*S,C,S*)-type with W–S(1), W–S(2), and W–C(8) bond lengths of 2.404(4), 2.401(4), and 2.142(10) Å, respectively, and with the C–S bond lengths practically equal to each other, 1.747(11) *vs* 1.766(11) Å. Also, the P(1)–C(8) distance of 1.82(1) Å is comparable to the typical P–Cy distances, in the range 1.82(1)–1.86(1) Å. The latter linkage is practically eclipsed to the carbynic W–C(1) linkage, the dihedral angles C(1A)WC(8)P(1) and C(1B)WC(8)P(1) being 6(1)° and −13(1)°, respectively. It is noteworthy that the bonding of the S_2C fragment to the tungsten atom in **4a** differs significantly from that observed in the metal-saturated complex[7a] [W{κ^3(*S,C,S*)-S_2CPMe_3}(CO)$_2$(PMe$_3$)$_2$] where the W–S bond lengths, 2.505(8) and 2.541(7) Å, are definitely longer and the W–C one is only slightly shorter, 2.12(2) Å. Another structure which is closely related to the present one is that of the formal 16-electron complex[8] [W(≡CBu^t)(CHBu^t)(CH$_2$Bu^t)(dmpe)]. Also, in the latter the carbyne group occupies the apex of the square pyramid (W≡C = 1.785(8) Å) while in the basal plane there are, besides the two phosphine donors of the chelate, adjacent alkyl and alkylidene groups.

Ketenyl Complexes. The facile substitution of the carbonyl groups with dithio ligands in complexes **1a** and **1b** prompted us to investigate their reactivity with dialkyldithiocarbamate, a typical monoanionic chelate ligand. The addition of a stoichiometric amount of NaS$_2$CNR$_2$ (R = Me, Et) to a solution of **1a** and **1b** in methanol at −20 °C gives a purple solution from which ketenyl complexes **5a–d** are obtained in good yields (Scheme 2). These complexes have been isolated as brown solids, and they are stable under N$_2$ atmosphere. They have been characterized by elemental analyses, mass spectrometry (FAB) (see Experimental Section), and IR and NMR spectroscopies (Tables 4 and 5).

The IR spectra (CH$_2$Cl$_2$) (Table 4) show two ν(CO) stretching carbonyl absorptions, one very strong at

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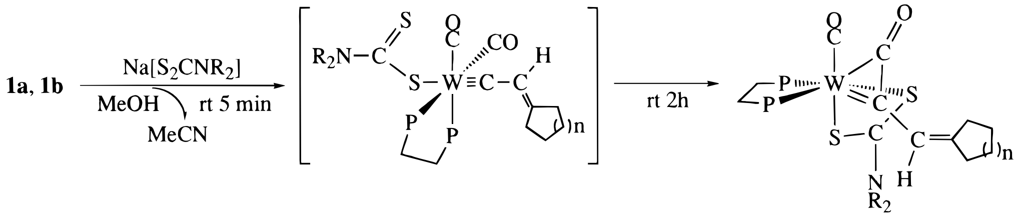
[8] Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

Scheme 2



R \ n	1	4
Me	**5a**	**5b**
Et	**5c**	**5d**

Table 4. IR[a] and $^{31}P\{^1H\}$ NMR[b] Data for the Alkenyl−Ketenyl Complexes

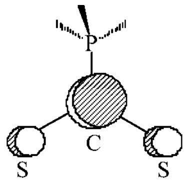
	IR		$^{31}P\{^1H\}$[c]	
	ν(CO)	ν(C=C=O)	P *trans* to κ^2-ketenyl	P *trans* to S
5a	1869 vs	1731 m	18.4 d (19.0, 72.3)	45.5 d (19.0, 312.7)
5b	1870 vs	1729 m	17.6 d (16.8, 67.9)	46.0 d (16.8, 315.1)
5c	1869 vs	1729 m	17.4 d (19.8, 73.1)	46.3 d (19.8, 310.8)
5d	1870 vs	1727 m	16.6 d (18.1, 68.1)	46.4 d (18.1, 313.3)

[a] Spectra recorded in CH_2Cl_2, ν (cm^{-1}). Abbreviations: m, medium; vs, very strong. [b] Spectra recorded in $CDCl_3$, δ in ppm, J in Hertz. Abbreviations: d, doublet. [c] J(P−P) and J(P−W).

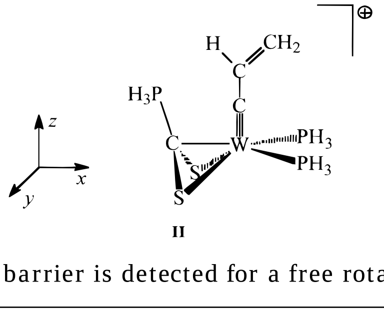
1869−1870 cm^{-1}, assigned to the terminal carbonyl ligand, and a second medium intensity absorption at 1729−1731 cm^{-1}, indicating the presence of the ketenyl group.[9] This is confirmed by the ketenyl carbon resonance in the ^{13}C NMR spectra (Table 5) which appears as an unresolved multiplet at δ 199.4−201.4 ppm due to the coupling with the unequivalent phosphorus nuclei. An additional doublet of doublets at δ 187.9−190.4 ppm (dd, ^2J(C−P) = 18, 10 Hz) are assigned to the α carbon of the ketenyl group [W{κ^2(*C*,*C*)=C−(C=O)-$CH{=}\overline{CCH_2(CH_2)_nCH_2CH_2}$}]. Further resonances attributable to the rest of the carbon nuclei of the alkenyl moieties and dithiocarbamate and dppe ligands can also be assigned (see Experimental Section). The ^{31}P NMR spectra of complexes **5a**−**d** (Table 4) consist of two doublets (^2J(P−P) = 16.8−19.8 Hz) along with the ^{183}W satellites. As expected for the high *trans* influence of the κ^2-ketenyl ligand, small values of J(P−W) coupling constants are observed (δ 16.6−18.4, ^1J(P−W) = 67.9−72.3 Hz, P *trans* to κ^2-ketenyl; δ 45.5−46.4, ^1J(P−W) = 310.8−315.1 Hz, P *trans* to S).[9a] Significantly, the former coupling constants are lower than those shown by the alkenyl−carbyne ligand.[4]

When the reactions are monitored by IR in the carbonyl region, the formation of an intermediate complex is observed. Thus, after 5 min the spectra show two new ν(CO) stretching absorptions at 1997 and 1933 cm^{-1}. The reactions are allowed to proceed until these absorptions totally disappear to give those corresponding to the final complexes **5a**−**d**. Although all attempts to isolate these intermediate species have failed, we believe that *cis*-dicarbonyl complexes containing monodentate dithiocarbamate ligands are formed (Scheme 2).[9b] The ability of dithiocarbamate ligands to chelate probably favors the substitution of an additional carbonyl ligand, promoting the coupling of the carbyne group and carbon monoxide to give the κ^2-alkenyl−ketenyl moiety. In contrast to this behavior, complexes **3a** and **3b** remain unchanged even when their solutions in methanol are heated under reflux. This probably indicates the unfavorable “bite angle” of the $S_2P(OR)_2$ ligands, although tungsten complexes in which dithiophosphate is acting as a chelate ligand have been reported.[10]

MO Analyses of Complexes 4a,b. The unit S_2CPR_3, formally resulting from the aggregation of carbon disulfide and a tertiary phosphine, is found to be a versatile ligand. The metal complexes show a variety of coordination modes, and up to four electron pairs can be involved in the bonding with the metal(s). In particular, the trihapto binding mode, M(κ^3-*S*,*C*,*S*), has been structurally characterized in a number of mononuclear[7] and binuclear[6,11] complexes. The trihapto coordination of S_2CPCy_3 in complexes **4a,b** is particularly interesting because it coexists with a carbyne group bonded to the same metal center. Also, the case is peculiar because a significant amount of back-donation into the empty π^* level of S_2CPCy_3 (see **I**) is expected to occur from a somewhat electron-deficient metal species (16 electrons). The EHMO calculations have been performed mainly based on the structural results obtained for **4a**. The working model **II** has the imposed C_s symmetry with the terminal alkenyl group, hanging from the carbyne, fixed in the mirror plane. No significant barrier is detected for a free rotation of the



I



II

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(9) (a) Similar data have been reported for analogous tungsten ketenyl complexes: Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474 and references therein. (b) An analogous intermediate has been postulated in the formation of related ketenyl complexes also generated by the reaction of tungsten carbonyl−carbyne complexes with dithiocarbamate ligands (see ref 9a). (c) Hill, A. F.; Malget, J. M.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 721. (d) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786. (e) Mayr, A.; Chang, R. T.; Lee, T. Y.; Cheung, O. K.; Kjelsberg, M. A.; McDermott, G. A.; Engen, D. V. *J. Organomet. Chem.* **1994**, *479*, 47.

(10) Haiduc, I.; Sowerby, D. B.; Lu, S. F. *Polyhedron* **1995**, *14*, 3389.

Table 5. Selected $^{13}C\{^1H\}$ NMR Data for the Alkenyl−Ketenyl Complexes[a]

	$^{13}C\{^1H\}$					
	$W{=}C_\alpha{=}C{=}O^b$	C_β	C_γ	2 *cis* CO[b]	$C_\alpha{=}C{=}O$	S_2CNR_2
5a	190.0 dd (18.6, 10.5)	119.5 s	150.0 s	221.9 dd (10.0, 2.8)	199.4 m	211.8 s
5b	190.4 dd (18.7, 9.7)	124.5 s	148.5 s	222.4 dd (10.4, 2.4)	201.4 m	211.3 s
5c	187.9 dd (17.8, 11.1)	119.6 s	149.9 s	221.5 m	201.2 m	211.5 s
5d	190.1 dd (18.4, 9.8)	124.9 s	147.1 s	221.8 dd (10.8, 3.6)	199.6 m	211.2 s

[a] Spectra recorded in $CDCl_3$, δ in ppm, *J* in Hertz. Abbreviations: s, singlet; d, doublet; m, multiplet. [b] In parenthesis $^2J(C-P)$.

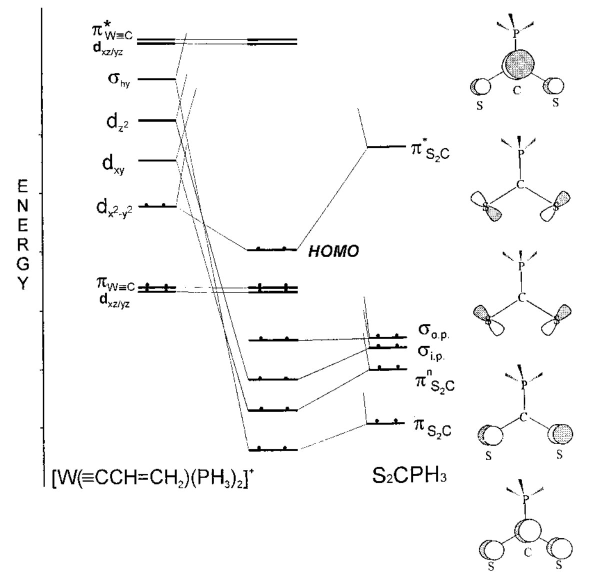


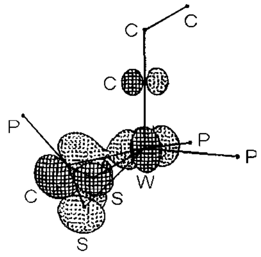
Figure 2. Diagram of the interactions between the dithio ligand S_2CPH_3 and the fragment $[W(\equiv CCH{=}CH_2)(PH_3)_2]^+$.

alkenyl−carbyne fragment about the extended W≡C−C vector nor do the main electronic features seem to be affected by the substitution of the terminal $CH{=}CH_2$ group with a single H atom.

Figure 2 shows the diagram for the interaction between the dithiocarboxylate ligand and the remaining part of the molecule. The frontier molecular orbitals (FMOs) of the ligand S_2CPH_3 (on the right side of the figure) have been described recently.[7c,12] Essentially, these consist of two major *in-plane* combinations of sulphur lone pairs (*in-phase* σ_{ip} and *out-of-phase*, σ_{op}), and three of the π-S_2C system containing four electrons. Besides the empty π^*-S_2C level, these include the π-S_2C and π^n-S_2C combinations.

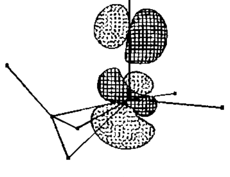
The fragment of the type ML_3 (with pseudo C_{3v} symmetry) is somewhat atypical because of the triple linkage between the metal and one of the ligands (W≡CR). In any case, by adopting a classic strategy[13] the frontier orbitals can still be thought to descend from an octahedron following the removal of three *fac* σ donors. Accordingly, there are two main subsets of levels, namely a lower t_{2g} and higher $e_g + \sigma_{hybrid}$. Two levels of the former subset, considered empty, have the proper d_π symmetry (*xz*, *yz* orbitals) to interact with the p_π orbitals of a formally trianionic carbyne. The interactions are also at the origin of the W≡C triple bond (the bonding/antibonding combinations are highlighted in Figure 2).

By considering the carbyne group as a formal trianion (π-donor), *versus* monocationic (π-acceptor) or a neutral moiety,[14] the metal can be regarded as a d^2 species. Indeed, several theoretical studies have already been devoted to octahedral metal−carbyne complexes,[15] but the situation may be simplified by thinking that the unique electron pair of the d^2 metal is hosted in the third t_{2g} orbital (x^2-y^2), hence, it is available for back-donation into the empty π^*-S_2C FMO. The bonding combination (the strongest observed in terms of overlap population between fragment orbitals) gives rise to the HOMO of the molecule, shown in **III**. It is noteworthy that the total energy as well as that of the HOMO are optimized for a value of the $C_{carbyne}-W-C_{dithioligand}$ bond angle very close to the experimental one (*ca.* 105°).

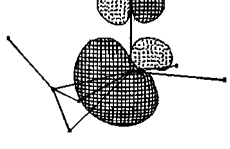


III

Previous MO studies[7c,12] on the interaction between the ligand S_2CPH_3 and metal fragments such as $[Fe(CO)_3]$ and $[W(CO)_2(PH_3)_2]$ also pointed out the extra stability of the back-donation into the FMO **I**, which adds to the four-electron donation involving the S_2C π system. The rest of metal orbitals lying above the t_{2g} set are also shown in Figure 2. One of them, *xy*, interacts more strongly with the π^n-S_2C antisymmetric combination. Finally, there are two possible candidates (see **IV** and **V**) which, being empty, can potentially interact with the symmetric π-S_2C bonding combination.



IV



V

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(11) See for example: (a) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1994**, *13*, 4667. (b) Barrado, G.; Li, J.; Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *Organometallics* **1994**, *13*, 2330. (c) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1994**, *13*, 1336. (d) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1993**, *12*, 2888. (e) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1993**, *12*, 1394. (f) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Angew. Chem.* **1992**, *31*, 76.

(12) Galindo, A.; Mealli, C. *Inorg. Chem.* **1996**, *35*, 2406.

(13) See for example: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(14) Neutral formalism avoids the oxidation state assignment, see for example: (a) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 535. (b) Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632.

The higher level σ_{hy} (**IV**) has sp hybrid character while the lower has d_{π} character (**V**). Since the main lobe of the latter points opposite to the W≡C linkage, it is indicated as z^2 in Figure 2.

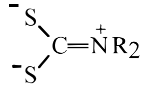
In principle, both of the FMOs **IV** and **V** could share the electrons donated from π-S_2C and the description of the whole complex as a 16-electron species could still be rational.[16] However, as a new piece of information provided by the calculations, the *in-plane* sulfur lone pair σ_{ip} (see Figure 2) contributes somehow to the bonding, in particular it overlaps preferentially with z^2. The 18-electron configuration can be achieved in this manner, *i.e.*, through the involvement of all of the nine metal orbitals in some different interaction. Experimentally, the participation of as many as three sulphur electron pairs in bonding to the metal is supported by the comparison of the W−S distances in the present and other 18-electron species also containing the same dithio ligand $\kappa^3(S,C,S)$ coordinated. As discussed during the description of the structure **4a**, the W−S distance in the 18-electron complex $[W\{\kappa^3(S,C,S)\text{-}S_2CPMe_3\}(CO)_2(PMe_3)_2]$[7a] is at least 0.1 Å longer than in our species, a fact which is nicely rationalized by the theoretical arguments which assign a certain double bond character to the W−S linkages.

The fragment molecular orbital (FMO) analysis highlights the importance of the relative orientation of S_2CPH_3 with respect to the fragment $[W(\equiv CCH{=}CH_2)(PH_3)_2]^+$. The dithio ligand is able to donate up to three electron pairs (two from the π and one from the σ system) only if the P−C bond of S_2CPH_3 eclipses the W−C triple bond, as occurs in the molecular structure of **4a**. Similar preferred orientations for π-acceptor ligands (alkenes and alkynes) have been reported in several d^2 complexes containing multiple-bonded ligands[17] (mainly oxo[18] and imido[18b,19] derivatives). While the metal achieves the formal 18-electron configuration, a fourth electron pair is backdonated into the electrophilic S_2C carbon atom (**I**). If the dithio ligand is turned upside down, the energetics of the system is disfavored by *ca.* 0.6 eV and, importantly, the fluxionality of the κ^3 bound S_2CPR_3 ligand is prevented by the highest energetics when the C−P vector is perpendicular to the W≡C linkage (ΔE > 1.4 eV).

The dichotomy between the $\kappa^3(S,C,S)$ and $\kappa^2(S,S)$ coordination modes of dithio ligands in a variety of saturated metal complexes has been previously addressed.[7c] For the model compound $[(PH_3)_2(S_2CPH_3)W(\equiv CCH{=}CH_2)]^+$, the complex with a $\kappa^3(S,C,S)$ bonding mode is more stable than the dihapto one by *ca.* 1 eV. The stabilization of the HOMO due to the back-donation is lost at the square pyramidal geometry if S_2CPH_3 is dihapto bonded. It is worth pointing out that although in the present complex the metal is electron poor (recall its apparent 16-electron configuration and, at the very best, the extra donation from the *in-plane* σ_{ip} S_2C lone pair), the back-donation from the unique electron pair in $dx^2{-}y^2$ is a major stabilizing force.

There still remains doubts on the reasons why in **4a** the ligand S_2CPCy_3 prefers the trihapto coordination while the metal center could be formally saturated by the dihapto $\kappa^2(S,S)$ coordination in the presence of an extra CO ligand. Evidently (see Scheme 1), the addition of S_2CPCy_3 forces the departure of as many as two CO ligands from the coordination sphere. As a possible explanation, if the S_2CPCy_3 group were dihapto coordinated, there could be a significant electron repulsion between its filled π MOs (at the sulfur atoms) and the metal *xz*, *yz* orbitals. The latter are expected to accumulate large electron density when involved in π interactions with the triply-bonded carbyne group. Similar points have been raised by other authors regarding the coexistence in the complex of a carbyne ligand with coligands capable of donating four π electrons such as an alkyne.[20] Along the same lines also, the deformation of the octahedral geometry in such complexes has been interpreted.[2b] In summary, the metal back-donation into the π^*-S_2C orbital at κ^3-(S,C,S) bonding and the loss of π repulsions due to the dihapto coordination seem to be the factors counterbalancing the loss of one carbonyl ligand. Hence, the preference for the five-coordinated complexes **4a,b** over the six-coordinated monocarbonyl species is reasonable.

The different behavior of $S_2CNR_2^-$ ligands *versus* S_2CPCy_3 on coordination to the alkenyl−carbyne core affords the ketenyl derivatives **5a−d** (Scheme 2). Although a theoretical analysis of such a different reactivity has not been carried out as yet, we want to comment on the evidently different electronic properties of the dithiocarbamate ligands *vs* S_2CPR_3. Indeed, the population of the dithiocarbamate π system is characterized by a total of six electrons, and the electrophilicity at the central carbon atom is evidently diminished. This feature is usually well-described by the VB representation **VI**.



VI

Importantly, the back-donation from the metal is greatly reduced as is the possibility of forming trihapto-adducts analogous to those obtained with S_2CPR_3. Also, since the π electron density accumulates less at the sulfur atoms, the $\kappa^2(S,S)$ coordination is less hindered and the octahedral geometry is more easily achieved.

The trihapto-pseudoallylic coordination of S_2CPCy_3 found in **4a,b** has been characterized by X-ray crystallography in other dithio ligands (xanthate and thioxanthate) bonded to d^2 oxo−molybdenum complexes, for example as in $[Mo(O)\{\kappa^2(S,S)\text{-}S_2CSPr^i\}\{\kappa^3(S,C,S)\text{-}S_2CSPr^i\}]$,[21] $[Mo(O)\{\kappa^2(S,S)\text{-}S_2CPh\}\{\kappa^3\text{-}(S,C,S)\text{-}S_2CPh\}]$,[22] $[Mo(O)\{\kappa^2(S,S)\text{-}S_2C(PMe_3)OPr^i\}\{\kappa^3(S,C,S)\text{-}$

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[15] (a) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489. (c) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 4677.

[16] See for example: Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

[17] Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988.

[18] See for example: (a) Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402. (b) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261. (c) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.

[19] See for example: (a) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1995**, 1907. (b) Clark, G. R.; Glenny, M. W.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1995**, 1147. (c) Montilla, F.; Galindo, A.; Carmona, E. Unpublished results.

[20] See for example: Atagi, L. M.; Mayer, J. M. *Organometallics* **1994**, *13*, 4794 and references therein.

[21] Hyde, J.; Venkatasubramanian, K.; Zubieta, J. *Inorg. Chem.* **1978**, *17*, 414.

$S_2COPr^i\}]$,[23] and $[Mo(O)\{\kappa^2(S,S)\text{-}S_2C(PMe_3)SPr^i\}\{\kappa^3\text{-}(S,C,S)\text{-}S_2CSPr^i\}]$.[24] These complexes are closely related with compounds **4a,b**, and all of them have been studied through the corresponding $[Mo(O)\{\kappa^3\text{-}(S,C,S)\text{-}S_2CX\}\text{-}(S\text{-}S)]$ models or, alternatively, by a general $[Mo(O)\text{-}\{\kappa^3(S,C,S)\text{-}S_2CH\}\{\kappa^2\text{-}(S,S)\text{-}S_2CH\}]$ model compound. The bonding of the dithio ligand to the ML_3 fragment (pseudo C_{3v}), containing the oxo group and the other κ^2-dithio ligand, can be described as previously done for a model of **4a**. The HOMO of the $[Mo(O)\{\kappa^3(S,C,S)\text{-}S_2CH\}\{\kappa^2\text{-}(S,S)\text{-}S_2CH\}]$ model is formed through the same interaction highlighted before, that is the overlap of the $\pi^*\text{-}S_2C$ FMO and the filled $dx^2{-}y^2$ orbital. Similar preferred orientations of the $\kappa^3\text{-}S_2CX$ group can be understood in terms of maximum overlap between FMOs as outlined for the carbyne example and need no further comments.

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 complexes $[(dppe)(CO)_2(MeCN)W{\equiv}CCH{=}CCH_2(CH_2)_nCH_2CH_2][BF_4]$ (n = 1 (**1a**), 4 (**1b**)) were prepared by the literature methods.[4] $[NBu_4][S_2P(OEt)_2]$, NaS_2CNR_2 (R= Me, Et) (Aldrich Chemical Co.), and S_2CPCy_3 (Strem 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 a Bruker AC300 spectrometer at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.5 MHz (^{13}C) using $CDCl_3$ as solvent. The spectral references used were tetramethylsilane for ^1H and ^{13}C NMR measurements and 85% H_3PO_4 for ^{31}P NMR measurements.

Selected IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopic data for the novel alkenyl−carbyne complexes and alkenyl−ketenyl complexes are collected in Tables 1, 2, 4, and 5.

$[(dppe)(CO)_2\{\kappa(S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}CCH_2(CH_2)_n\text{-}CH_2CH_2][BF_4]$ (n = 1 (2a), 4 (2b)). General Procedure. An equimolar amount of complex **1a** or **1b** (0.2 mmol) and S_2CPCy_3 in methanol (20 mL) was stirred at room temperature for 10 min. The color of the solution changed from orange to red. Removal of the solvent and washing the resulting solid with diethyl ether (5 mL) and hexane (2 × 5 mL) gave **2a** or **2b** as orange solids. Yield: **2a** and **2b**, 90%. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): **2a**, 136; **2b**, 140.

Spectral data for **2a**: IR (KBr, ν(CO) and ν(B−F)) 1989 (s), 1923 (vs), 1055 (s, br). ^1H NMR (δ, $CDCl_3$): 1.09 (m, 14H, 7 CH_2), 1.38 (m, 10H, 5 CH_2), 1.69 (m, 10H, 5 CH_2), 1.91 (m, 4H, 2 CH_2), 2.35 (m, 3H, $P(CH(CH_2)_5)_3$), 2.50−3.20 (m, 4H, $P(CH_2)_2P$), 7.27−7.70 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 24.9−34.6 (m, 19 CH_2), 29.5 (m, $P(CH_2)_2P$), 32.4 (d, J(C−P) = 36.1 Hz, $P(CH(CH_2)_5)_3$), 128.1−135.0 (m, C_β, PPh_2).

Spectral data for **2b**: ^1H NMR (δ, $CDCl_3$) 1.12 (m, 12H, 6 CH_2), 1.42 (m, 14H, 7 CH_2), 1.74 (m, 16H, 8 CH_2), 2.44 (m, 5H, CH_2, $P(CH(CH_2)_5)_3$), 2.82 (m, 2H, $P(CH_aH_b)_2P$), 3.06 (m, 2H, $P(CH_aH_b)_2P$), 7.30−7.73 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 23.1−35.6 (m, 22 CH_2), 29.6 (m, $P(CH_2)_2P$), 32.4 (d, J(C−P) = 36.2 Hz, $P(CH(CH_2)_5)_3$), 128.1−135.7 (m, C_β, PPh_2).

$[(dppe)(CO)_2\{\kappa(S)\text{-}S_2P(OEt)_2\}W{\equiv}CCH{=}CCH_2(CH_2)_n\text{-}CH_2CH_2]$ (n = 1 (3a), 4 (3b)). General Procedure. A mixture of **1a** or **1b** (0.2 mmol) and $[NBu_4][S_2P(OEt)_2]$ (0.2 mmol) in dichloromethane (10 mL) was stirred at room temperature for 0.5 h. After evaporation of the solvent to dryness, the residue was extracted with toluene and filtered off on Alox. Removal of the solvent gave **3a** or **3b** as bright yellow solids. Yield: **3a**, 85%; **3b**, 82%.

Spectral and analytical data for **3a:** IR (KBr, ν(CO)) 1995 (vs), 1928 (vs). ^1H NMR (δ, $CDCl_3$): 1.20 (t, J(H−H) = 7.1 Hz, 6H, $P(OCH_2CH_3)_2$), 1,48 (m, 4H, 2 CH_2), 1.93 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 2.60 (m, 2H, $P(CH_aH_b)_2P$), 2.80 (m, 2H, $P(CH_aH_b)_2P$), 3.78 (m, 4H, $P(OCH_2CH_3)_2$), 7.33−7.74 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 15.6 (d, ^3J(C−P) = 9.0 Hz, $P(OCH_2CH_3)_2$), 25.4 (s, CH_2), 26.1 (s, CH_2), 27.2 (m, $P(CH_2)_2P$), 31.5 (s, CH_2), 34.4 (s, CH_2), 61.8 (d, ^2J(C-P) = 6.6 Hz, $P(OCH_2\text{-}CH_3)_2$), 128.2−136.6 (m, C_β, PPh_2). MS (FAB, *m/e*): 860 [M^+ − 2CO], 731 [M^+ − $(EtO)_2PS_2$], 645 [M^+ − 2CO − 2EtO − S − C_7H_9]. Anal. Calcd for $C_{39}H_{43}O_4P_3S_2W$: C, 51.1; H, 4.7. Found: C, 51.0; H, 4.8.

Spectral and analytical data for **3b:** IR (KBr, ν(CO)) 1991 (vs), 1921 (vs). ^1H NMR (δ, $CDCl_3$): 1.19 (t, J(H−H) = 7.0 Hz, 6H, $P(OCH_2CH_3)_2$), 1.42 (m, 4H, 2 CH_2), 1.50 (m, 4H, 2 CH_2), 1.77 (m, 4H, 2 CH_2), 2.38 (m, 2H, CH_2), 2.60 (m, 2H, $P(CH_aH_b)_2P$), 2.80 (m, 2H, $P(CH_aH_b)_2P$), 3.77 (m, 4H, $P(OCH_2\text{-}CH_3)_2$), 7.33−7.70 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 15.7 (d, ^3J(C−P) = 9.2 Hz, $P(OCH_2CH_3)_2$), 25.5 (s, CH_2), 26.8 (s, CH_2), 27.0 (s, 3 CH_2), 27.4 (m, $P(CH_2)_2P$), 31.8 (s, CH_2), 35.9 (s, CH_2), 62.0 (d, ^2J(C−P) = 6.7 Hz, $P(OCH_2CH_3)_2$), 128.3−136.4 (m, PPh_2). MS (FAB, *m/e*): 902 [M^+ − 2CO], 773 [M^+ − $(EtO)_2PS_2$], 645 [M^+ − 2CO − 2EtO − S − $C_{10}H_{15}$]. Anal Calcd for $C_{42}H_{49}O_4P_3S_2W$: C, 52.6; H, 5.2. Found: C, 52.8; H, 4.8.

$[(dppe)\{\kappa^3(S,C,S)\text{-}S_2CPCy_3\}W{\equiv}CCH{=}CCH_2(CH_2)_n\text{-}CH_2CH_2][BF_4]$ (n = 1 (4a), 4 (4b)). General Procedure. A mixture of complex **1a** or **1b** (0.2 mmol) and S_2CPCy_3 (0.2 mmol) in methanol (20 mL) was stirred at room temperature for 24 h. The color of the solution changed from orange to deep red, and a red crystalline solid precipitated. Complete precipitation took place by addition of diethyl ether (20 mL). The solvent was decanted, and the resulting solid was washed with diethyl ether (5 mL) and hexane (2 × 5 mL) to give the compounds **4a** or **4b** as red crystalline solids. Yield: **4a** and **4b**, 90%. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): **4a**, 121; **4b**, 118.

Spectral and analytical data for **4a**: IR (KBr, ν(B−F)) 1056 (s, br). ^1H NMR (δ, $CDCl_3$): 1.28 (m, 14H, 7 CH_2), 1.67 (m, 8H, 4 CH_2), 1.80 (m, 10H, 5 CH_2), 2.15 (m, 6H, 3 CH_2), 2.70 (m, 3H, $P(CH(CH_2)_5)_3$), 3.14 (m, 2H, $P(CH_aH_b)_2P$), 3.52 (m, 2H, $P(CH_aH_b)_2P$), 7.13−7.96 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 25.0 (s, CH_2), 25.5 (m, 3 CH_2), 26.3 (s, CH_2), 26.9 (d, ^2J(C−P) = 11.8 Hz, 6 CH_2), 27.4 (m, 6 CH_2), 29.6 (m, $P(CH_2)_2P$), 30.2 (s, CH_2), 32.8 (s, CH_2), 33.9 (d, J(C−P)= 41.4 Hz, $P(CH\text{-}(CH_2)_5)_3$), 128.7−132.9 (m, C_β, PPh_2). MS (FAB, *m/e*): 1031 [M^+ − BF_4], 751 [M^+ − BF_4 − PCy_3], 646 [M^+ − BF_4 − PCy_3 − C − C_7H_9]. Anal. Calcd for $C_{52}H_{66}BF_4P_3S_2W$: C, 55.8; H, 6.0. Found: C, 55.6; H, 6.0.

Spectral and analytical data for **4b**: IR (KBr, ν(B−F)) 1065 (s, br). ^1H NMR (δ, $CDCl_3$): 0.84 (m, 2H, CH_2), 1.10 (m, 2H, CH_2), 1.19 (m, 6H, 3 CH_2), 1.29 (m, 10H, 5 CH_2), 1.38 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.70 (m, 4H, 2 CH_2), 1.78 (m, 4H, 2 CH_2), 1.84 (m, 6H, 3 CH_2), 2.14 (m, 6H, 3 CH_2), 2.72 (m, 3H, $P(CH(CH_2)_5)_3$), 3.23 (m, 2H, $P(CH_aH_b)_2P$), 3.48 (m, 2H, $P(CH_aH_b)_2P$), 7.11−7.99 (m, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 23.2 (s, CH_2), 25.3 (s, CH_2), 25.5 (s, CH_2), 25.6 (s, 3 CH_2), 27.0 (d, ^2J(C−P) = 11.7 Hz, 6 CH_2), 27.6 (d, ^3J(C−P) =

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2.1 Hz, 6 CH_2), 27.9 (s, CH_2), 29.7 (m, $P(CH_2)_2P$), 30.2 (s, CH_2), 31.8 (s, CH_2), 32.6 (s, CH_2), 33.9 (d, J(C−P)= 41.6 Hz, P(*C*H-$(CH_2)_5)_3$), 128.8−132.8 (m, PPh_2). MS (FAB, *m*/*e*): 1073 [$M^+ - BF_4$], 793 [$M^+ - BF_4 - PCy_3$], 646 [$M^+ - BF_4 - PCy_3 - C - C_7H_9$]. Anal. Calcd for $C_{55}H_{72}BF_4P_3S_2W$: C, 56.9; H, 6.2. Found: C, 56.3; H, 6.2.

[(dppe)(CO){*κ*²(*S*,*S*)-S_2CNR_2}W{*κ*²(*C*,*C*)=C(C=O)-CH=$\overline{CCH_2(CH_2)_nCH_2C}H_2$}] (R = Me, *n* = 1 (5a), 4 (5b); R = Et, *n* = 1 (5c), 4 (5d)). General Procedure. A mixture of **1a** or **1b** (0.2 mmol) and NaS_2CNR_2 (0.2 mmol) in methanol (20 mL) was stirred at room temperature for 2 h. The color of the solution changed from orange to reddish-purple. The solvent was removed under vacuum, the solid residue was extracted with dichloromethane, and the extract was filtered. The solution was concentrated to *ca.* 2 mL, and methanol (10 mL) was added. Slow evaporation of the solvents gave **5a**−**d** as red solids. Yield: **5a**, 85%; **5b**, 80%; **5c**, 80%; **5d**, 88%.

Spectral and analytical data for **5a**: IR (KBr, *ν*(CO); *ν*(C=C=O)) 1870 (vs); 1731 (m). ^1H NMR (*δ*, $CDCl_3$): 1.48 (m, 4H, 2 CH_2), 2.53 (m, 4H, 2 CH_2), 2.58 (s, 3H, NCH_3), 2.60 (m, 2H, P(C*H*$_a$H$_b$)$_2$P), 2.69 (s, 3H, NCH_3), 3.10 (m, 2H, P(CH$_a$*H*$_b$)$_2$P), 7.10−8.04 (m, 21H, $C_\beta H$, PPh_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 24.6 (m, P*C*$_a$H$_2$C$_b$H$_2$P), 26.1 (s, CH_2), 26.5 (s, CH_2), 30.2 (m, PC$_a$H$_2$*C*$_b$H$_2$P), 31.5 (s, CH_2), 34.4 (s, CH_2), 38.5 (s, NCH_3), 39.7 (s, NCH_3), 126.3−135.9 (m, PPh_2). MS (FAB, *m*/*e*): 852 [M^+], 795 [$M^+ - 2CO - H$], 702 [$M^+ - 2CO - H - C_7H_9$], 646 [$M^+ - 2CO - H - C_7H_9 - CNMe_2$]. Anal. Calcd for $C_{38}H_{39}NO_2P_2S_2W$: C, 53.6; H, 4.6; N, 1.6. Found: C, 54.1; H, 4.4; N, 1.5.

Spectral and analytical data for **5b**: IR (KBr, *ν*(CO); *ν*(C=C=O)) 1869 (vs); 1722 (m). ^1H NMR (*δ*, $CDCl_3$): 1.39 (m, 6H, 3 CH_2), 1.59 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 2.00 (m, 2H, CH_2), 2.20−3.50 (m, 4H, $P(CH_2)_2P$), 2.32 (m, 2H, CH_2), 2.56 (s, 3H, NCH_3), 2.67 (s, 3H, NCH_3), 7.02−8.33 (m, 21H, $C_\beta H$, PPh_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 23.7 (m, P*C*$_a$H$_2$C$_b$H$_2$P), 25.5 (s, CH_2), 26.3 (s, CH_2), 26.5 (s, CH_2), 27.3 (s, CH_2), 27.4 (s, CH_2), 30.1 (m, PC$_a$H$_2$*C*$_b$H$_2$P), 31.0 (s, CH_2), 37.7 (s, CH_2), 38.5 (s, NCH_3), 39.7 (s, NCH_3), 126.4−134.9 (m, PPh_2). MS (FAB, *m*/*e*): 894 [M^+], 838 [$M^+ - 2CO$], 702 [$M^+ - 2CO - H - C_{10}H_{15}$], 646 [$M^+ - 2CO - H - C_{10}H_{15} - CNMe_2$]. Anal. Calcd for $C_{41}H_{45}NO_2P_2S_2W$: C, 55.1; H, 5.1; N, 1.6. Found: C, 54.8; H, 5.0; N, 1.5.

Spectral and analytical data for **5c**: IR (KBr, *ν*(CO); *ν*(C=C=O)) 1869 (vs); 1726 (m). ^1H NMR (*δ*, $CDCl_3$): 0.93 (t, J(H−H) = 7.2 Hz, 3H, NCH$_2$C*H$_3$*), 0.96 (t, J(H−H) = 7.2 Hz, 3H, NCH$_2$C*H$_3$*), 1.50 (m, 4H, 2 CH_2), 2.05 (m, 2H, CH_2), 2.50 (m, 2H, CH_2), 2.50−3.30 (m, 4H, $P(CH_2)_2P$), 3.00 (m, 2H, NC*H$_2$*CH$_3$), 3.27 (m, 2H, NC*H$_2$*CH$_3$), 7.00−8.00 (m, 21H, $C_\beta H$, PPh_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 12.19 (s, NCH$_2$*C*H$_3$), 12.24 (s, NCH$_2$*C*H$_3$), 25.2 (m, P*C*$_a$H$_2$C$_b$H$_2$P), 26.2 (s, CH_2), 26.6 (s, CH_2), 30.2 (m, PC$_a$H$_2$*C*$_b$H$_2$P), 31.5 (s, CH_2), 34.4 (s, CH_2), 44.1 (s, N*C*H$_2$CH$_3$), 45.3 (s, N*C*H$_2$CH$_3$), 127.1−136.3 (m, PPh_2). MS (FAB, *m*/*e*): 880 [M^+], 823 [$M^+ - 2CO - H$], 730 [$M^+ - 2CO - H - C_7H_9$], 646 [$M^+ - 2CO - H - C_7H_9 - CNEt_2$]. Anal. Calcd for $C_{40}H_{43}NO_2P_2S_2W$: C, 54.6; H, 4.9; N, 1.6. Found: C, 55.4; H, 5.0; N, 1.5.

Spectral and analytical data for **5d**: IR (KBr, *ν*(CO); *ν*(C=C=O)) 1869 (vs); 1725 (m). ^1H NMR (*δ*, $CDCl_3$): 0.90 (t, J(H−H) = 7.1 Hz, 3H, NCH$_2$C*H$_3$*), 0.97 (t, J(H−H) = 7.1 Hz, 3H, NCH$_2$C*H$_3$*), 1.42 (m, 6H, 3 CH_2), 1.75 (m, 4H, 2 CH_2), 2.20 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 2.70−3.40 (m, 4H, $P(CH_2)_2P$), 2.95 (m, 2H, NC*H$_2$*CH$_3$), 3.25 (m, 2H, NC*H$_2$*CH$_3$), 7.00−8.00 (m, 21H, $C_\beta H$, PPh_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 12.2 (s, N(CH$_2$*C*H$_3$)$_2$), 24.7 (m, P*C*$_a$H$_2$C$_b$H$_2$P), 25.6 (s, CH_2), 26.2 (s, CH_2), 26.4 (s, CH_2), 27.3 (s, CH_2), 27.5 (s, CH_2), 30.3 (m, PC$_a$H$_2$*C*$_b$H$_2$P), 30.9 (s, CH_2), 37.8 (s, CH_2), 44.0 (s, N*C*H$_2$CH$_3$), 45.2 (s, N*C*H$_2$CH$_3$), 127.0−134.5 (m, PPh_2). MS (FAB, *m*/*e*): 922 [M^+], 866 [$M^+ - 2CO$], 730 [$M^+ - 2CO - H - C_{10}H_{15}$], 646 [$M^+ - 2CO - H - C_{10}H_{15} - CNEt_2$]. Anal. Calcd for $C_{43}H_{49}NO_2P_2S_2W$: C, 56.0; H, 5.4; N, 1.5. Found: C, 56.8; H, 5.4; N, 1.4.

Table 6. Experimental Data for the X-ray Diffraction Study of Complex 4a

formula	$C_{52}H_{66}BF_4P_3S_2W$
M_r	1118.79
cryst syst	monoclinic
space group	$P2_1/n$
radiation (λ,Å)	graphite-monochromated (Mo Kα, 0.710 73)
a, Å	16.864(4)
b, Å	17.940(5)
c, Å	17.506(5)
β, deg	99.39(2)
V, Å^3	5225(2)
Z	4
D_{calc}, g cm^{-3}	1.422
F(000)	2280
cryst size, mm	0.16 × 0.22 × 0.28
μ (Mo Kα), cm^{-1}	24.30
θ range, deg	3−27
no. of reflns measd	$\pm h,k,l$
unique total no. of data	11384
unique no. of obsd data	4555 [$I > 2\sigma(I)$]
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.0493
$R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$	0.0558

Crystal Structure Determination of Complex 4a. Selected crystallographic data for complex **4a** are listed in Table 6. 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 3−27° were measured; of 11 384 independent reflections, 4555, 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 0.612).[25]

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, excluding the carbon atoms of the alkenyl−carbyne ligand and of the phenyl rings and the atoms of the BF_4^- anion (both the ligand and anion were found disordered and distributed in two positions, A and B, of equal occupancy factors). The hydrogen atoms were placed at their geometrically calculated positions (C−H = 0.96 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 435 variables; after the last cycles, no parameters shifted by more than 0.9 esd. The highest remaining peak (close to the W atom) in the final difference map was equivalent to about 1.50 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 0.738 and 0.0017. Final *R* and R_w values were 0.0493 and 0.0558, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 26. 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.[27]

The extended Hückel parameters were taken from ref 28, and the graphic interpretation of the MO calculations has been performed by using the package CACAO.[29] The geometry of the model used for the calculations is fully consistent with that obtained from the X-ray analysis of compound **4a**.

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940501). L.Z. thanks the Spanish Ministerio de Educación y Ciencia and Ministerio de Asuntos Exteriores (Agencia Española de Cooperación Internacional) for grants. A bilateral Italo-Spanish research project (CNR-CSIC) is gratefully acknowledged (A.G. and C.M.). Preliminary MO studies have been carried out by Mr. Rafael Fernández.

Supporting Information Available: Tables of 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) (8 pages). Ordering information is given on any current masthead page.

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