The ^{31}P NMR spectrum shown in Figure 2 was simulated by using the 1180/1280 ITRCAL routine (an adaptation of the Laocoon III) of the Nicolet software. This routine is designed for simulation of systems with a maximum of seven nuclei with spin $^1/_2$. Since our complexes involve six phosphorus and three rhodium atoms (nine spin $^1/_2$ nucleii in all), we had to carry out the calculations in three parts. To do this we performed individual simulations using all six phosphorus atoms, with full coupling between them, and one rhodium atom which was placed at Rh$_a$, Rh$_b$, and Rh$_c$ in successive calculations.[29] As a result the calculations cannot include any Rh–Rh coupling nor can they include Rh–P coupling other than one-bond coupling. However this is not a major limitation since these particular coupling constants are known from work on simpler molecules to be much smaller (<10 Hz) than most of the coupling constants used in the simulations.[18] The calculations produced satisfactory simulations of the spectra at both 145.8 and 81 MHz.

X-ray Data Collection, Refinement, and Solution. Well-formed red crystals were obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution of $[Rh_3(\mu\text{-}dpmp)_2(\mu\text{-}CO)(CO)(\mu\text{-}Cl)(Cl)][BPh_4]$. Crystal data, data collection procedure, and refinement of the structure are summarized in Table V. The lattice was found to be monoclinic by standard procedures using the software associated with the Syntex P2$_1$ diffractometer. Quick scans of the reflections for space group determination yielded the conditions $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$, consistent with the space group $P2_1/n$. The data were collected at 140 K by using a locally modified LT-1 low-temperature apparatus on the Syntex P2$_1$ diffractometer. The data were corrected for Lorentz, polarization, and extinction effects. The structure was solved by locating the three rhodium atoms using the Patterson map generated using the FMAP8 routine of SHELXTL, version 4, 1984 (Nicolet Instrument Corporation, Madison, WI). Other atoms were located from successive difference Fourier maps. Final cycles of refinement were made with anisotropic thermal parameters for rhodium, phosphorus, and chlorine and isotropic thermal parameters for all remaining atoms. Hydrogen atoms were not located. Scattering factors and corrections for anomalous dispersion was taken from a standard source.[30] An absorption correction (XABS) was applied. A conventional R factor of 0.072 was obtained. The final difference Fourier map showed a feature at 0.532, 0.071, 0.025 (3.4 e Å^{-3}) which was 1.33 Å away from a feature at 0.5, 0, 0 (2.3 e Å^{-3}). These produce a linear triatomic molecule (by inversion of the first peak) which may represent a disordered remnant of a solvent molecule which largely vaporized from the crystal.

Acknowledgment. We thank the National Science Foundation (No. CHE8217954) for financial support and Mr. M. V. Nguyen for experimental assistance.

Registry No. 2, 84774-75-4; 3, 86372-62-5; 4 (X = Cl), 95045-36-6; 4 (X = Br), 95045-39-9; 4 (X = I), 95045-41-3; 4·CH$_2$Cl (X = Cl), 95045-37-7; $[Rh_3(\mu\text{-}dpmp)_2(^{13}CO)_3Br_2][BPh_4]$, 95045-43-5; $[Rh_3(\mu\text{-}dpmp)_2(CO)_3Br_2][BPh_4]$, 95045-45-7.

Supplementary Material Available: A listing of anisotropic thermal parameters, hydrogen atom positions, and structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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Transition-Metal Ketenes. 25.[1] Bis(trimethylphosphine)-Substituted η^2-Alkyne Complexes of Tungsten. Synthesis, Structure, and Extended Hückel MO Calculations

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Bis(trimethylphosphine)-substituted, cationic η^2-alkyne complexes of tungsten $(\eta^5\text{-}C_5H_5)[P(CH_3)_3]_2W(\eta^2\text{-}RC{\equiv}COR')[BF_4]$ (R = CH_3, $C_6H_4CH_3$-4; R′ = CH_3, C_2H_5) were prepared by treatment of the corresponding mixed carbonyl–trimethylphosphine alkyne complexes with trimethylphosphine. The substitution is accompanied by an unexpected color change from yellow to violet which can be explained on the basis of extended Hückel MO calculations. The structures of the new compounds were determined by spectroscopy and, in the case of the η^2-methoxy(4-methylphenyl)ethyne complex **2b**, additionally by X-ray analysis.

Introduction

The intramolecular carbonylation of suitable carbyne complexes leads via CC bond formation to η^1- and η^2-ketenyl complexes.[2-5] These show pronounced reactivity toward Lewis basis to afford new ketenyl,[4,5] σ-bonded alkynyl,[6] arsino- and phosphinoketene[7,8] as well as η^3-phosphinoketene complexes.[9,10] On the other hand, the η^2-ketenyl complexes add Lewis acids to the ketene oxygen atom with concomitant conversion of the η^2-ketenyl into an η^2-alkyne ligand. This reaction allows an easy access

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Table I. $^{13}C\{^1H\}$ NMR Spectral Data (ppm) of 2a–c (δ)

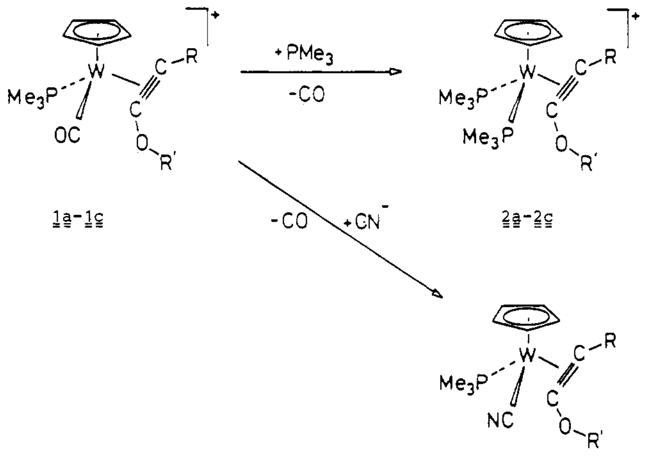
	2a	2b	2c
$C\equiv CO$	227.9	225.5 (17.1)^a	223.9 (15.0)^a
$C\equiv CO$	200.5	199.8 (5.8)^a	200.0 (6.0)^a
$C_6H_4CH_3$		138.6, 138.2	138.8, 138.6
		129.5, 127.8	129.4, 127.4
		21.4	21.5
C_5H_5	90.7	91.5	91.2
OR′	64.4	65.2	74.5, 15.8
PCH_3	24.1 (34.2)^b	23.8 (35.4)^b	24.1 (34.2)^b
CH_3	22.4		

^{a} $^2J(^{31}P-^{13}C)$ pseudotriplet. ^{b} $N(^{31}P-^{13}C)$.

to neutral and cationic η^2-alkyne complexes.[11,12] Comparable alkyne complexes have been obtained in the reactions of Cl [P(CH$_3$)$_3$]$_4$WCH with aluminium trichloride or aluminum trimethyl and CO.[13,14]

Results and Discussion

We have now found that the substitution of the carbonyl ligand in the cationic alkyne complexes using an excess of trimethylphosphine leads to a surprising change of color from yellow to violet and generates the species **2a–c** in good yields from **1a–c**. A similar phenomenon was observed on the substitution of the carbonyl ligand in **1b** by a cyanide group to yield **3b**. Green cationic acetylene complexes have been obtained by treating [Mo(CO)(Me$_3$SiC$_2$H)$_2$(η^5-C$_9$H$_7$)][BF$_4$] with P(OMe)$_3$.[15]



a, R = R′ = CH$_3$; b, R = C$_6$H$_4$CH$_3$, R′ = CH$_3$; c, R = C$_6$H$_4$CH$_3$, R′ = C$_2$H$_5$

The violet diamagnetic compounds are slightly soluble in dichloromethane. The composition and structure of these complexes were confirmed by elemental analysis and proton, carbon-13, and phosphorus NMR spectroscopy, and, in the case of **2b**, by X-ray structure analysis.

The carbon-13 NMR spectra are in agreement with those of the proposed structures of **2a–3b** (Table I). The strong low-field shift of the alkyne carbon atoms suggest a 4π-electron alkyne ligand,[16] whereas the accompanying tungsten carbon coupling constants indicate high σ-bond contributions between tungsten and the two alkyne carbon atoms.[17] Thus, the description as a metallacyclopropene seems comparably appropriate.

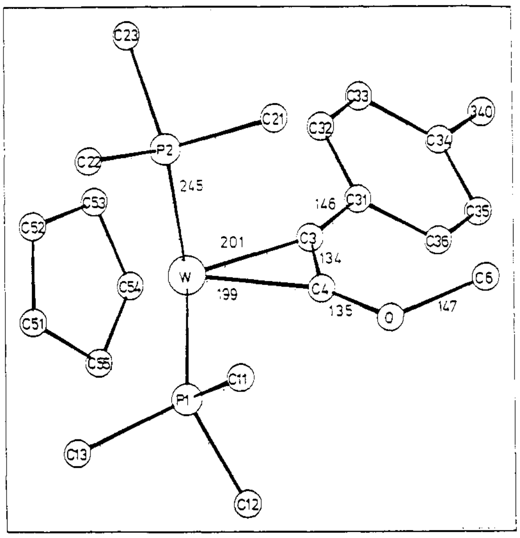


Figure 1.

For all complexes the $^{31}P\{^1H\}$ NMR spectra exhibit a singlet accompanied by tungsten satellites. In view of the appearance of only one signal the two trimethylphosphine ligands must be magnetically equivalent, at least on the NMR time scale.

The structure of **2b** was solved by conventional Patterson and Fourier techniques and is shown in Figure 1. The atomic positional and thermal parameters for the complex are listed in Table II and the intramolecular distances and angles in Table III. The distances from tungsten to the cyclopentadienyl and the two trimethylphosphine ligands are comparable to those found for similar organometallic tungsten complexes. As generally observed for acetylene complexes, the C≡C bond [1.339 (14) Å] is lengthened compared to C$_2$Ph$_2$ [1.198 (3) Å],[18] but this CC distance is not very sensitive to the number of electrons donated to the metal. Within the W–C(3)–C(4) ring the W–C(3) [2.007 (11) Å] and the W–C(4) bonds [1.990 (10) Å] are nearly equivalent and distinctly shorter than a tungsten–carbon single bond.[19] Short metal–carbon bonds as in W, Mo, and Ta complexes have been discussed in terms of two- and four-electron donor alkyne ligands,[20,21] but the conclusions drawn are not of general significance since the comparisons were made between complexes with different metals, ligands, or acetylenic groups. The change in the –C≡C– angles upon coordination is also noticeable and in line with other systems: from 178.1 (2)° in the essentially linear free ligand C$_2$Ph$_2$[18] the angle decreases to 143.2 (10)° as a result of rehybridization of the acetylenic carbons. So, equally justified, the structure of **2b** can be regarded as a metallacyclopropene complex (I ↔ II). The

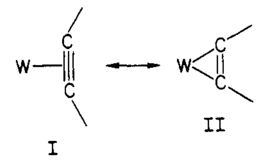


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Table II. Positional and Thermal Parameters for Hydrogen and Non-Hydrogen Atoms of $C_{21}H_{33}BF_4OP_2W$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
W	0.46174 (4)	0.21323 (3)	0.10969 (1)	C(21)	0.159 (2)	0.4078 (13)	0.1381 (5)
P(1)	0.2768 (3)	0.0302 (3)	0.10055 (10)	C(22)	0.0631 (13)	0.3407 (12)	0.0385 (4)
P(2)	0.2438 (3)	0.3703 (3)	0.08666 (11)	C(23)	0.3019 (15)	0.5261 (12)	0.0699 (5)
C(4)	0.4374 (11)	0.1957 (10)	0.1767 (4)	O	0.3541 (8)	0.1505 (8)	0.2076 (3)
C(3)	0.5624 (11)	0.2735 (10)	0.1767 (4)	C(6)	0.389 (2)	0.206 (2)	0.2560 (4)
C(31)	0.7028 (11)	0.3357 (10)	0.2081 (4)	B	0.1778 (13)	0.2128 (15)	0.4128 (5)
C(32)	0.7833 (12)	0.4393 (10)	0.1929 (4)	F(1)	0.2301 (10)	0.1027 (7)	0.4412 (3)
C(33)	0.9257 (12)	0.4904 (11)	0.2196 (4)	F(2)	0.0141 (9)	0.2038 (8)	0.3929 (3)
C(34)	0.9993 (12)	0.4379 (11)	0.2640 (4)	F(3)	0.2037 (10)	0.3181 (7)	0.4413 (3)
C(340)	0.1548 (14)	0.4861 (13)	0.2932 (5)	F(4)	0.2553 (12)	0.2231 (12)	0.3766 (4)
C(35)	0.9265 (12)	0.3343 (11)	0.2802 (4)	C(51)	0.4991 (11)	0.1490 (12)	0.0332 (4)
C(36)	0.7794 (11)	0.2857 (12)	0.2533 (4)	C(52)	0.5070 (11)	0.2802 (13)	0.0330 (4)
C(11)	0.0839 (12)	0.0462 (12)	0.1177 (4)	C(53)	0.6321 (12)	0.3237 (10)	0.0707 (4)
C(12)	0.3692 (12)	−0.1056 (10)	0.1369 (5)	C(54)	0.7040 (10)	0.2152 (14)	0.0933 (4)
C(13)	0.2078 (13)	−0.0499 (12)	0.0421 (4)	C(55)	0.6290 (12)	0.1034 (11)	0.0732 (4)

atom	*x/a*	*y/b*	*z/c*	*B*, Å²	atom	*x/a*	*y/b*	*z/c*	*B*, Å²
H131	0.173	0.006	0.017	3.0	H62	0.307	0.193	0.273	3.5
H232	0.237	0.586	0.072	3.0	H63	0.491	0.185	0.277	3.5
H233	0.347	0.534	0.046	3.0	H222	0.092	0.298	0.012	3.5
H33	0.973	0.554	0.205	3.0	H223	−0.010	0.286	0.050	3.5
H341	1.197	0.432	0.314	3.0	H132	0.294	−0.098	0.035	3.5
H342	1.141	0.561	0.311	3.5	H133	0.120	−0.106	0.042	3.5
H343	1.229	0.503	0.274	3.5	H32	0.738	0.477	0.163	3.5
H212	0.087	0.480	0.131	3.5	H35	0.976	0.297	0.310	3.5
H213	0.239	0.425	0.166	3.5	H111	0.024	−0.032	0.112	3.5
H122	0.467	-0.131	0.129	3.5	H112	0.018	0.113	0.099	3.5
H123	0.297	−0.177	0.133	3.5	H113	0.100	0.068	0.151	3.5
H36	0.728	0.215	0.264	3.5	H121	0.392	−0.077	0.169	3.0
H51	0.422	0.097	0.011	3.5	H211	0.096	0.334	0.142	3.0
H52	0.437	0.337	0.009	3.5	H221	0.010	0.419	0.027	3.0
H53	0.662	0.410	0.079	3.5	H231	0.396	0.534	0.094	3.0
H54	0.797	0.217	0.120	3.5	H61	0.391	0.299	0.250	3.0
H55	0.657	0.016	0.083	3.5					

atom	*B*(1)	*B*(22)	*B*(33)	1 *B*(12)	*B*(13)	*B*(23)
W	1.26 (1)	1.64 (2)	1.58 (2)	−0.01 (2)	0.32 (1)	−0.03 (2)
P(1)	1.5 (1)	1.6 (1)	2.0 (1)	−0.1 (1)	0.3 (1)	0.0 (1)
P(2)	2.2 (1)	2.1 (1)	2.8 (1)	0.4 (1)	0.9 (1)	0.3 (1)
C(4)	3.0 (4)	1.6 (5)	1.2 (4)	0.4 (4)	0.8 (3)	0.3 (4)
C(3)	2.1 (4)	1.5 (4)	3.1 (5)	−0.4 (4)	1.2 (3)	−1.3 (4)
C(31)	2.2 (4)	1.9 (4)	2.0 (5)	0.1 (3)	0.9 (4)	−0.0 (4)
C(32)	2.2 (4)	2.0 (5)	2.9 (6)	−0.8 (4)	0.8 (4)	−0.5 (4)
C(33)	3.2 (5)	2.4 (5)	2.8 (6)	−0.7 (4)	0.8 (4)	−0.6 (5)
C(34)	2.3 (4)	3.8 (6)	1.5 (5)	0.2 (4)	0.0 (4)	−1.4 (4)
C(340)	2.9 (5)	3.9 (7)	4.4 (7)	−1.9 (5)	0.4 (5)	−1.6 (6)
C(35)	3.1 (5)	2.3 (5)	2.2 (5)	−0.4 (4)	0.4 (4)	0.0 (4)
C(36)	2.5 (4)	2.5 (5)	3.0 (5)	−1.1 (4)	0.4 (4)	−0.7 (5)
C(11)	2.4 (4)	4.2 (6)	2.8 (6)	−0.3 (4)	1.2 (4)	−0.0 (5)
C(12)	2.8 (4)	1.9 (5)	3.9 (6)	−0.5 (4)	0.7 (4)	0.2 (4)
C(13)	2.7 (5)	3.5 (6)	3.2 (6)	−1.0 (4)	0.4 (4)	−0.4 (5)
C(21)	4.6 (6)	3.7 (7)	4.3 (7)	1.9 (5)	2.2 (5)	−0.1 (6)
C(22)	3.1 (5)	4.0 (6)	2.4 (6)	0.8 (4)	0.7 (4)	0.5 (5)
C(23)	3.9 (6)	2.7 (6)	5.7 (8)	0.9 (5)	2.1 (5)	1.4 (6)
O	3.5 (3)	3.9 (4)	1.9 (4)	−1.7 (3)	1.4 (3)	−0.1 (3)
C(6)	5.6 (6)	6.6 (8)	1.9 (5)	−2.0 (7)	1.9 (5)	−1.5 (7)
B	2.6 (5)	2.2 (5)	2.8 (6)	−0.0 (5)	0.0 (4)	−0.2 (6)
F(1)	7.1 (4)	3.0 (4)	4.5 (5)	-1.1 (3)	0.1 (3)	−0.1 (3)
F(2)	4.5 (4)	5.1 (4)	7.0 (5)	−1.0 (3)	−1.1 (3)	1.4 (5)
F(3)	7.4 (5)	2.4 (4)	5.9 (5)	−0.7 (3)	−2.3 (4)	−0.7 (3)
F(4)	7.3 (5)	11.7 (8)	6.8 (6)	1.8 (5)	3.3 (4)	2.0 (6)
C(51)	1.7 (4)	3.0 (5)	1.6 (5)	−0.0 (4)	0.5 (3)	−0.2 (5)
C(52)	2.5 (4)	2.4 (5)	2.1 (5)	0.2 (5)	1.1 (3)	−0.3 (6)
C(53)	2.1 (4)	2.8 (6)	2.6 (6)	−0.6 (4)	0.6 (4)	−0.0 (4)
C(54)	1.0 (3)	5.2 (6)	2.1 (5)	−0.3 (5)	0.2 (3)	0.2 (6)
C(55)	2.3 (4)	3.1 (6)	2.4 (6)	0.7 (4)	1.5 (4)	−0.3 (4)

drastic color change from yellow (**1b**, λ_{max} = 465 nm (ϵ 1640 mol^{-1} cm^{-1})) to violet (**2b**, λ_{max} = 562 nm by trimethylphosphine roused our interest in the nature of the electronic transition and in the difference of the MO descriptions of the mixed carbonyl–phosphine and bis(phosphine)-substituted complexes. A simple description can be found on the basis of extended Hückel MO calculations. The electronic structure as well as conformational details of half-sandwich d^4-alkyne complexes such as **1a**–**3b** can be conveniently described in terms of interacting d^4 CpMLL′ metal fragments and alkyne ligands. This has been shown in detail by Hoffmann and Schilling[22] for the $CpMo(CO)(PH_3)^+$ fragment and its bonding capability

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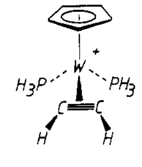
Table III. Intramolecular Distances (A) and Angles (deg) of 2b

	Bond Distances		
W-C(3)	200.7 (11)	W-C(51)	238.6 (11)
W-C(4)	199.0 (10)	W-C(52)	242.5 (11)
W-P(1)	245.0 (3)	W-C(53)	233.5 (11)
W-P(2)	244.5 (3)	W-C(54)	222.1 (9)
		W-C(55)	227.0 (11)
C(3)-C(4)	133.9 (14)	C(4)-O	134.5 (12)
C(3)-C(31)	146.3 (15)	C(6)-O	146.8 (15)
P(1)-C(11)	183.1 (11)	P(2)-C(21)	183.4 (14)
P(1)-C(12)	182.4 (12)	P(2)-C(22)	183.0 (12)
P(1)-C(13)	184.0 (13)	P(2)-C(23)	179.9 (13)
	Bond Angles		
P(1)-W-P(2)	95.95 (10)	W-C(3)-C(31)	145.64 (80)
P(1)-W-C(3)	117.58 (31)	W-C(3)-C(4)	69.17 (62)
P(1)-W-C(4)	79.53 (29)	C(31)-C(3)-C(4)	143.15 (101)
P(2)-W-C(3)	99.77 (31)	W-C(4)-O	149.48 (76)
P(2)-W-C(4)	94.29 (30)	W-C(4)-C(3)	71.14 (63)
		C(3)-C(4)-O	139.20 (98)
C(4)-O-C(6)	117.62 (89)		

toward the C_2H_2 group. In connection with the experimental findings presented here, we have performed model EH MO calculations[23] for **4**, the basic model for systems **2a–c**, in order to have a direct comparison to the electronic structure of **5**, the parent compound for **1a–c**.



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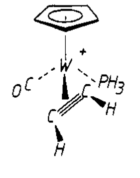


5

Figure 2 shows an interaction diagram for **4**, constructing its valence MOs from those of a d^4 $CpW(PH_3)_2^+$ fragment and a bent acetylene unit. The orientation of the C_2H_2 ligand is as indicated in **4** (overall C_s symmetry) and represents the computed minimum energy conformation for the model. Due to a minimization of steric repulsions with the PMe_3 groups or due to packing effects, the frozen conformation of the methoxy(4-methylphenyl)ethyne ligand in the crystal structure of **3b** is skewed (see Figure 1). The computed energy of rotation for the C_2H_2 ligand in **4** indeed indicates, that it only requires about 4–5 kcal to rotate the C_2H_2 group by as much as 40°. This is easily understood, as the two orthogonal metal fragment MOs a″ and 1a′ (see Figure 2 and text below) are nearly degenerate. Facile alkyne rotation or, in the case of **2a–3b** at least a facile windshield wiper motion, is reflected in the magnetic equivalence of the two PMe_3 ligands in **2a–2c**. The relevant orbitals of $CpW(PH_3)_2^+$, **1a′–3a′**, typical for a $CpML_2$ fragment[24] with σ-donor ligands L, are shown in a simplified manner on the left of Figure 2 and need not be reiterated here. Both donor orbitals of the bent acetylene unit, 1π and 2π (HOMO, rehybridized by bending), interact with the appropriate metal orbitals 2a′ and 3a′. The antibonding linear combination of 1π with 2a′ forms the LUMO of the complex cation, localized only 12% within the acetylene ligand and 83% on tungsten, therefore being essentially an empty d level. Strong interaction and back-bonding occur from a″ of the metal unit to the lowest acceptor MO 3π* of the C_2H_2. As in other cases[25] the alkyne utilizes its two occupied π levels to interact with the tungsten center; the strongest ligand–metal interaction, however, comes from 3π* back-bonding to a″.

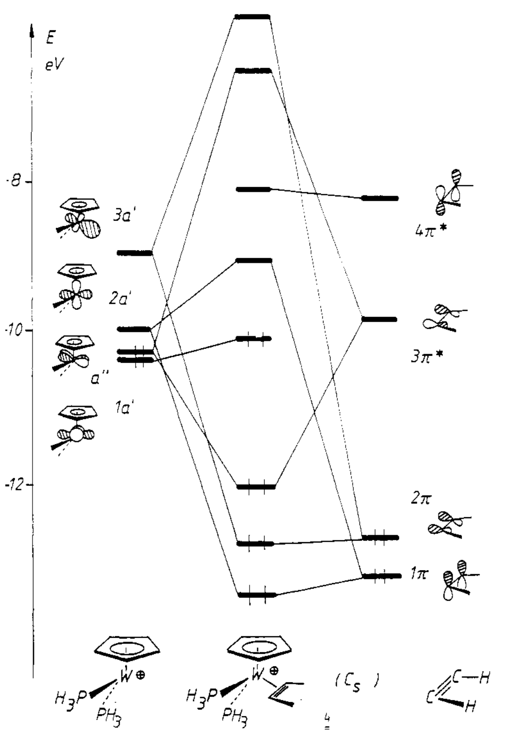
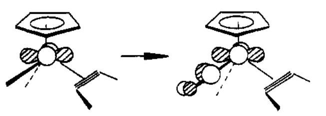


Figure 2.

The HOMO of **4** is the "left over" metal fragment orbital 1a′, slightly destabilized by 2π within a three-orbital pattern of MOs 2π, 1a′, and 3a′. This highest occupied orbital appears only 1 eV below the LUMO, which makes the energy gap here 0.73 eV smaller than that computed for the carbonyl-substituted analogue **5**. The comparison of **4** and **5** (in their computed minimum energy conformations with the C≡C vector parallel to the W–CO bond[23] for **5** as in a related experimental structure[26]) reveals the most pronounced orbital energy difference for the HOMO, which, as qualitatively shown in **6**, is stabilized by 0.96 eV



6

through back-bonding, when one PH_3 of **4** is replaced by a carbonyl ligand. The LUMO energy is less different for **4** and **5**, only 0.23 eV higher for the bis(phosphine) complex. Both frontier level energy changes make up for the 0.73 eV HOMO–LUMO gap reduction on going from **5** to **4**. Thus the violet-blue color of the bis(phosphine) substitution products **2a–c** is in contrast to that of the yellow precursor compounds **1a–c** with mixed $CO/P(CH_3)_3$ ligand pattern, and the differences in their electronic spectra become understandable on the basis of the reduced d–d excitation energy. The same arguments of course apply if the strong π-acceptor CO is replaced by the weaker CN^- ligand.

Experimental Section

All manipulations were carried out under purified argon atmosphere with use of conventional Schlenk techniques. The solvents ether and pentane were distilled over sodium/potassium

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(23) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. The parameters used for W and P (sp basis) are taken from: Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320. The structural data are adapted from the X-ray structures of $(\eta^5\text{-}C_5H_5)(CO)[P(CH_3)_3]W(\eta^2\text{-}C_6H_4CH_3C{\equiv}COB_{10}H_{14}]$[26] and of **2b**.

(24) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. Hofmann, P. *Angew. Chem.* **1977**, *89*, 551; *Angew. Chem., Int. Ed. Engl.* **1977**, 16.

(25) Tatsumi, K.; Hoffmann, R.; Tempelton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

(26) Sieber, W. J.; Neugebauer, D.; Kreissl, F. R., unpublished results.

and dichloromethane was distilled over sodium/lead alloy prior to use. Dichloromethane-d_2 was purchased from Merck and used without further purification.

The proton and carbon-13 NMR spectra were recorded in dichloromethane-d_2 solution at 90 MHz on a JEOL FX 90-Q spectrometer; chemical shifts are reported relative to $CDHCl_2$, 5.40 ppm, for ^1H and CD_2Cl_2, 54.2 ppm, for ^{13}C. The ^{31}P NMR spectra were recorded in dichloromethane-d_2 at 36.4 MHz on a Bruker HFX-90 spectrometer with the chemical shifts relative to 85% H_3PO_4 external. Mass spectra were recorded on a Varian MAT 311A spectrometer using the FD technique.

(η^5-Cyclopentadienyl)(η^2-methoxymethylethyne)bis(trimethylphosphine)tungsten Tetrafluoroborate (2a). A solution of 0.42 g (0.8 mmol) of **1a**[12] in 20 mL of dichloromethane was treated with 0.15 g (2.0 mmol) of trimethylphosphine at −78 °C. On warming up to room temperature the yellow color of the solution turned to violet. After 1 h the solvent and the excess of trimethylphosphine were removed under vacuum. The oily residue was dissolved in 5 mL of dichloromethane, and the crude product then was precipitated with ether/pentane. Further purification by recrystallization from a mixture of dichloromethane/ether/pentane yielded, after being dried under vacuum at room temperature, 0.44 g (96%) of **3a**, a red-violet powder: ^1H NMR δ 5.40 (t, J = 1.8 Hz, C_5H_5), 4.26 (s, OCH_3), 2.98 (s, CH_3), 1.70 (d, J = 9.0 Hz, PCH_3); ^{31}P NMR δ −21.5 [$^1J(^{183}W-^{31}P)$ = 324.7 Hz]; MS, m/z 471 cation. Anal. Calcd for $C_{15}H_{29}BF_4OP_2W$ (558.00): C, 32.29; H, 5.24. Found: C, 31.83; H, 5.40.

(η^5-Cyclopentadienyl)[η^2-methoxy(4-methylphenyl)ethyne]bis(trimethylphosphine)tungsten Tetrafluoroborate (2b). The analogous reaction of 1.17 g (2.0 mmol) of **1b**[12] with 0.23 g (3.0 mmol) of trimethylphosphine yielded, after purification, 1.20 g (95%) of **3b**, violet crystals: ^1H NMR δ 7.22 (m, C_6H_4), 5.48 (t, J = 1.5 Hz, C_5H_5), 4.17 (s, OCH_3), 2.47 (s, CH_3), 1.76 (d, J = 9.0 Hz, PCH_3); ^{31}P NMR δ −23.0 [$^1J(^{183}W-^{31}P)$ = 320.5 Hz]; MS, m/z 547 cation. Anal. Calcd for $C_{21}H_{33}BF_4OP_2W$ (634.10): C, 39.78; H, 5.25; P, 9.77; W, 28.99. Found: C, 39.59; H, 5.29; P, 9.46; W, 28.62.

(η^5-Cyclopentadienyl)[η^2-ethoxy(4-methylphenyl)ethyne]bis(trimethylphosphine)tungsten Tetrafluoroborate (2c). The reaction of 0.90 g (1.5 mmol) of **1c**[12] with 0.15 g (2.0 mmol) of trimethylphosphine yielded, after purification and drying under vacuum, 0.87 g (90%) of **5b**, violet crystals: ^1H NMR δ 7.27 (m, C_6H_4), 5.40 (t, J = 1.8 Hz, C_5H_5), 4.51 (q, OCH_2), 2.56 (s, CH_3), 1.86 (d, J = 9.0 Hz, PCH_3), 1.50 (t, CH_2CH_3); ^{31}P NMR δ −23.0 [$^1J(^{183}W-^{31}P)$ = 320.4 Hz]; MS, m/z 561 cation. Anal. Calcd for $C_{22}H_{35}BF_4OP_2W$ (648.13): C, 40.77; H, 5.44; P, 9.56; W, 28.37. Found: C, 40.81; H, 5.36; P, 9.35; W, 28.33.

Cyano(η^5-cyclopentadienyl)[η^2-methoxy(4-methylphenyl)ethyne](trimethylphosphine)tungsten Tetrafluoroborate (3b). The treatment of 0.59 g (1.0 mmol) of **1b**[12] in methanol with 0.07 g (1.0 mmol) of KCN yielded, after purification, 0.17 g (34%) of **5b**, red-violet powder ($C_{19}H_{24}NOPW$ (497.23): ^1H NMR δ 7.67 (m, C_6H_4), 5.33 (s, C_5H_5), 4.33 (s, OCH_3), 2.50 (s, CH_3), 1.60 (d, J = 9.1 Hz, PCH_3); ^{31}P NMR δ −19.9 [$^1J(^{183}W-^{31}P)$ = 381.5 Hz]; MS, m/z 497 (M^+); IR 2080 cm^{-1} (ν_{CN}).

X-ray Crystallography of 2b ($C_{21}H_{33}BF_4OP_2W$). Suitable crystals were obtained by cooling a dichloromethane solution of **2b**. The measurements were carried out at −40 °C with a crystal mounted in a glass capillary on a Syntex $P2_1$ instrument using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The lattice constants at −40 °C obtained from θ values for 15 reflections are a = 8.506 (2) Å, b = 10.447 (2) Å, c = 28.668 (7) Å, β = 103.87 (2)°, and V = 2473.3 (9) Å^3. The calculated density (d_{calcd}) is 1.70 g/cm^3 for z = 4. The space group, derived from systematic absent reflections, is $P2_1/c$.

Intensity data were collected by the ω scan technique ($\Delta\omega$ = 1°; 29.3°/min $\geq$ scan rate $\geq$ 1.2°/min; $2\theta_{max}$ = 48.0°). Lorentz–polarization and an empirical absorption correction were applied (μ = 51.1 cm^{-1}). The absorption correction was based on ψ scan measurements for nine reflections with χ near 270°. After averaging of equivalent reflections, a total of 3880 independent reflections were obtained of which 3172 reflections ($I > 1.96\sigma(I)$) were used in the subsequent calculations. The structure was solved by Patterson and Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were located in difference Fourier maps. They were not refined; however, their contribution to F_c was taken into account in the least-squares calculations. Scattering factors for neutral atoms were applied. The calculations were done on a Nova 1200 computer using the Syntex XTL program package. The resulting R values are $R(F)$ = 0.045 and $R_w(F)$ = 0.046. The observed and calculated structure factor amplitudes are available as supplementary material.

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Registry No. **1a**, 89041-51-0; **1b**, 85748-31-8; **1c**, 85735-53-1; **2a**, 94993-10-9; **2b**, 94993-12-1; **2c**, 94993-14-3; **3b**, 94993-15-4; **4**, 94993-16-5; **5**, 94993-17-6; PMe_3, 594-09-2; HC≡CH, 74-86-2.

Supplementary Material Available: A listing of structure factor amplitudes (36 pages). Ordering information is given on any current masthead page.