Induction of Carbonyl–Carbyne Coupling by Chelating Schiff Base Ligands. Crystal and Molecular Structure of Carbonyl(methoxyphenylacetylene)-bis(pyrrole-2-carboxaldehyde methyliminato)tungsten

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Reaction of the tungsten carbyne complexes [(W≡CR)Cl(CO)$_2$(py)$_2$] (**1a**, R = C_6H_5; **1b**, R = CH_3) with pyrrole-2-carboxaldehyde methylimine ($C_6H_8N_2$)/KOH in THF followed by metathesis with NEt_4Cl in CH_2Cl_2 gives the anionic tungsten ketenyl complexes [NEt_4][W($C_6H_7N_2$)$_2$(RCCO)(CO)] (**3a**, R = C_6H_5; **3b**, R = CH_3). Alkylation of **3** with methyl fluorosulfate provides the neutral tungsten alkoxyacetylene complexes W($C_6H_7N_2$)$_2$(RC≡COCH$_3$)(CO) (**4a**, R = C_6H_5; **4b**, R = CH_3). The molecular structure of **4a** has been determined by X-ray crystallography: space group $P2_1/n$, a = 9.568 (2) Å, b = 20.884 (4) Å, c = 10.597 (2) Å, β = 98.25 (2)°, Z = 4, R = 2.8%, R_w = 2.4%.

Introduction

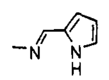
Transition-metal carbyne complexes of the group 6 transition metals[1] have become easily available through the recent development of new synthetic methods.[2,3] For the investigation of the reactivity of this type of compound it is important to have access to stable complexes containing coordinatively labile ligands and it is desirable to be able to control the number of those ligands. The bis(pyridine)-substituted complexes [(W≡CR)Cl(CO)$_2$(py)$_2$] (**1**)[2] (py = pyridine) possess two labile pyridine ligands. Substitution of only one pyridine ligand was demonstrated in the reaction with excess chloride which leads quantitatively to [NEt_4][(W≡CR)Cl$_2$(CO)$_2$(py)].[4] Substitution of both pyridine ligands is easily achieved by the addition of strong donor ligands, e.g. PMe$_3$ or Ph$_2$PCH$_2$CH$_2$PPh$_2$.[2] We have been interested in devising transition-metal carbyne complexes containing only a single labile ligand.[5] In the course of this work we have investigated reactions of complexes **1** with monoanionic bidentate ligands (XL$^-$) in the hope to obtain complexes of the type [(W≡CR)(XL)(CO)$_2$(py)]. However, these reactions did not proceed in the intended way. Complexes **1** easily take up 2 equiv of monoanionic bidentate ligands. With dithiocarbamate ligands we observed, depending upon the counterion, Na$^+$ or H$_2$NEt$_2$$^+$, formation of tungsten ketenyl complexes [W(RCCO)(Et$_2$NCS$_2$)$_2$(CO)]$^-$ or thioaldehyde complexes [W(Et$_2$NCS$_2$)(Et$_2$NCS)(CO)(S=CHR)], respectively.[6] Here we report reactions of **1** with an anionic chelating Schiff base ligand, pyrrole-2-carboxaldehyde methyliminate, which also lead to formation of ketenyl complexes by carbonyl–carbyne coupling.

Results and Discussion

Reactions. The bis(pyridine)-substituted tungsten carbyne complexes [(W≡CR)Cl(CO)$_2$(py)$_2$] (**1a**,**b**) react in

$$\underset{\substack{\textbf{1a},\ R = C_6H_5\\ \textbf{1b},\ R = CH_3}}{[(W{\equiv}CR)Cl(CO)_2(py)_2]} \xrightarrow[\text{2. NEt}_4\text{Cl, CH}_2\text{Cl}_2]{\text{1. }\mathbf{2}\text{/KOH, THF}} \underset{\substack{\textbf{3a},\ R = C_6H_5\\ \textbf{3b},\ R = CH_3}}{[NEt_4][W(RCCO)(NN)_2(CO)]} \qquad (1)$$

tetrahydrofuran (THF) with 2 equiv of pyrrole-2-carboxaldehyde methylimine, **2** (NN = anion of **2**), in the pres-



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ence of solid KOH to give anionic tungsten ketenyl complexes which are isolated as their tetraethylammonium salts **3a** and **3b** in 95 and 80% yield, respectively. Compounds **3** are air-sensitive and hygroscopic but may be handled as solids in the atmosphere for short periods of time without visible decomposition. When reaction 1 is followd by IR, an intermediate is observed in the initial phase of the reaction in which both carbonyl stretching frequencies are shifted by a few wavenumbers to lower frequencies. This is evidence for a stepwise incorporation of the Schiff base ligand into the metal complex. It is not possible to decide on the basis of the IR spectrum, however, whether the first chelating ligand is replacing two pyridine ligands or one pyridine ligand and the chloride ligand. Isolation of the intermediate was not achieved successfully. Even in the presence of only 1 equiv of Schiff base **2** a significant fraction of the intermediate reacts with a second Schiff base ligand to give the ketenyl complex **3**. In the analogous reaction of **1a** with the anionic chelate ligand sodium diethyldithiocarbamate, which provides the anionic ketenyl complex [W(PhCCO)(Et$_2$NCS$_2$)$_2$(CO)]$^-$, no intermediate at all could be observed spectroscopically. Compounds **3** exhibit a strong absorption for a terminal carbonyl ligand around 1830 cm^{-1}. A broad absorption of medium intensity at approximately 1670 cm^{-1} is assigned to the ν(C=O) stretch of the η^2-ketenyl ligand. Two absorptions centered around 1600 cm^{-1} are assigned to the imine groups of the Schiff base ligands.

Formation of ketenyl ligands by carbonyl–carbyne coupling was first discovered by Kreissl and co-workers[7a] and is now a well-established process in mononuclear[6-8] as well

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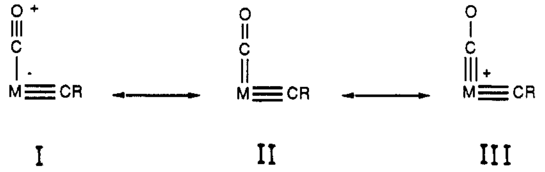
as polynuclear[9] transition-metal complexes. Mechanistic details of the coupling step remain uncertain at this point; in particular, the question whether carbonyl–carbyne coupling is a spontaneous insertion process leading to a 16-electron intermediate (counting the η^2-ketenyl ligand as a four-electron donor) which subsequently is trapped by the added ligand or whether insertion is induced via an associative attack by the added ligand and the question which electronic factors favor the coupling step. Reversibility of carbonyl–carbyne coupling[7e,8f] indicates that the ligand coupling step occurs very easily. Induction of carbonyl–carbyne coupling by the addition of phosphine ligands to $[(W{\equiv}CR)(\eta^5\text{-}C_5H_5)(CO)_2]$[7] as well as by coordination of chelating dithiocarbamate[6,8f] and pyrrole-2-carboxaldiminate ligands (this work) to other systems indicates the operation of an associative mechanism. Recently photochemical induction of the coupling step in $[(W{\equiv}CC_6H_4\text{-}4\text{-}CH_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ has been observed.[8g] An important electronic factor favoring the coupling step appears to be electron-richness of the metal complex system. While induction of carbonyl–carbyne coupling has not yet been reported for trans halo transition-metal carbyne complexes, this reaction seems to be common in systems where the halide is substituted by better donor ligands, e.g., cyclopentadienyl,[7] cyanide,[8b,c] dithiocarbamate,[6,8f] pyrrole-2-carboxaldiminate ligands (this work), or tris(pyrazolyl)borate.[8h] Strong trans donor ligands cause the buildup of charge on the carbyne ligand. Increasing electron density on the metal center also increases π-back-bonding to carbonyl ligands, i.e., enhances contribution of the bis(carbyne) form III to the bonding in metal carbonyl carbyne complexes. If contribution of resonance structure III with the carbyne form of the carbonyl ligand facilitates the coupling step, one may expect promotion of carbonyl–carbyne coupling by Lewis acids, since it is well-established that interaction of Lewis acids with the oxygen atom of carbonyl ligands increases metal–carbonyl π-back-bonding.[10] There are only a few potential examples for this effect. $[W(CH)Cl(PMe_3)_4]$ reacts with CO in the presence of $AlCl_3$ to give $[W(Cl)(CO)(\eta^2\text{-}HC{\equiv}COAlCl_3)(PMe_3)_3]$.[8e] $[W(CPh)Cl(CO)_4]$ reacts with acetylacetone under irradiation with ultraviolet light at −60 °C to afford $[W(acac)(Cl)(\eta^2\text{-}PhC{\equiv}COH)(CO)_2]$.[8a] In this second reaction the proton could play the role of the Lewis acid, although the possibility of photoinduced carbonyl–carbyne coupling in this system has been pointed out.[8g] Interestingly, these two reactions are the only reported examples of carbonyl–carbyne coupling in trans halo metal carbyne complexes. Proton-induced carbonyl–carbyne coupling has also been observed on trinuclear cobalt cluster systems.[9f] Lewis acids may also be actively involved in the related coupling of two carbonyl ligands[11] on a tantalum and a diiron center and the coupling of two isocyanide ligands[12] on molybdenum, tungsten, and niobium centers. The role of Lewis acids in these reactions is reminiscent of Lewis acid promoted migrations of alkyl ligands to carbonyl ligands[13] and acyl ligands.[14] The coupling of two carbyne ligands—corresponding to the extreme of resonance form III—has recently been demonstrated to proceed under very mild conditions on a tungsten center.[15]



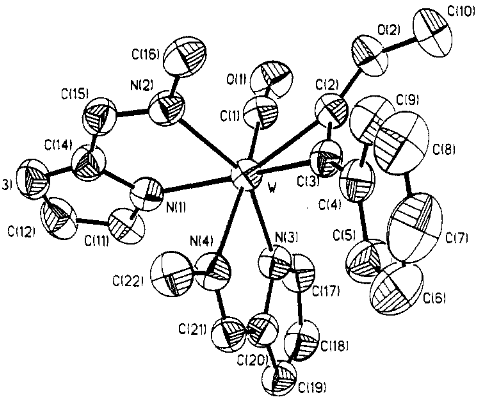


Figure 1. Structure of compound **4a** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Table I. Selected Bond Lengths (Å)

W–C(1)	1.968 (4)	N(2)–C(15)	1.300 (5)
W–C(2)	2.019 (4)	N(2)–C(16)	1.466 (5)
W–C(3)	2.034 (4)	C(11)–C(12)	1.387 (7)
W–N(1)	2.183 (3)	C(12)–C(13)	1.386 (7)
W–N(2)	2.180 (3)	C(13)–C(14)	1.390 (6)
W–N(3)	2.070 (3)	C(14)–C(15)	1.410 (6)
W–N(4)	2.231 (3)	N(3)–C(17)	1.357 (5)
C(1)–O(1)	1.154 (5)	N(3)–C(20)	1.402 (5)
C(2)–C(3)	1.310 (5)	N(4)–C(21)	1.293 (5)
C(2)–O(2)	1.337 (5)	N(4)–C(22)	1.459 (6)
C(3)–C(4)	1.476 (6)	C(17)–C(18)	1.379 (6)
O(2)–C(10)	1.431 (6)	C(18)–C(19)	1.394 (7)
N(1)–C(11)	1.347 (6)	C(19)–C(20)	1.376 (6)
N(1)–C(14)	1.378 (6)	C(20)–C(21)	1.416 (6)

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Table II. Selected Bond Angles (deg)

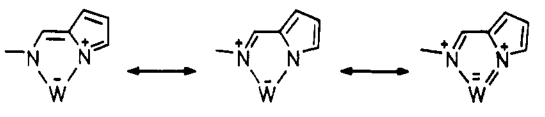
C(1)-W-C(2)	72.8 (2)	W-N(1)-C(11)	136.7 (3)
C(1)-W-C(3)	110.4 (2)	W-N(1)-C(14)	116.4 (3)
C(2)-W-C(3)	37.7 (2)	C(11)-N(1)-C(14)	106.9 (3)
C(1)-W-N(1)	85.0 (1)	N(1)-C(11)-C12)	109.9 (4)
C(2)-W-N(1)	153.1 (1)	C(11)-C(12)-C(13)	107.4 (4)
C(3)-W-N(1)	160.3 (1)	C(12)-C(13)-C(14)	106.2 (4)
C(1)-W-N(2)	99.3 (1)	N(1)-C(14)-C(13)	109.6 (4)
C(2)-W-N(2)	95.6 (1)	N(1)-C(14)-C(15)	115.1 (4)
C(3)-W-N(2)	92.2 (1)	C(13)-C(14)-C(15)	135.0 (4)
N(1)-W-N(2)	72.7 (1)	C(14)-C(15)-N(2)	117.0 (4)
C(1)-W-N(3)	93.4 (1)	W-N(2)-C(15)	118.5 (3)
C(2)-W-N(3)	111.4 (1)	W-N(2)-C(16)	122.7 (3)
C(3)-W-N(3)	106.1 (1)	C(15)-N(2)-C(16)	118.5 (4)
N(1)-W-N(3)	84.4 (1)	W-N(3)-C(17)	137.4 (3)
N(2)-W-N(3)	152.6 (1)	W-N(3)-C(20)	116.6 (3)
C(1)-W-N(4)	163.8 (1)	C(17)-N(3)-C(20)	105.7 (3)
C(2)-W-N(4)	122.0 (1)	N(3)-C(17)-C(18)	110.3 (4)
C(3)-W-N(4)	84.4 (1)	C(17)-C(18)-C(19)	107.8 (4)
N(1)-W-N(4)	82.2 (1)	C(18)-C(19)-C(20)	106.2 (4)
N(2)-W-N(4)	86.4 (1)	N(3)-C(20)-C(19)	110.0 (4)
N(3)-W-N(4)	75.6 (1)	N(3)-C(20)-C(21)	115.7 (3)
W-C(1)-O(1)	176.5 (4)	C(19)-C(20)-C(21)	134.0 (4)
W-C(2)-C(3)	71.7 (2)	C(i0)-C(21)-N(4)	118.2 (4)
W-C(2)-O(2)	145.0 (3)	W-N(4)-C(21)	113.9 (3)
C(3)-C(2)-O(2)	143.2 (4)	W-N(4)-C(22)	128.0 (2)
W-C(3)-C(2)	70.5 (2)	C(21)-N(4)-C(22)	118.0 (3)
W-C(3)-C(4)	144.9 (3)		
C(2)-C(3)-C(4)	144.0 (4)		
C(2)-O(2)-C(10)	115.6 (3)		

The electronic features and relationship of coupling of carbonyl and carbyne, two carbonyl, two isocyanide, and two carbyne ligands on metal centers have been the subject of recent theoretical investigations.[16]

Kreissl and others demonstrated transformation of η^2-ketenyl ligands into η^2-acetylene ligands by addition of electrophiles to the oxygen atom of the ketenyl ligand.[7f,8f,h,17] Complexes **3** react with methyl fluorosulfate in CH_2Cl_2 at low temperatures to give the neutral methoxyacetylene complexes $[W(NN)_2(CO)(RC{\equiv}COCH_3)]$ (**4a**, R = C_6H_5; **4b**, R = CH_3) (eq 2). This transformation is

$$\mathbf{3a,b} \xrightarrow[CH_2Cl_2]{FSO_3CH_3} [W(NN)_2(RC{\equiv}COCH_3)(CO)] \quad (2)$$
$$\mathbf{4a}, R = C_6H_5$$
$$\mathbf{4b}, R = CH_3$$

accompanied by an upward shift of ν_{CO} in the infrared spectrum of about 100 cm^{-1}. The ketenyl absorption is replaced by a new weak band at 1680 cm^{-1} for the acetylene ligand. The absorptions for the imino groups remain almost unchanged. Complexes **4a** and **4b** are isolated after chromatography (SiO_2/CH_2Cl_2) and recrystallization from CH_2Cl_2/hexane in 58 and 67% yields, respectively.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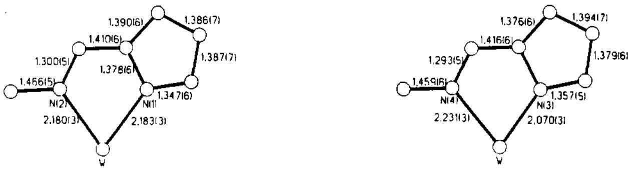

Figure 2. Intraligand bond distances of pyrrole-2-carboxaldehyde methyliminate ligands.

The structural and spectroscopic data (vide infra) indicate that complexes **4** are related to a well-established class of molybdenum and tungsten alkyne complexes of the type $[M(R_2NCS_2)_2(RC{\equiv}CR')(CO)]$[18] (M = Mo, W) where the monoanionic bidentate chelate ligands are dithiocarbamates. These compounds have been investigated in detail both experimentally[18] and theoretically.[19]

Structure of $[W(C_6H_7N_2)_2(C_6H_5C{\equiv}COCH_3)(CO)]$ (4a). The molecular structure of complex **4a** is shown in Figure 1. The bond lengths and bond angles are listed in Tables I and II. The coordination geometry around the tungsten atom can be described as octahedral, if the acetylene is considered to occupy one coordination site. The alkoxyacetylene ligand is cis to carbon monoxide and oriented parallel to the metal–carbonyl axis with the methoxy group proximal and the phenyl group distal to the carbonyl. The short distances between the tungsten atom and the acetylene carbon atoms, 2.019 (4) and 2.034 (4) Å for W–C(2) and W–C(3), respectively, reflect metal–carbon multiple-bond character and indicate π-donation by the acetylene (vide infra). The acetylene C≡C separation is 1.310 (5) Å. These bond lengths are very similar to the corresponding distances in the related tungsten acetylene complex $[W(Et_2NCS_2)_2(CO)(HC{\equiv}CH)]$ (**5**).[18a] The W–C(acetylene) distances in **5** are 2.038 (8) and 2.015 (9) Å, although in this compound the shorter W–C distance belongs to the carbon atom proximal to carbon monoxide. The C≡C distance in **5** is 1.29 (1) Å. The W–C(1)(CO) distance in **4b** of 1.968 (4) Å also corresponds well to the W–C(CO) distance of 1.936 (7) Å in **5**. Of interest are also the bonding distances between the tungsten center and the nitrogen atoms of the two pyrrole-2-carboxaldehyde methyliminate ligands. The nitrogen atoms of Schiff base N(1)/N(2), which is oriented perpendicular to the metal–carbonyl axis, are equidistant to the tungsten atom, 2.183 (3) Å for W–N(1) and 2.180 (3) Å for W–N(2). The other Schiff base N(3)/N(4) is coordinated with the imine nitrogen N(4) trans to carbon monoxide and with the pyrrole nitrogen N(3) trans to the imine nitrogen N(2). It has two distinctly different W–N distances. The W–N(4) distance to the imine nitrogen atom is long, 2.231 (3) Å; the W–N(3) distance to the pyrrole nitrogen atom is short, 2.070(3) Å. Generally, in complexes with electronically equivalent coordination sites, the metal–pyrrole nitrogen distance is found to be 0.05–0.10 Å shorter than the metal–imine nitrogen distance.[20] Thus, the W–N(1) distance can be considered elongated compared to W–N(2), most likely due to the trans influence[21] of the strongly

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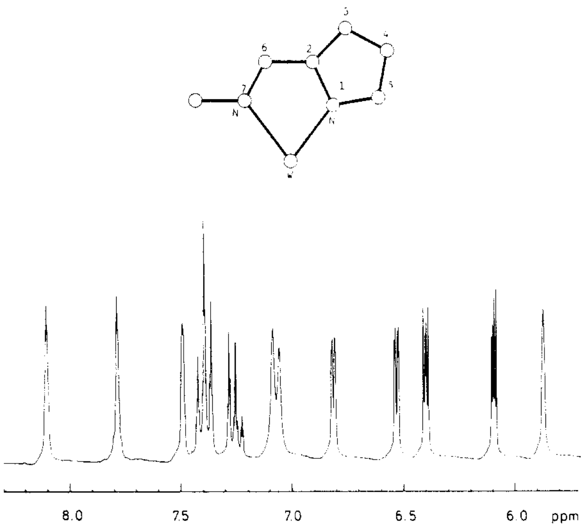

Figure 3. Partial ^1H NMR spectrum of **4a**.

bonded acetylene ligand. The elongation of the W–N(4) distance compared to W–N(2) may be the result of the trans influence of the carbonyl ligand, which is very strongly bonded to the metal. The very short W–N(3) distance is the consequence of π-donation of the pyrrole nitrogen into an empty metal d orbital (vide infra). This difference in coordination of the two Schiff base ligands is also reflected in slight changes of the *intraligand* bond distances. The bond distances C(17)–C(18), C(19)–C(20), and C(21)–N(4) in Schiff base N(3)/N(4) are shorter; the distances N(3)–C(17), N(3)–C(20), C(18)–C(19), and C(20)–C(21) are longer than the corresponding distances in Schiff base N(1)/N(2). Thus, the bonding of the Schiff base ligand N(1)/N(2) may be described adequately with resonance structures IV and V as the main contributors, whereas resonance structure VI seems to contribute significantly to the bonding of Schiff base N(3)/N(4).

NMR Spectra. The ^1H NMR spectra of complexes 3 and 4 show ten signals for the two Schiff base ligands. The spectral appearance is very similar for all compounds, indicating that the relative arrangement of the two chelate ligands is the same in all compounds. The spectrum of complex **4a**, part of which is shown in Figure 3, is discussed as a representative example using the usual numbering scheme for pyrrole derivatives. On the basis of double irradiation experiments two sets of three signals belonging to the two ligands are distinguished. The resonances at 7.49 (C^5–H), 6.81 (C^3–H), and 6.40 ppm (C^4–H) form one set. In this set the chemical shifts and the multiplicities of the pyrrole hydrogen signals are very similar to those found in other metal complexes of pyrrole-2-carboxaldimines or in the free ligand 2.[22] Assignment of the signal for C^4–H is unambiguous on the basis of the coupling pattern. The resonances of C^3–H and C^5–H have not been assigned consistently in the literature.[20b,22] We assign the resonance at lower field to C^5–H in analogy to the assignment made for pyrrolecarboxaldehyde[23] and several metal complexes of pyrrole-2-carboxaldimines.[20b,22a] This leaves the signal at 6.81 ppm for C^3–H. The other set is formed by the resonances at 6.53 (C^3–H′), 6.10 (C^4–H′), and 5.87 ppm (C^5–H′). The resonances for C^3–H′ and C^4–H′ correlate well with those of the other set. The signal for C^5–H′, however, is experiencing a strong upfield shift of 1.62 ppm relative to the resonance of C^5–H. Inspection of the structure of **4a** reveals that the hydrogen on C(11), C^5–H′, of Schiff base N(1)/N(2) is located directly in the shielding region of the pyrrole ring of Schiff base N(3)/N(4). This is shown in Figure 4. The shielding experienced by C^5–H′ provides additional support for the assignment of the hydrogen atoms in the pyrrole positions 3 and 5. Thus, the first set of signals belongs to Schiff base N(3)/N(4), and the second, primed, set belongs to Schiff base N(1)/N(2). The resonances at 8.10 and 7.78 ppm are tentatively assigned to C^6–H and C^6–H′, respectively.

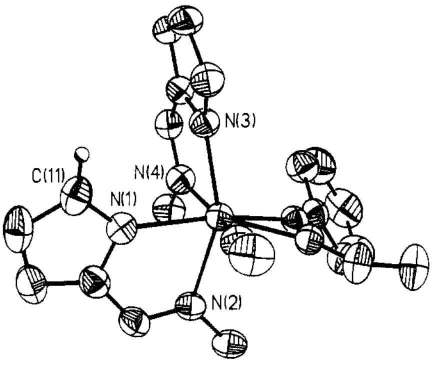

Figure 4. Perspective of the structure of compound **4a** showing the location of the hydrogen on C(11) above the plane of the pyrrole ring of Schiff base N(3)/N(4).

The ^{13}C NMR resonances of the carbonyl and ketenyl ligands appear at values comparable to those found for other anionic tungsten ketenyl complexes.[7f,g,8b,c] For **3a**, the carbon atom of the carbonyl ligand exhibits a resonance at 228.9 ppm (J_{CW} = 172.3 Hz), the ketenyl carbonyl carbon at 208.6 ppm, and the phenyl-substituted carbon atom at 174.0 ppm. The ^{13}C NMR spectra of the neutral acetylene complexes 4 show the expected resonances for the ligands. For **4a**, the carbonyl ligand gives rise to a signal at 220.6 ppm. The two acetylene carbon atoms exhibit resonances at 232.1 and 182.0 ppm. Following the assignment by Kreissl[17a,b] the signal at lower field is attributed to the carbon atom carrying the methoxy group and the signal at higher field is attributed to the phenyl-substituted carbon atom. These chemical shift values are characteristic for four-electron-donor acetylene ligands.[24]

Qualitative Bonding Description. The structure of complex **4a** is related to that of the acetylene complex $[W(Et_2NCS_2)_2(HC{\equiv}CH)(CO)]$;[18a] it is derived by replacing the two dithiocarbamates with two pyrrole-2-carboxaldiminate ligands. The bonding picture developed for these systems[19] adequately describes the qualitative aspects of bonding in complexes 4. In the idealized octahedral coordination geometry, as shown in Figure 5, the carbonyl ligand is oriented along the z axis, the acetylene ligand is centered on the x axis, and the pyrrole nitrogen N(3) lies on the y axis. The arrangement of the ligands is governed by metal–ligand π-interactions. Of the three metal $d\pi$ orbitals (d_{xy}, d_{xz}, d_{yz}) the d_{xz} and d_{yz} orbitals are stabilized by interaction with the carbonyl ligand. Thus, the four d electrons of the formal tungsten(II), d^4, system will occupy these orbitals. The acetylene ligand, which is binding with its filled $\pi_{\parallel}$ orbital to a metal σ_x orbital, is oriented parallel to the z axis for π-interaction between filled d_{xz} and empty $\pi_{\parallel}^*$. In this orientation the second filled acetylene π-orbital ($\pi_{\perp}$) is properly aligned for interaction with empty d_{xy}. Both metal alkyne π-interactions are

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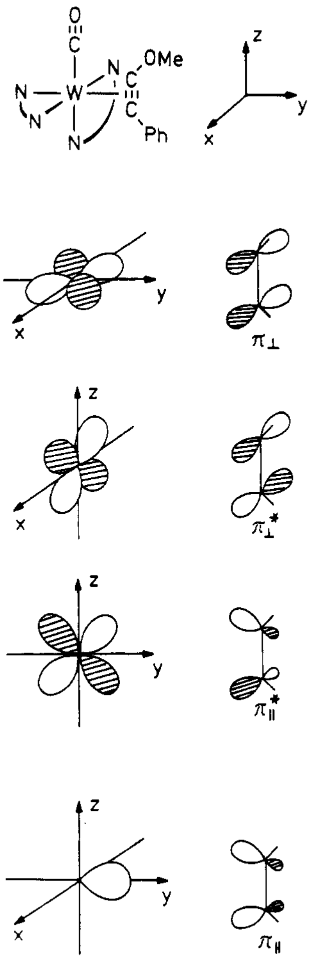

Figure 5. Qualitative molecular orbitals of 4.

strongest in this orientation. The nitrogen donor ligands have π-systems whose nodal planes coincide with the molecular planes of the Schiff base ligands. Of the four nitrogen atoms only N(3) is oriented in the appropriate way for π-donation into empty d_{xy}. This π-donation by the pyrrole nitrogen is significant, leading to the shortest W–N separation in the molecule as well as partial localization of the pyrrole-2-carboxaldiminate π-system. We conclude that in these Schiff base ligands the pyrrole nitrogen atom is a better π-donor site than the imine nitrogen atom.

Experimental Section

Standard inert atmosphere techniques were used. The solvents CH_2Cl_2 (P_2O_4), tetrahydrofuran, and diethyl ether (Na/benzophenone) were dried and distilled prior to use. Pyrrole-2-carboxaldehyde methylimine[25] was prepared as described in the literature. The NMR spectra were recorded on a Bruker W250 spectrometer in $CDCl_3$ solution and the IR spectra on a Digilab FT-20 spectrometer in CH_2Cl_2 solution. Elemental analyses were performed by Schwarzkopf Analytical Laboratory.

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
W	3034 (1)	4223 (1)	2618 (1)	35(1)
C(1)	5042 (4)	4186 (2)	2410 (4)	44(1)
O(1)	6204 (3)	4137 (2)	2251 (3)	62(1)
C(2)	3842 (4)	3421 (2)	3503 (4)	41(1)
C(3)	2484 (4)	3433 (2)	3554 (3)	39(1)
C(4)	1337 (4)	3117 (2)	4115 (4)	45(1)
C(5)	32 (5)	3029 (2)	3406 (5)	61(2)
C(6)	−1070 (6)	2772 (3)	3974 (6)	83(2)
C(7)	−854 (7)	2598 (3)	5250 (6)	84(2)
C(8)	415 (6)	2685 (3)	5934 (5)	75(2)
C(9)	1538 (5)	2938 (2)	5404 (4)	58(2)
O(2)	5017 (3)	3081 (1)	3852 (3)	54(1)
C(10)	4839 (5)	2498 (2)	4519 (5)	69(2)
N(1)	3155 (3)	5222 (2)	2034 (3)	43(1)
C(11)	3271 (4)	5541 (2)	949 (4)	52(1)
C(12)	3337 (5)	6194 (2)	1183 (5)	64(2)
C(13)	3279 (5)	6282 (2)	2471 (5)	60(2)
C(14)	3168 (4)	5674 (2)	2982 (4)	49(1)
C(15)	3181 (4)	5426 (2)	4221 (4)	48(1)
N(2)	3199 (3)	4806 (2)	4339 (3)	43(1)
C(16)	3190 (5)	4530 (2)	5610 (4)	53(1)
N(3)	2354 (3)	4060 (2)	702 (3)	42(1)
C(17)	2944 (5)	3928 (2)	−359 (4)	49(1)
C(18)	1926 (5)	3925 (2)	−1420 (4)	57(2)
C(19)	638 (5)	4075 (2)	−1023 (4)	52(1)
C(20)	915 (4)	4157 (2)	277 (4)	43(1)
C(21)	101 (4)	4363 (2)	1216 (4)	44(1)
N(4)	731 (4)	4441 (2)	2369 (3)	44(1)
C(22)	−107 (4)	4662 (2)	3329 (4)	54(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

[NEt$_4$][W($C_6H_7N_2$)$_2$(OCCPh)(CO)] (3a). Approximately 50 KOH pellets are added to a stirred solution of [(W≡CPh)Cl(CO)$_2$(py)$_2$] (**1a**) (1.045 g, 2.0 mmol) and pyrrole-2-carboxaldehyde methylimine (**2**) (0.454 g, 4.2 mmol) in THF (50 mL). A green color develops which slowly darkens to a brownish green. The reaction is monitored by IR. When the reaction is completed (1.25 h), the solvent is removed and the residue washed with pentane. The solid is suspended in CH_2Cl_2 (30 mL), and NEt_4Cl (0.335 g, 2.02 mmol) is added. The product dissolves, and a fine precipitate of KCl forms. After being stirred for 30 min, the solution is filtered through a pad of cellulose. The volume is reduced to 5 mL, and ether is added dropwise until an oily precipitate starts to form. Upon trituration of the precipitate and further addition of ether dark brown crystals form (1.283 g, 95%) (mp 105 °C dec): ^{1}H NMR δ 8.08 (s, br, 1 H, C^6–H), 7.71 (s, br, 1 H, C^6–H′), 7.37 (t, 2 H, *m*-Ph), 7.32 (d, 2 H, *o*-Ph), 7.19 (m, 1 H, C^5–H), 7.09 (t, 1 H, *p*-Ph), 6.66 (d, J = 3 Hz, 2 H, C^3–H), 6.33 (d, J = 3 Hz, 1 H, C^3–H′), 6.19 (m, 1 H, C^4–H), 5.94 (s, br, 1 H, C^4–H′), 5.62 (s, br, 1 H, C^5–H′), 3.21 (s, 3 H, N-CH_3), 3.11 (s, 3 H, N-CH_3), 2.50 (q, 8 H, NCH_2CH_3), 0.75 (t, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$NMR δ 228.9 (J_{CW} = 172.3 Hz, *CO*), 208.6 (C═O), 174.0 (CPh), 158.7, 152.2, 143.3, 142.7, 139.1, 133.2, 128.2, 127.0, 124.5, 113.5, 112.2, 110.9 (C_6H_5 and NC_4H_3CHNMe) 51.6 (CH_2CH_3), 50.4, 43.4 (NCH_3), 7.0 (CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1839 (s), $\nu_{C=O}$ 1665 (m), $\nu_{C=N}$ 1605 (m), 1582 (m). Anal. Calcd for $C_{29}H_{39}N_5O_2W$ (mol wt 673.51): C, 51.72; H, 5.84; N, 10.4. Found: C, 50.75; H, 6.00; N, 9.66.

[NEt$_4$][W($C_6H_7N_2$)$_2$(OCCMe)(CO)] (3b). The procedure described for **3a** is followed to give a dark red powder (2.277 g, 80%) (mp 70–74 °C dec): ^{1}H NMR δ 8.02 (s, br, 1 H, C^6–H), 7.74 (s, br, 1 H, C$_6$–H′), 7.12 (s, br, 1 H, C^5–H), 6.59 (m, 1 H, C^3–H), 6.35 (m, 1 H, C^3–H′), 6.15 (m, 1 H, C^4–H), 5.96 (m, 1 H, C^4–H′), 5.60 (s, br, 1 H, C^5–H′), 3.31 (s, 3 H, NCH_3), 3.21 (s, 3 H, NCH_3), 3.15 (q, 8 H, CH_2CH_3), 2.86 (s, 3 H, CCH_3), 1.20 (t, 12 H, CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1827 (s), $\nu_{C=O}$ 1683 (m), $\nu_{C=N}$ 1606 (m), 1582 (m).

W($C_6H_7N_2$)$_2$(CH_3OC_2Ph)(CO) (4a). CH_3OSO_2F (0.2 mL, 2.5 mmol) is added to a solution of **3a** (1.35 g, 2.0 mmol) in CH_2Cl_2 (50 mL) at −78 °C. After the solution is warmed to room temperature, the solvent is removed in vacuo. The product is chromatographed through a 5-cm high layer of silica gel with a solvent mixture of CH_2Cl_2/pentane, 2:1. The product is recrystallized from CH_2Cl_2/pentane to yield deep green crystals (650 mg, 58%) (mp 212 °C): ^{1}H NMR δ 8.10 (s, br, 1 H, C^6–H), 7.78 (s, br, 1 H, C^6–H′), 7.49 (s, br, 1 H, C^5–H), 7.39 (t, 2 H, *m*-Ph), 7.25 (t, 1 H, *p*-Ph), 7.08 (d, 2 H, *o*-Ph), 6.81 (dd, 1 H, ^1J = 3 Hz, ^2J = 1 Hz, C^3–H), 6.53 (dd, 1 H, ^1J = 3 Hz, ^2J = 1 Hz, C^3–H′), 6.40 (dd, 1 H, ^1J = 3 Hz, ^2J = 2 Hz, C^4–H), 6.10 (dd, 1 H, ^1J = 3 Hz, ^2J = 2 Hz, C^4–H′), 5.87 (s, br, 1 H, C^5–H′), 4.26 (s, 3 H, OCH_3), 3.29 (s, 3 H, N–CH_3), 3.08 (s, br, 3 H, NCH_3); $^{13}C\{^1H\}$NMR δ 232.1 (br, COMe), 220.6 (br, CO), 182.0 (br, CPh), 160.1, 155.0, 143.4, 141.5, 139.7, 139.5, 135.9, 128.1, 127.1, 127.0, 115.7, 114.3,

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Table IV. Experimental Data for the X-ray Diffraction Study

Crystal Parameters	
molecular formula	$C_{22}H_{22}N_4O_2W$
mol wt	558.3
cryst color	black
cryst size, mm	0.20 × 0.25 × 0.50 mm
a, Å	9.568 (2)
b, Å	20.884 (4)
c, Å	10.597 (2)
β, deg	98.25 (2)
V, Å^3	2095.4 (8)
Z	4
space group	$P2_1/n$
ρ(calcd), g/cm^3	1.77
$F(000)$, e	1088
μ(Mo Kα), cm^{-1}	58.4
Data Measurements	
diffractometer	Nicolet R3m
Radiatn	Mo Kα
monochromater	graphite single crystal
2θ range, deg	3–55
scan type	$0-2\theta$
scan speed, deg/min	3.91–29.30
scan width, deg	1.0 + 0.35 tan
reflctns measd	$+h,+k,\pm l$
unique reflctns	4817
obsd reflctns	4226
transmissn coeff	max 0.560 min 0.280
parameters	262
R	0.028
R_w	0.024
GOF	1.73

113.8, 112.7 (C_6H_5 and NC_4H_3CHNMe), 65.0 (OCH_3), 50.8, 43.6 (NCH_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1927 (s), $\nu_{C\equiv C}$ 1691 (w), $\nu_{C=N}$ 1603 (m), 1584 (m). Anal. Calcd for $C_{22}H_{22}N_4O_2W$ (mol wt 558.29): C, 47.33; H, 3.97. Found: C, 47.34; H, 3.98.

$W(C_6H_7N_2)_2(CH_3OC_2Me)(CO)$ (4b). $CH_3OSO_2CF_3$ (0.17 mL, 1.5 mmol) is added to a solution of **3b** (0.974 g, 1.5 mmol) in CH_2Cl_2 (40 mL) at −78 °C. After the solution is warmed to 0 °C, the solvent is removed. The product is purified by chromatography on silica gel (8 × 2 cm) at −10 °C. The product is eluted with CH_2Cl_2/pentane, 2:1 (1 L). Recrystallization from CH_2Cl_2/ether gives red crystals (0.527 g, 67%) (mp 77–85 °C dec): ^{1}H NMR δ 8.06 (s, br, 1 H, C^6–H) 7.77 (s, br, 1 H, C^6–H′), 7.36 (s, br, 1 H, C^5–H), 6.70 (m, 1 H, C3–H), 6.54 (m, 1 H, C^3–H′), 6.31 (m, 1 H, C^4–H), 6.09 (m, 1 H C^4–H′), 5.88 (s, br, 1 H, C^5–H′), 4.28 (s, 3 H, OCH_3), 3.43 (d, 3 H, J_{HH} = 1 Hz, NCH_3), 3.18 (d, 3 H, J_{HH} = 1 Hz, NCH_3), 3.12 (s, 3 H, CCH_3); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1917 (s), $\nu_{C=N}$ 1604 (m), 1585 (m). Anal. Calcd for $C_{17}H_{20}N_4O_2W$: C, 41.14; H, 4.03; N, 11.29. Found: C, 41.24; H, 4.32; N, 11.47.

Crystal Structure Determination of 4a. A single crystal of $C_{22}H_{22}N_4O_2W$ measuring 0.20 × 0.25 × 0.50 mm was mounted on a glass fiber and centered on Nicolet R3m diffractometer. Cell constants and their estimated standard deviations were determined by a least-squares fit of 25 diffractometer-measured reflections with $20° \leq 2\theta \leq 25°$. The material belongs to the monoclinic crystal class, space group $P2_1/n$ (standard $P2_1/c$), with a = 9.568 (2) Å, b = 20.884 (4) Å, c = 10.597 (2) Å, and β = 98.25 (2)°. A density of 1.77 g/cm^3 was calculated for Z = 4, mol wt 558.3 g, and a unit cell volume of 2095.4 (8) Å^3.

All intensity measurements were made at room temperature by using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a $\theta-2\theta$ scan technique with a variable scan rate of 3.91–29.30°/min. The scan range was (1.0 + 0.35 tan)°, and background counts were taken for half the scan time at each extreme of the scan range. All data (5450) having $h, k \geq 0$ with $3° \geq 2\theta \geq 55°$ were measured in this manner. Crystal decomposition was monitored throughout data collected by remeasuring two standard reflections after every 50 data measurements; no significant variations were recorded. The intensities were reduced by applying Lorentz and polarization corrections. Empirical absorption corrections were applied on the basis of azimuthal scans of suitable reflections; the maximum and minimum relative transmission values were 0.560 and 0.280, respectively. Equivalent reflections were averaged (R_{merge} = 0.004) to give 4817 unique data of which 4226 were considered to be observed [$|F_o| > 3\sigma(F_o)$].

The structure was solved by standard heavy-atom techniques. Following refinement of the non-hydrogen atoms with anisotropic temperature factors, a difference map showed peaks at plausible hydrogen positions. Hydrogen atoms were included in refinement in ideal positions (C–H = 0.96 Å; CCH = 120° or 109.5°). In the final cycles of blocked-cascade least-squares refinement, the non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogens were varied by using a riding model. Refinement converged (shift/error ≤ 0.1) at R = 0.028 and R_w = 0.024. A final difference map displayed a maximum peak of 0.85 e/Å^3 in the vicinity of the tungsten atom. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where w is the weight of a given observation.[26] The analytical forms for the scattering factors of the neutral atoms were used.[27,28]

Acknowledgment. We thank B. Cannon for experimental work. This work was supported by the National Science Foundation (CHE-8411023), by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by an Atlantic Richfield Foundation Grant of Research Corp.

Registry No. **1a**, 99630-91-8; **1b**, 99630-62-3; **2**, 15191-65-8; **3a**, 108452-78-4; **3b**, 108510-43-6; **4a**, 108452-79-5; **4b**, 108452-80-8.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters (6 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(26) $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$. Final value of g = 0.00007.

(27) *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, pp 99, 149.

(28) $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = \sum[w(|F_o| - |F_c|)^2]^{1/2}/\sum(w|F_o|^2)^{1/2}$.