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Supplementary Material Available: Complete details of crystal data, data collection, and solution and refinement (Table S1), complete lists of bond lengths (Table S2) and bond angles (Table S3), anisotropic thermal parameters (Table S4), and hydrogen atom coordinates and isotropic thermal parameters (Table S5), and a drawing showing the complete labeling scheme for **3b** (Figure S1) (8 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Ynol Ester Complexes of Molybdenum and Tungsten: Cleavage of the RCCO–C(O)R′ Bond and of the RCC–OC(O)R′ Bond of Ynol Ester Ligands

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Reaction of the ketenyl complexes $NEt_4[M(\eta^2\text{-RCCO})(S_2CNR''_2)_2(CO)]$ (**3**, M = Mo, R = Ph, R″ = Et; **4**, M = W, R = Ph, R″ = Et (**a**), R = $C_6H_4CMe_3$-4, R″ = Et (**b**), R = Ph, R″ = Me (**c**)) and $K[W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(N_2C_6H_7)_2(CO)]$ (**5**) with acyl halides R′COCl (or R′COBr) affords the (ynol ester)metal complexes $[M(S_2CNR'')_2(CO)(\eta^2\text{-RCCOCOR}')]$ (**8**: M = Mo, R = Ph, R′ = Ph, R″ = Et) (**9**: M = W, R = Ph, R′ = Me (**a**), Ph (**b**), $CHCH_2$ (**c**), *trans*-CHCHMe (**d**), *trans*-CHCHPh (**e**), R″ = Et; R = $C_6H_4CMe_3$-4, R′ = Me (**f**), CH_2Ph (**g**), CMe_3 (**h**), R″ = Et; R = Ph, R′ = CMe_3, R″ = Me (**i**)) and $[W(N_2C_6H_7)_2(CO)(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOR')]$ (**10**: R = $C_6H_4CMe_3$-4, R′ = CMe_3 (**a**), CH_2Ph (**b**), C_6H_4-OMe-4 (**c**)). Reaction of the ynol ester complexes $[W(S_2CNEt_2)_2(CO)(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOCH_2R)]$ (R = H (**9f**), Ph (**9g**)) with dimethylamine affords the ketenyl complex $[H_2NMe_2][W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(S_2CNEt_2)_2(CO)]$. The ynol ester complexes $[W(LL)_2(CO)(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOCH_2Ph)]$ (LL = S_2CNEt_2 (**9g**), $N_2C_6H_7$ (**10b**)) react with $NaN(SiMe_3)_2$ to give the ketenyl complexes $Na[W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(LL)_2(CO)]$. Reaction of $[W(S_2CNEt_2)_2(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCOCOCMe_3)(CO)]$ (**9h**) with $HNMe_2$ gives $[W(S_2CNEt_2)_2(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCNMe_2)(CO)]$ (**11**). Reaction of **9h** with PMe_3 gives $[W(S_2CNEt_2)_2(\eta^3\text{-}4\text{-}Me_3C\text{-}C_6H_4CCSCSNEt_2)(CO)][Me_3CO_2]$ (**12**). The reaction of **4b** with PMe_3 affords $[W(\eta^2\text{-}4\text{-}Me_3C\text{-}C_6H_4CCO)(S_2CNEt_2)(CO)(PMe_3)_2]$ (**13**). The (ynol ether)metal complexes $[M(S_2CNEt_2)_2(CO)(\eta^2\text{-RCCOMe})]$ (**6**, M = Mo, R = Ph; **7**, M = W, R = $C_6H_4CMe_3$-4) were prepared by reaction of $NEt_4[M(\eta^2\text{-RCCO})(S_2CNR''_2)_2(CO)]$ with $CF_3SO_3CH_3$.

Introduction

Ketenyl, or ynolate, ligands ($RCCO^-$) have become easily accessible by the coupling of alkylidyne and carbonyl ligands.[4] Kreissl and co-workers observed in 1976 the first alkylidene–carbonyl coupling in the reaction of $[W(CC_6H_4\text{-}CH_3\text{-}4)(\eta^5\text{-}C_5H_5)(CO)_2]$ with PMe_3.[5] In subsequent years additional examples of nucleophile-induced alkylidyne–carbonyl coupling reactions were described.[4] Geoffroy and co-workers reported photoinduction of alkylidyne–carbonyl coupling in the presence of donor ligands.[6] We have recently demonstrated that photogenerated ketenyl ligands may also be trapped by electrophiles.[7] Induction of alkylidyne–carbonyl coupling by electrophiles is not yet firmly established but may be involved in the formation of aluminum-substituted ynolate ligands reported by Schrock and co-workers,[8] which takes place upon reaction of a methylidyne complex with carbon monoxide in the presence of aluminum Lewis acids. The reductive coupling of two carbonyl ligands developed by Lippard and co-workers[9] also involves an alkylidyne (siloxycarbyne)–carbonyl coupling step. The formation of sulfur-substituted ketenyl ligands by coupling of thiocarbyne and carbonyl ligands was reported by Angelici and co-workers.[10]

Our knowledge of the reactivity of ketenyl ligands rests primarily on the pioneering work by Kreissl and his group.[4] Depending on the electronic requirements of the metal

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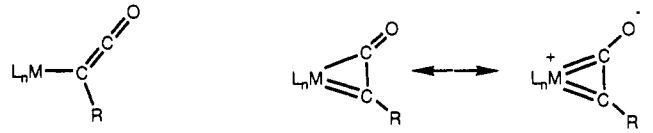
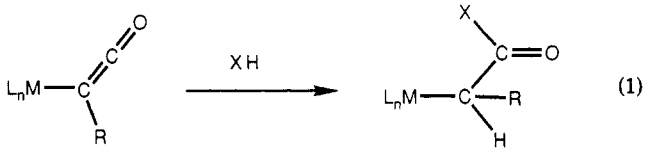
center, (formally anionic) ketenyl ligands may act as η^1 two-electron-donor ligands (I) or as η^2 four-electron-donor ligands (II). The bonding mode strongly influences the



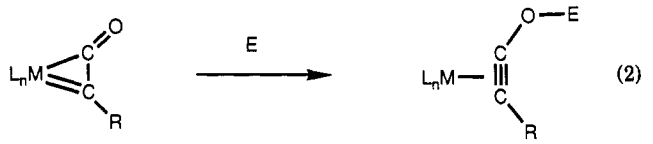
I II

reactivity of ketenyl ligands. A characteristic reaction of η^1-ketenyl complexes is the addition of HX molecules across the ketenyl CC bond to give metallo–acetic acid derivatives (eq 1).[11] Thus, (η^1-ketenyl)metal complexes



(1)

may be considered as transition-metal-substituted ketenes. The most common reaction of (η^2-ketenyl)metal complexes is the addition of electrophiles to give (oxoalkyne)metal complexes (eq 2).[12] A variety of metal-coordinated ynols and ynol derivatives were synthesized by this method, e.g. RC≡COCH$_3$, RC≡COH, [RC≡COBR$_3$]$^-$, and RSC≡COCH$_3$.[4]



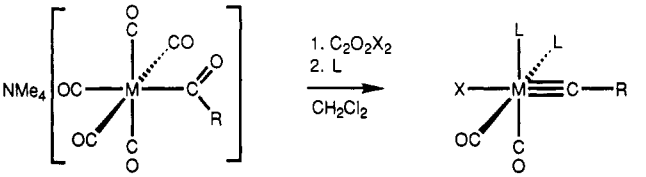
(2)

The chemistry of "free" ketenide, or ynolate, ions (e.g., alkali-metal salts of RCCO$^-$) has been little developed.[13] With most electrophiles, addition occurs at the terminal carbon atom to give ketenes. This reactivity prevents the general use of ynolate ions as starting materials into the chemistry of ynol derivatives. It was demonstrated several years ago by Stang et al.[14] and by Kowalski et al.[15] that addition of electrophiles to the oxygen atom is feasible when bulky silylating agents, such as *i*-Pr$_3$SiCl, are used. In recent years methods for the preparation of ynol ethers and ynol esters, which do not depend on ynolate ions as intermediates, were developed in Stang's group.[16] It has quickly become apparent that ynol derivatives are useful synthetic reagents.[17]

Since transition-metal-coordinated ynol derivatives are easily accessible by addition of electrophiles to η^2-ketenyl ligands, it appears likely that this route will provide an attractive entry into the coordination chemistry of this little-studied family of compounds. It is evident from the partial list of ligands mentioned above that even representatives that are unable to exist as free molecules, e.g. the parent ynols, form stable transition-metal complexes. The synthesis of ynol derivatives within the coordination sphere of a transition metal is especially attractive due to the potential of further transition-metal-mediated transformations. Here we describe the synthesis of new transition-metal ynol ester complexes and report our first attempts to elucidate the reaction behavior of this type of metal complex.

Results and Discussion

Synthesis and Characterization of the (Ynol ester)metal Complexes. The anionic ketenyl complexes **3–5** were prepared by following a previously developed procedure, reaction of the pyridine-substituted metal alkylidyne complexes **1** and **2** with anionic bidentate ligands.[18,19] The carbyne complexes **1** and **2** were synthesized as shown in eq 3. Equation 4 shows the reaction of complexes **3** and

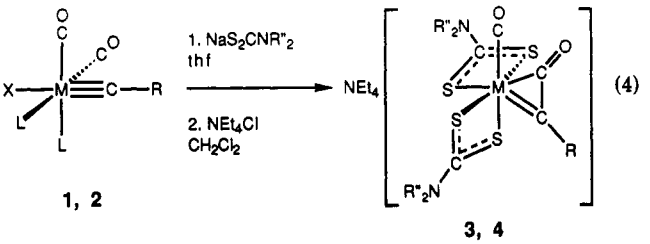


1, 2

1: M = Mo, R = Ph, L = 4-picoline, X = Br
2a: M = W, R = Ph, L = pyridine, X = Cl
2b: M = W, R = C$_6$H$_4$-CMe$_3$-4, L = pyridine, X = Cl

(3)

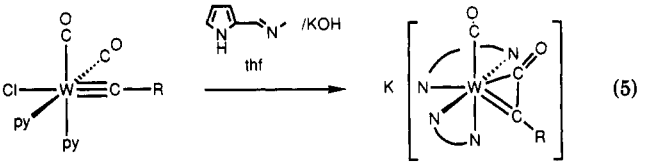
4 with dithiocarbamate ligands; eq 5 shows the reaction of complex **5** with pyrrolecarboxaldehyde methylimine in the presence of base. The reactivity of ketenyl complexes



1, 2 **3, 4**

(4)

3: M = Mo, R = Ph, R" = Et
4a: M = W, R = Ph, R" = Et
4b: M = W, R = C$_6$H$_4$-CMe$_3$-4, R" = Et
4c: M = W, R = Ph, R" = Me



2a **5**

R = C$_6$H$_4$-CMe$_3$-4
N⌒N = C$_6$H$_7$N$_2$

(5)

of the type [M(RCCO)(LL)$_2$(CO)]$^-$ toward alkylating agents has previously been established.[19,20] Similarly, the ketenyl complexes **3** and **4b** react with CF$_3$SO$_3$Me to give the ynol ether complexes **6** and **7** (eq 6).

The anionic ketenyl complexes **3–5** react in methylene chloride solution with acyl halides to give the neutral ynol

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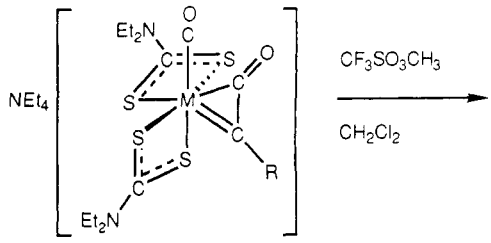
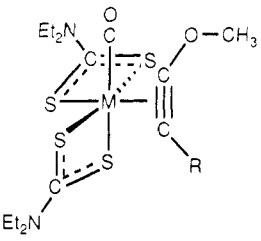


3, 4b



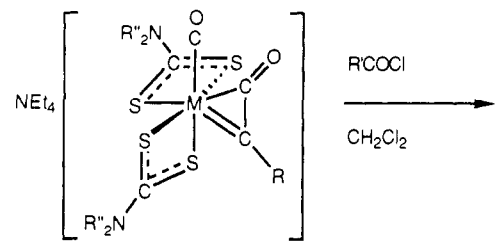
(6)

6, 7

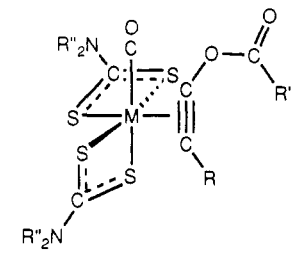
6: M = Mo, R = Ph
7: M = W, R = C_6H_5-CMe_3-4

ester complexes **8**, **9** and **10** (eqs 7 and 8, respectively) in synthetically useful yields (in most cases above 60%). The products are easily purified by chromatography on silica gel using methylene chloride or mixtures of methylene chloride and hexane as the eluant and/or by recrystallization from the same solvent systems. All tungsten ynol ester complexes are stable in solution in the absence of air. The tungsten complexes also tolerate short exposure to air in solution without noticeable decomposition. The molybdenum complex **8** decomposes at room temperature; it was handled at temperatures below 0 °C. The ynol ester complexes **8–10** are all green solids. The compounds were obtained in microcrystalline form or as powders. Despite several variations of the ligands or of the substituents on the ynol ester ligands, we were not able to obtain crystals suitable for an X-ray structure analysis of any of the new complexes. We have, however, studied the solid-state structure of the tungsten ynol ester complex $WCl_2(\eta^2$-$PhC{\equiv}COCOC_6H_4$-OMe-4)$(CO)(PMe_3)_2$, which was obtained by a photochemical route.[7]

Acylation of the ketenyl complexes **3–5** is accompanied by a shift of the carbonyl ligand stretching frequency from about 1830–1850 cm^{-1} to about 1910–1940 cm^{-1} for the neutral ynol ester complexes **8–10**. In addition to the strong absorption of the terminal carbonyl ligand the products also exhibit a characteristic absorption of medium intensity at 1730–1780 cm^{-1} for the ester carbonyl group. The infrared absorption of the carbonyl group of uncoordinated ynol esters is found in the range of 1755–1800 cm^{-1}, i.e. at slightly higher frequencies.[21] The ^{13}C NMR resonances of the two alkyne carbon atoms are found from δ 188 to 196 ppm and from δ 215 to 221 ppm. These values are characteristic of four-electron-donor alkyne ligands.[22] The values of the resonances for the alkyne carbon atoms are very similar to those previously found for ynol ether ligands (RCCOR').[23] On the basis of the established assignments for this type of ligand the signal for the alkyne carbon at lower field is assigned to the oxygen-substituted carbon atom, while the signal at higher field is assigned to the aryl-substituted carbon atom. This assignment is confirmed by the observation of a triplet ($^3J_{CH}$ = 5 Hz) at



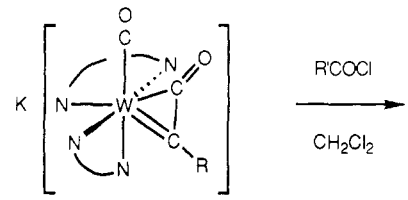
3, 4



(7)

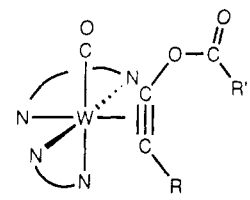
8, 9

8: M = Mo, R = Ph, R' = Ph, R" = Et
9a: M = W, R = Ph, R' = Me, R" = Et
9b: M = W, R = Ph, R' = Ph, R" = Et
9c: M = W, R = Ph, R' = $CHCH_2$, R" = Et
9d: M = W, R = Ph, R' = *trans*-CHCHMe, R" = Et
9e: M = W, R = Ph, R' = *trans*-CHCHPh, R" = Et
9f: M = W, R = C_6H_4-CMe_3-4, R' = Me, R" = Et
9g: M = W, R = C_6H_4-CMe_3-4, R' = CH_2Ph, R" = Et
9h: M = W, R = C_6H_4-CMe_3-4, R' = CMe_3, R" = Et
9i: M = W, R = C_6H_4-CMe_3-4, R' = CMe3, R" = Me



5

R = C_6H_4-CMe_3-4
N⌒N = $C_6H_7N_2$



(8)

10

10a: R' = CMe_3
10b: R' = CH_2Ph
10c: R' = C_6H_4-OMe-4

δ 193.3 ppm for the ^{13}C NMR signal of the CPh carbon atom in complex **9e**. The resonances for the ester carbonyl carbon atoms are found between δ 161 and 174 ppm. These values are in the established region for ester carbonyl groups.[24] The corresponding signals for free ynol esters RC≡COCOR' (R = alkyl, R' = alkyl, aryl) are found in the same range.[21]

Reactions of (Ynol ester)metal Complexes. Several experiments were carried out to test the reactivity of the new ynol ester complexes. The reaction of organic esters with primary and secondary amines to give amides by cleavage of the R'C(O)–OR bond is a common reaction.[25]

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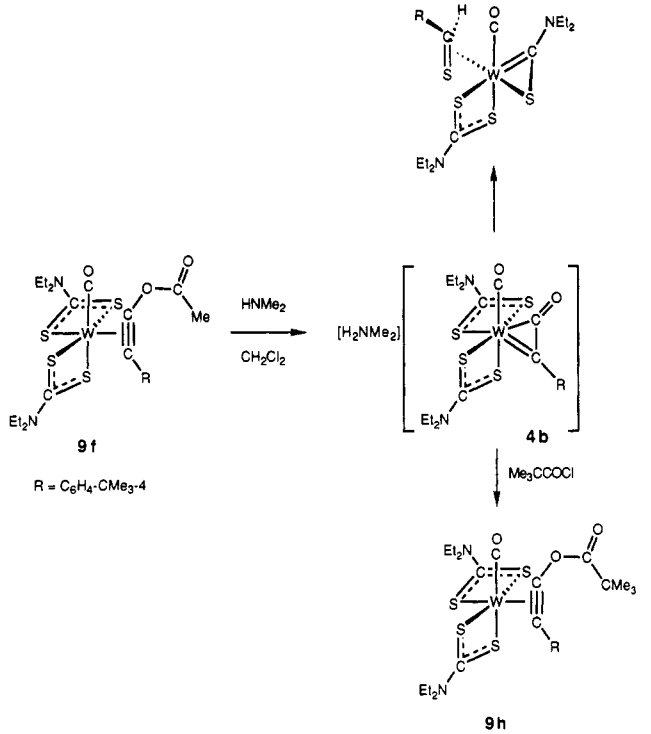
We chose to study this reaction for the ynol ester ligands with the expectation to establish that the ester group of the coordinated ynol esters would behave the same way, i.e. undergo cleavage of the RCCO–C(O)R′ bond. We were able to confirm this, but we found that the RCC–OC(O)R′ bond is also subject to cleavage under certain circumstances. We were furthermore interested to see whether the ynol ester ligands could be cleaved intact from the metal center by substitution with other ligands. This goal has not yet been reached, but attempts to do so led to the discovery of unexpected transformations of ynol ester ligands.

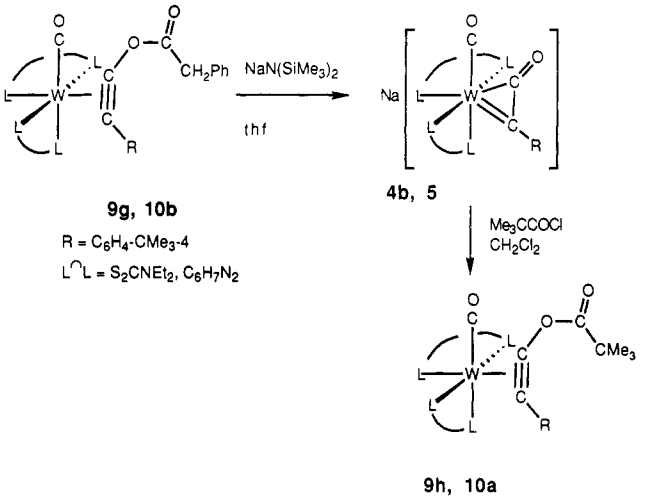
Cleavage of Ynol Ester Ligands at the RCCO–C(O)R′ Linkage. Addition of excess dimethylamine to a methylene chloride solution of complex **9f** causes a rapid change of color from deep green to forest green (eq 9). An



(9)

IR spectrum of the reaction solution, taken within less than 5 min, exhibits two strong absorptions at 1847 and 1640 cm^{-1}. These absorptions are assigned to $[W(4\text{-}Me_3CC_6H_4CCO)(S_2CNEt_2)_2(CO)]^-$ (**4b**, dimethylammonium salt) and dimethylacetamide.[26] Formation of **4b** and of dimethylacetamide was expected as the products of aminolysis of the ester group. The nature of complex **4b** was confirmed by transformation into the ynol ester complex **9h** by reaction with trimethylacetyl chloride, after removal of excess amine. The IR spectrum of the reaction solution also exhibits an absorption of medium intensity at 1920 cm^{-1}, which becomes dominant when the reaction solution is allowed to stand for several hours. The ketenyl complex **4b** (dimethylammonium salt) apparently transforms slowly into a second product. This compound was identified by ^1H NMR spectroscopy as the thioaldehyde complex $[W(\eta^2\text{-}SCNEt_2)(S_2CNEt_2)(CO)(SCHC_6H_4\text{-}CMe_3\text{-}4)]$. The phenyl analogue $[W(\eta^2\text{-}SCNEt_2)(S_2CNEt_2)(CO)(SCHPh)]$ had previously been synthesized by the reaction of complex **4a** with $[H_2NEt_2][S_2CNEt_2]$.[18] The thioaldehyde complex may thus be considered a secondary reaction product formed from **4b**, the primary product of aminolysis of the ynol ester complex **9f**. The IR spectrum of the reaction solution also exhibits a weak peak at 2015 cm^{-1}. The origin of this absorption was not determined.

The phenylacetic acid ynol ester complexes **9g** and **10b** react rapidly (less than 5 min) with $Na[N(SiMe_3)_2]$ in THF to form the ketenyl complexes **4b** and **5**, as indicated by the appearance of characteristic IR absorptions at about 1820 and 1660 cm^{-1} (eq 10). The nature of these products



(10)

was confirmed by transformation into the ynol ester complexes **9h** and **10a** by reaction with trimethylacetyl chloride (eq 10). Under the same conditions, cleavage of the ynol ester ligand $4\text{-}Me_3C\text{-}C_6H_4CCOCOC_6H_4\text{–}OMe\text{-}4$ in complex **10c** by reaction with $Na[N(SiMe_3)_2]$ takes more than 18 h. Formation of the ketenyl complexes **4b** and **5** from **9g** and **10b** could conceivably occur by one of two routes: direct attack of bis(trimethylsilyl)amide at the ester carbonyl group or deprotonation of the CH_2Ph group and cleavage of phenylketene from the deprotonated ynol ester complex. We have not been able to observe any evidence of phenylketene formation based on the infrared spectrum of the reaction solution, but the significantly lower reactivity of complex **10c** toward $Na[N(SiMe_3)_2]$ suggests that cleavage of the ynol ester ligands in complexes **9g** and **10b** is initiated by deprotonation of the phenylacetyl group. Phenylketene, if liberated, may not be stable under the reaction conditions. The trimethylacetyl ynolate ligands in complexes **9h** and **10a** are also cleaved by $Na[N(SiMe_3)_2]$ to give the ketenyl complexes **4b** and **5**, but also significantly more slowly than in phenylacetyl ynolate ligands in **9g** and **10b** (eq 10).

Cleavage of the Ynol Ester Group at the RCC–OC(O)R′ Linkage. The reaction of the ynol ester complex **9h** with dimethylamine (eq 11) did not lead to the formation of the expected anionic ketenyl complex **4b**. Rather, the infrared spectrum of the reaction solution showed a strong absorption at 1901 cm^{-1}, indicating the formation of a neutral product. The product was easily isolated and purified by chromatography on silica gel using CH_2Cl_2/hexane as the eluant. On the basis of IR and ^1H NMR spectroscopic information it was obvious that the trimethylacetate group was lost from the starting complex and that a dimethylamino group was incorporated in the product. The presence of five peaks in the ^{13}C NMR spectrum between δ 250 and 190 ppm signaled the presence of a (dimethylamino)alkyne ligand, in addition to the

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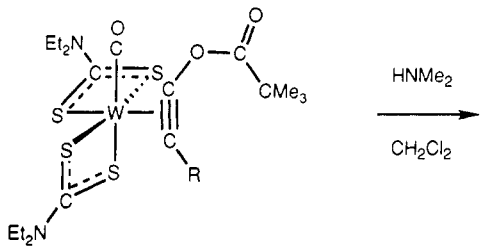
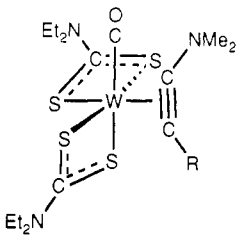


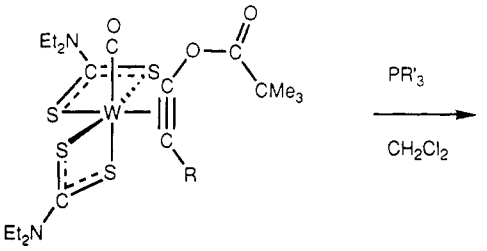
9h



11 (11)

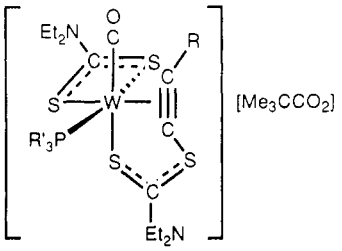
carbonyl ligand and the two (diethylamino)dithiocarbamate ligands. A resonance at δ 246.7 ppm is due to the carbonyl ligand. Resonances at δ 211.9, 203.9, 200.5, and 199.3 ppm are due to the dithiocarbamate carbon atoms and the alkyne carbon atoms. The reaction thus amounts to substitution of trimethylacetate at the alkyne carbon by dimethylamide to give the aminoalkyne complex **11**. Since the reaction of the analogous acetic acid ynol ester ligand of complex **9f** with dimethylamine (eq 9) leads to cleavage of the RCCO–C(O)CH_3 bond, it appears that the attack of dimethylamine at the carbonyl group of the trimethylacetic acid ynol ester ligand in **9h** is hindered by the bulky acid residue.

Another cleavage of the RCC–OC(O)R′ bond of an ynol ester ligand was observed in the reactions of **9h** with trimethylphosphine and triethylphosphine to form **12a** and **12b** (eq 12). The reactions with phosphines were con-



9h

R = C_6H_4-CMe_3-4



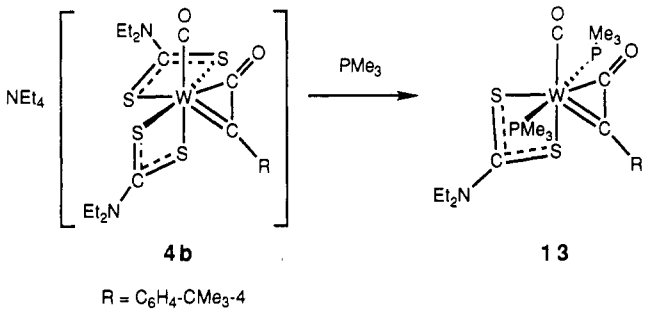
12 (12)

12a: R′ = Me
12b: R′ = Et

ducted with the intent to displace ynol ester ligands from the metal center. Templeton has previously reported facile substitution of alkyne ligands in molybdenum complexes of the type $[Mo(S_2CNMe_2)_2(CO)(alkyne)]$.[27] Substitution of ynol ester ligands, however, was not achieved. Instead, an unexpected reaction involving replacement of the carboxylate group of the ynol ester ligand by dithiocarbamate took place.

Addition of trimethylphosphine to a THF solution of **9h** causes a change of color from green to red within about 15 min. The reaction is accompanied by a shift of the IR absorption of the carbonyl ligand from 1924 to 1955 cm^{-1}. The absorption of the ester carbonyl group at 1760 cm^{-1} is replaced by a new absorption at 1634 cm^{-1}, indicating the presence of a free carboxylate group.[26] However, the possibility of direct substitution of trimethylacetate by trimethylphosphine is excluded by the presence of a large W–P coupling constant (J_{WP} = 309 Hz) for the ^{31}P NMR signal of the phosphorus atom. This coupling constant is clear evidence that trimethylphosphine is coordinated directly to the metal center.[28] The ^{13}C NMR spectrum exhibits five peaks in the range from δ 230 to 190 ppm, which indicate the presence of a carbonyl ligand, two dithiocarbamate groups, and one alkyne ligand. To accommodate all of the observed spectroscopic parameters, we formulate the product as the cationic complex **12**, with trimethylacetate as the counterion (eq 12). Complex **12** contains an unusual chelating dithiocarbamate-substituted alkyne ligand. The formation of complex **12** may be envisaged to occur by nucleophilic attack of phosphine at the metal center with concomitant (or subsequent) displacement of the sulfur atom of a dithiocarbamate ligand from the metal center. The noncoordinated sulfur atom of the η^1-dithiocarbamate ligand may then substitute the carboxylate group at the alkyne ligand, thereby generating complex **12**. The intermediacy of an η^1-dithiocarbamate ligand seems reasonable, considering the existence of well-characterized (η^1-dithiocarbamato)metal complexes.[29]

Reaction of Ketenyl Complex 4b with Trimethylphosphine. To test the possibility that a sulfur atom of a dithiocarbamate ligand may be displaced from the metal center upon the addition of a phosphine ligand, we studied the reaction of ketenyl complex **4b** with trimethylphosphine (eq 13). Reaction of **4b** with PMe_3 could be



4b **13**

R = C_6H_4-CMe_3-4

(13)

expected to result in displacement of a sulfur atom from the metal center or η^2–η^1 transformation of a ketenyl ligand. Upon addition of trimethylphosphine to a THF solution of **4b** the solution turns from green to purple within 15 min. The infrared absorption of the carbonyl ligand of complex **4b** at 1831 cm^{-1} disappears and is replaced by a new absorption at 1871 cm^{-1}. The absorption at 1670 cm^{-1} for the ketenyl ligand shifts to 1700 cm^{-1}. The ^1H NMR spectrum shows the presence of only one dithio-

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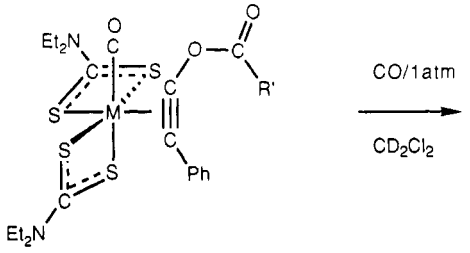
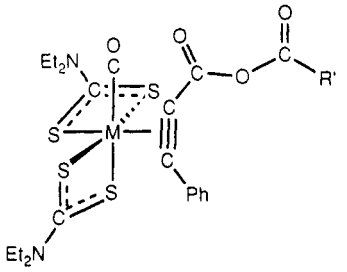
carbamate ligand and the presence of two trimethylphosphine ligands. The product is formulated as the neutral ketenyl complex $[W(4\text{-}Me_3C\text{-}C_6H_4CCO)(S_2CNEt_2)(CO)(PMe_3)_2]$ (**13**). This result establishes that dithiocarbamate ligands are subject to substitution by trimethylphosphine ligands and lends support to the possible intermediacy of an η^1-dithiocarbamate intermediate in the formation of complex **12**.

Reaction of Ynol Ester Complexes 8 and 9c with Carbon Monoxide. Templeton et al.[27] reported the displacement of alkyne ligands by carbon monoxide under atmospheric pressure from complexes of the type $[Mo(S_2CNR'_2)_2(RCCR)(CO)]$. We therefore hoped to release the ynol ester ligands from the metal center by reaction with carbon monoxide. Complexes **8** and **9c** do react with carbon monoxide under atmospheric pressure, but substitution of the ynol ester ligands does not occur (eq 14).



8, 9c



(14)

14, 15

14: M = Mo, R' = Ph
15: M = W, R' = CH=CH_2

When solutions of **8** and **9c** in CH_2Cl_2 are placed under an atmosphere of carbon monoxide, the color changes slowly from green to brown (30 min and 4 h, respectively). The reaction is accompanied by a slight shift of the IR absorption of the carbonyl ligand, e.g. from 1940 cm^{-1} in **8** to 1946 cm^{-1}. In most runs of this experiment a second (weak) IR absorption of varying intensity at 2003 cm^{-1} is observed, apparently due to a minor side product, which could not be isolated. In the region typical for organic carbonyl groups two absorptions are observed, e.g. at 1775 and 1745 cm^{-1} for **14**. Both the molybdenum complex **14** and the tungsten complex **15** are very air-sensitive. Upon exposure to air, solutions of both compounds darken. Nevertheless, the tungsten complex **15** could be purified by chromatography on silica gel, using methylene chloride as the eluant, and was isolated as a green powder.

The ^1H NMR spectrum of **15** is uninformative, except that it indicates no significant changes for the proton-containing parts of the molecule. The ^{13}C NMR spectra of **14** and **15** indicate that the products have structural features very similar to those of the starting ynol ester complexes **8** and **9c**. The ^{13}C NMR spectrum of **15** features five peaks in the region from δ 240 to 190 ppm. The resonance at δ 236.7 is assigned to a terminal carbonyl ligand (J_{WC} = 139.4 Hz). Two resonances at δ 212.3 and 199.5, both quintets due to coupling to four hydrogen atoms, are assigned to the dithiocarbamate carbon atoms. The remaining two signals at δ 214.9 and at 203.3 are indicative of the presence of an alkyne ligand. The signal at δ 214.9 ppm is a triplet and is therefore assigned to the alkyne carbon carrying the phenyl group (^{183}W satellites were not clearly observed for this resonance). The signal at δ 203.3 ppm is a singlet and features ^{183}W satellites (J_{WC} = 40.79 Hz). Two signals are found in the region for organic carbonyl groups. The resonance at δ 169.9 ppm is a singlet. The signal at δ 161.2 is a multiplet (ddd) and is assigned to the acryloyl carbonyl group. The ^{13}C NMR spectrum of the molybdenum complex **14** features very similar resonances. On the basis of the available spectroscopic information, the products **14** and **15** are formulated as shown in eq 14.

Complexes **14** and **15** are postulated to arise from the formal insertion of carbon monoxide into the RCC–OC(OR)R′ bond of the ynol ester ligands. However, we would expect such compounds to be about as stable as the ynol ester complexes toward air. Due to the observed high air sensitivity of the products we consider the proposed structures **14** and **15** as preliminary. A reviewer suggested that complexes **14** and **15** could also be formulated as complexes containing ynol oxalate moieties, i.e. RC≡CCOC(O)C(O)R′. The ynol ether complex $[W(S_2CNEt_2)_2(PhCCOMe)(CO)]$ did not exhibit any reactivity toward carbon monoxide at atmospheric pressure.

Conclusion

Ynol ester ligands are easily accessible by acylation of η^2-ketenyl ligands. First reactivity studies show that ynol ester ligands are able to undergo reactions involving cleavage of the RCCO–C(O)R′ bond as well as the RCC–OC(O)R′ bond. The cleavage of ynol ester ligands from the metal center in intact form has not yet been achieved.

Experimental Section

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents methylene chloride (CaH_2), tetrahydrofuran (Na/benzophenone), and hexane (CaH_2) were dried and distilled prior to use.

Materials. $[W(CPh)(Cl)(CO)_2(py)_2]$ (**2a**),[30] $NEt_4[W(PhCCO)(S_2CNEt_2)_2(CO)]$[18] (**4a**), and $NEt_4[W(PhCCO)(C_6H_7N_2)_2(CO)]$[19] (**5a**) were prepared as previously described. Reagents were obtained from commercial sources and used without further purification. NaS_2CNEt_2 and NEt_4Cl were dried at 110 °C under vacuum for 6 h prior to use. *N*-Methylpyrrole-2-carboxaldimine[31] was prepared as described in the literature. The NMR spectra were measured at magnetic field strengths of 5.87 or 7.05 T in $CDCl_3$ at room temperature unless otherwise noted; solvent peaks were used as internal reference, and the data are reported in δ relative to TMS. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

$[NMe_4][W\{C(O)(C_6H_4\text{-}CMe_3\text{-}4)\}(CO)_5]$ was prepared by following the procedure developed by Fischer and Maasböl.[32] $LiC_6H_4\text{-}CMe_3\text{-}4$ is prepared by reaction of Li clippings (3.05 g, 439 mmol) with 4-bromo-*tert*-butylbenzene (21.6 mL, 124 mmol) in diethyl ether (300 mL) for 2 h at reflux. The resulting solution is slowly added to a stirred suspension of $W(CO)_6$ (31.30 g, 88.94 mmol) in ether (100 mL). A glass wool plug is used to retain residual lithium particles. The reaction solution is stirred at room temperature for 30 min. The solvent is then removed in vacuo, and the orange residue is redissolved in a minimum amount of cold (0 °C) N_2-saturated water. The solution is filtered over a pad of Celite to remove unreacted tungsten hexacarbonyl. The product is precipitated by adding aqueous NMe_4Cl (14.6 g, 133 mmol). The solid is collected by filtration and redissolved in CH_2Cl_2 (200 mL) and the solution dried over $MgSO_4$. The solution

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is decanted off and reduced in volume, and the product is precipitated with hexane as an orange crystalline solid (39.9 g, 80%): mp 88.4–88.6 °C dec.; ^{1}H NMR δ 7.54 (d, 2 H, J = 8.37 Hz, C_6H_4), 7.35 (d, 2 H, J = 8.45 Hz, C_6H_4), 3.45 (s, 12 H, $N(CH_3)_4$), 1.31 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 279.3 ($C(O)C_6H_4$-CMe_3-4), 209.0 (trans CO), 204.7 (cis CO), 155.5, 152.2, 126.4, 125.2 (C_6H_4), 56.3 [$N(CH_3)_4$], 35.2 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$); IR (CH_2Cl_2, cm^{-1}) 2042 (w, CO), 1901 (vs, CO). Anal. Calcd for $C_{20}H_{25}NO_6W$: C, 42.95; H, 4.51. Found: C, 42.39; H, 4.39.

[Mo(CPh)Br(CO)$_2$(4-picoline)$_2$] (1) was prepared by following a previously described procedure.[31] During the entire experiment light sources near the working area were turned off. A solution of [NMe_4][Mo(COPh)(CO)$_5$][33] (5.62 g, 13.54 mmol) in CH_2Cl_2 (200 mL) was cooled to −78 °C. A fine orange precipitate formed, and a cold (−78 °C) solution of $C_2O_2Br_2$ (3.04 g, 14.07 mmol) was added. The color darkened to orange-red immediately. The solution was warmed up. At −20 °C the solution had turned bright yellow and 4-picoline (12.44 g, 133.6 mmol) was added. The solution was stirred at 0 °C for 50 min, and evolving gas was allowed to escape. The color was now orange. The solvent was removed at room temperature and the solid washed with hexane (3 × 15 mL) to remove excess 4-picoline. The product was dissolved in CH_2Cl_2 (4 × 40 mL) at 0 °C and the solvent removed from the filtered solution to give a brown-yellow residue. The product was purified by column chromatography on silica gel (14 × 5 cm) at −25 °C. Elution was begun with a 1:1 mixture of CH_2Cl_2/pentane, which was gradually changed to pure CH_2Cl_2. An initial yellow fraction was discarded. The product was collected in three major fractions (~850 mL). The fractions were stored in the dark at −10 °C until the solvent could be removed at temperatures below 0 °C. The solid from each fraction was redissolved in a small amount of CH_2Cl_2. Slow addition of hexane produced several crops of fine light orange crystals or precipitates contaminated with brown material. The combined yield of product was 4.21 g (61.4%). The product was stored in the dark at −78 °C for use without further purification: ^{1}H NMR δ 8.86 (m, 4 H), 7.42–7.46 (m, 2 H), 7.28–7.34 (m, 3 H), and 7.12 (br d, 4 H) (NC_5H_4Me and C_6H_5), 2.37 (s, 6 H, CH_3); IR (CH_2Cl_2, cm^{-1}) 1990 (s, CO), 1917 (s, CO).

[W(CC$_6$H$_4$-CMe$_3$-4)Cl(CO)$_2$(py)$_2$] (2b) was prepared by following a previously described procedure.[31] A solution of [NMe_4][W{C(O)(C_6H_4-CMe_3-4)}$(CO)_5$] (6.02 g, 11.0 mmol) in CH_2Cl_2 (50 mL) is cooled to −78 °C. A cold (−78 °C) solution of $C_2O_2Cl_2$ (0.96 mL, 11.0 mmol) in CH_2Cl_2 (10 mL) is quickly added to the well-stirred suspension/solution. The reaction mixture is warmed in an ice bath until the color changes from dark orange to light yellow (−15 to −5 °C). Then pyridine (10 equiv) is added, the temperature is raised to 40 °C, and evolving CO gas is allowed to escape. After complete formation of the product (~1.5 h) the solvent is removed and the residue washed with hexane (2 × 30 mL) to remove excess pyridine. The product is redissolved in cold (0 °C) CH_2Cl_2 (30 mL) and filtered over a layer of silica gel/CH_2Cl_2 on a dry-ice-jacketed fritted disc. Cold (−78 °C) CH_2Cl_2 is used to wash all of the product out of the silica layer. The solvent is reduced in volume (20 mL), and the product is precipitated with hexane as an orange crystalline solid (4.56 g, 72%): mp 131–133 °C; ^{1}H NMR δ 9.06–9.04 (m, 4 H, α-C_5H_5N), 7.76–7.70 (m, 4 H, β-C_5H_5N), 7.32–7.20 (m, 6 H, γ-C_5H_5N, C_6H_4), 1.24 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR δ 263.5 (W≡C), 220.5 (CO), 152.6, 150.8, 146.5, 138.1, 129.0, 124.9 (C_6H_4, C_5H_5N), 34.7 ($C(CH_3)_3$), 30.9 ($C(CH_3)_3$); IR (CH_2Cl_2, cm^{-1}) 1984 (s, CO), 1901 (s, CO). Anal. Calcd for $C_{23}H_{23}ClN_2O_2W$: C, 47.73; H, 4.00. Found: C, 48.31; H, 4.14.

[NEt$_4$][Mo(S$_2$CNEt$_2$)$_2$(CO)(PhCCO)] (3). A dark orange solution of [Mo(CPh)Br(CO)$_2$(4-pic)$_2$] (0.781 g, 1.540 mmol) in tetrahydrofuran (30 mL) was stirred at −78 °C as a solution of NaS_2CNEt_2 (0.580 g, 3.388 mmol) in tetrahydrofuran (4 mL) was added. The solution was removed from the cold bath and stirred at ambient temperature for 1.45 h. The reaction solution turned initially green and then changed to brown during this period. The solvent was removed under reduced pressure. The product was redissolved in methylene chloride (20 mL) to give a green solution. Et_4NCl (0.281 g, 1.693 mmol ≡ 1.10 equiv) was added, and the solution was stirred for 45 min. The mixture was filtered through a pad of well-dried cellulose to remove finely divided NaBr. The solvent was removed from the green solution, and the resulting residue was dried under vacuum for 2.5 h. The product was treated with tetrahydrofuran (20 mL) to give a dark brown solution over a green powder. The mixture was cooled at −8 °C for 30 min, and then the supernatant was decanted and the solid washed with tetrahydrofuran (2 × 5 mL). The product was recrystallized from methylene chloride/diethyl ether to give forest green microcrystals of [NEt_4][Mo(S$_2$CNEt$_2$)$_2$(CO)(CPhCO)] (1.00 g, 1.50 mmol, 97.5%): ^{1}H NMR (CD_2Cl_2) δ 7.89 (d, J = 8.37 Hz, 2 H, Ph), 7.37 (t, J = 7.67 Hz, 2 H, Ph), 7.13 (t, J = 7.43 Hz, 1 H, Ph), 3.42–3.83 (br m, 8 H, NCH_2), 3.18 (q, J = 7.29 Hz, 8 H, NCH_2), 1.12–1.26 (m, 24 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K) δ 237.21 (CO) 214.20, 208.48, 204.71, 200.87 (CCO and CS_2) 139.39, 128.45, 126.50, 125.74 (C_6H_5) 52.24, 45.78, 44.99, 44.51, 44.19 (NCH_2), 12.78, 12.52, 12.37, 12.21, 7.53 (CH_3); IR (CH_2Cl_2, cm^{-1}) 1842 (s, CO) 1697 (m, br, CCO).

[NEt$_4$][W(S$_2$CNEt$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$CCO)] (4b). A solution of **2** in THF was cooled to 0 °C, and NaS_2CNEt_2 (2.2 equiv) was added. Immediately the color changed from orange to green-orange. After 5 min the solution was warmed to room temperature and stirring was continued for 40 min. NEt_4Cl (1.5 equiv) was added, and within 10 min the product precipitated as a green solid. Stirring was continued for an additional 20 min. The reaction mixture was filtered and the solid was collected, washed with hexane, and dried in vacuo. The solid was used as obtained for further reactions: ^{1}H NMR δ 7.92 (d, 2 H, J = 8.37 Hz, C_6H_4), 7.34 (d, 2 H, J = 8.44 Hz, C_6H_4), 3.51–3.72 (m, 8 H, NCH_2CH_3), 3.25 (q, 8 H, NCH_2CH_3), 1.27 [s, 9 H, $C(CH_3)_3$], 1.17–1.33 (m, 24 H, NCH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1831 (s, CO), 1670 (m, CCO).

[NEt$_4$][W(S$_2$CNMe$_2$)$_2$(CO)(PhCCO)] (4c). Complex **2a** (1.106 g, 2.12 mmol) was dissolved in 60 mL of THF, and sodium dimethyldithiocarbamate (2.2 equiv) was added with stirring. The IR spectrum of the reaction solution indicated the formation of a side product with an absorption at 1925 cm^{-1}. The side product is believed to be the thioaldehyde complex W(S_2CNMe_2)-($SCNMe_2$)(SCHPh)(CO). After 1 h the solvent is removed in vacuo. The residue was washed with hexane (2 × 50 mL) and redissolved in 60 mL of CH_2Cl_2. Tetraethylammonium bromide (0.356 g) was added, and the solution was filtered through Celite. The volume of the solution was reduced to 30 mL, and 40 mL of ether was added. Slow cooling to −8 °C resulted in the formation of a green microcrystalline solid. The supernatant was decanted, and the product was dried in vacuo; it contains excess tetraethylammonium bromide but was used for further reactions as obtained (1.129 g): ^{1}H NMR (273 K) δ 7.98 (d, 2 H), 7.36 (t, 2 H), 7.10 (m, 1 H) (C_6H_5), 3.34–3.35 (12 H, NCH_3), 3.35–3.12 (m, CH_2CH_3), 1.30 (t, CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1833 (s, CO), 1676 (m, CCO).

[Mo(S$_2$CNEt$_2$)$_2$(CO)(PhC≡COCH$_3$)] (6). A solution of **3** (0.203 g, 0.304 mmol) in CH_2Cl_2 (9 mL) is cooled to −78 °C. $CF_3SO_3CH_3$ (0.065 g, 0.398 mmol) is added. The solution is slowly warmed to room temperature, and Na_2CO_3 (100 mg) is added. The solvent is reduced to about 2 mL, and the product is purified by column chromatography at room temperature on silica gel (1.5 cm × 7 cm) using CH_2Cl_2 as the eluant. A green fraction is collected (about 15 mL), and the solvent is removed to obtain a green powder. The residue is redissolved in a 5:1 mixture of CH_2Cl_2/hexane (12 mL), and the solvent is slowly removed in vacuo until a crystalline precipitate forms. Then the mixture is slowly cooled to −78 °C. The supernatant is decanted and the green crystalline product is dried in vacuo (0.089 g, 0.161 mmol). An additional 11 mg of product was isolated from the residue of the supernatant by recrystallization from CH_2Cl_2/hexane: ^{1}H NMR δ 7.51 (d, 2 H, C_6H_4), 7.38 (d, 2 H, 7.25 (t, 1 H, C_6H_4), 4.43 (s, 3 H, OCH_3), 3.61–3.90 (m, 8 H, NCH_2CH_3), 1.16–1.30 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (273 K) δ 238.6 (CO), 225.8 (CCO), 207.6, 200.1 (S_2CNEt_2), 197.95 (CCO), 137.8, 128.2, 128.1, 127.8 (C_6H_4), 65.5 (OCH_3), 45.6, 44.7, 44.3, 44.1 (NCH_2CH_3), 12.8, 12.4 (NCH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1933 (s).

[W(S$_2$CNEt$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COCH$_3$)] (7). A solution of **4b** (0.977 g, 1.31 mmol) in CH_2Cl_2 (25 mL) is cooled to 0 °C. $CF_3SO_3CH_3$ (0.180 mL, 1.57 mmol) is added dropwise. The solution is warmed to room temperature, and within 15 min the mossy green solution turns bright green. Solvent is removed, and the product is purified by column chromatography on silica gel (2 cm × 15 cm) using CH_2Cl_2/hexane (1:1, 200 mL) (0.688 g, 75%):

mp 145–146 °C; ^{1}H NMR δ 7.55 (d, 2 H, J = 8.41 Hz, C_6H_4), 7.42 (d, 2 H, J = 8.43 Hz, C_6H_4), 4.44 (s, 3 H, OCH_3), 3.58–4.48 (m, 8 H, NCH_2CH_3), 1.33 (s, 9 H, $C(CH_3)_3$), 1.19–1.37 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 241.5 (CO), 255.0 (CCO), 212.6, 202.0 (S_2CNEt_2), 190.9 (CCO), 150.7, 135.2, 128.6, 125.0 (C_6H_4), 65.0 (OCH_3), 45.6, 44.6, 44.2, 43.9 (NCH_2CH_3), 34.6 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 12.8, 12.4 (NCH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1917 (s, CO). Anal. Calcd for $C_{24}H_{36}O_2S_4N_2W$: C, 41.38; H, 5.21. Found: C, 40.07; H, 5.04.

[Mo(S$_2$CNEt$_2$)$_2$(CO)(PhCCOC(O)Ph)] (8). A solution of **3** (0.204 g, 0.305 mmol) in CH_2Cl_2 (50 mL) was cooled to −78 °C. Benzoyl chloride (0.036 mL, 0.31 mmol) was added. After the mixture was warmed to 0 °C, the solvent was removed in vacuo. The product was redissolved in a few milliliters of CH_2Cl_2, and the solution was filtered through a layer of silica gel (1 cm × 1 cm) at room temperature. The product was washed out from the silica layer with about 25 mL of CH_2Cl_2. The volume of the solution was reduced to 5 mL, and about 8 mL of hexane was added. Slow reduction of the volume in vacuo resulted in the formation of green microcrystals, which were washed with hexane (2 mL) and with ether (1 mL) and dried in vacuo (0.154 g, 0.240 mmol). The product is very air sensitive and turns red upon exposure to air: ^{1}H NMR (CD_2Cl_2) δ 8.31 (m, 2 H), 7.73–7.67 (m, 1 H), 7.63–7.54 (m, 4 H), 7.48–7.41 (m, 2 H), 7.37–7.31 (m, 1 H) (2 C_6H_5), 3.90–3.64 (m, 8 H, NCH_2CH_3), 1.29–1.14 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 236.3 (CO), 216.6 (CCO), 206.7, 199.0 (CS_2), 195.9 (CPh), 160.9 (C=O), 136.6, 134.5, 130.9, 129.5, 129.1, 128.6, 128.2, 128.0 (C_6H_5), 46.3, 45.1, 44.7, 44.5 (NCH_2CH_3), 12.9, 12.4, 12.3, 12.2 (NCH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1940 (s, CO), 1755 (m, C=O).

[W(S$_2$CNEt$_2$)$_2$(PhC≡COC(O)CH$_3$)(CO)] (9a). A solution of **4a** (0.435 g, 0.58 mmol) in 50 mL of CH_2Cl_2 was cooled to −78 °C, and acetyl chloride (0.041 mL, 0.58 mmol) was added. The solution turned immediately from dull green to bright green. The solution was warmed to room temperature, and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel (12 cm × 2 cm) using CH_2Cl_2 as the eluant. The volume of the eluted solution was reduced to 25 mL, and an equal volume of hexane was added. Slow reduction of the volume in vacuo resulted in the formation of bright green microcrystals (0.24 g, 63.4%): mp 132–135 °C dec; ^{1}H NMR δ (CD_2Cl_2, 277 K) δ 7.52–7.56 (m, 2 H), 7.43 (t, J = 7.51 Hz, 2 H), and 7.25–7.33 (m, 1 H) (C_6H_5), 3.56–3.76 (m, 8 H, CH_2CH_3), 2.41 (s, 3 H, CH_3), 1.17–1.30 (m, 12 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K): δ 237.0 (J_{WC} = 138.5 Hz, CO), 218.2 (J_{WC} = 32.7 Hz, CCO), 211.5 and 200.1 (CS_2), 192.9 (CCO), 165.9 (C=O), 136.7, 130.2, 128.7, 128.0 (C_6H_5), 46.3, 45.0, 44.7, 44.4 (CH_2CH_3), 21.2 (CH_3), 1.17–1.30 (CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1925 (s, CO), 1695 (m, C=O).

[W(S$_2$CNEt$_2$)$_2$(CO)(PhCCOC(O)Ph)] (9b). A solution of **4a** (0.105 g, 0.139 mmol) in 5 mL of CH_2Cl_2 was cooled to −78 °C, and a slight excess of benzoyl chloride, dissolved in CH_2Cl_2, was added. After being warmed to room temperature, the solution was filtered through silica gel. Additional CH_2Cl_2 was used to wash the product out of the silica gel. The volume was reduced to 5 mL, and an equal volume of hexane was added. Slow reduction of the volume in vacuo resulted in the formation of bright green microcrystals (0.076 g, 74.5%): mp 121–123 °C dec; ^{1}H NMR (CD_2Cl_2, 277 K) δ 8.26–8.30 (m, 2 H), 7.66–7.73 (m, 1 H), 7.52–7.62 (m, 4 H), 7.41–7.48 (m, 2 H) (C_6H_5), 3.55–3.83 (m, 8 H, CH_2CH_3), 1.18–1.31 (m, 12 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K) δ 237.0 (J_{WC} = 135.9 Hz, CO), 218.1 (J_{WC} = 31.2 Hz, CCO), 211.6 (CS_2), 200.1 (CS_2), 193.2 (CCO), 161.6 (C=O), 136.9, 134.3, 130.8, 130.3, 129.0, 128.7, 128.6, 128.1 (C_6H_5), 46.4, 45.0, 44.7, 44.4 (CH_2CH_3), 12.9, 12.4, 12.2 (CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1920 (s, CO), 1745 (m, C=O). Anal. Calcd for $C_{26}H_{30}N_2O_3S_4W\cdot0.5CH_2Cl_2$: C, 41.17; H, 4.04. Found: C, 40.72; H, 4.22.

[W(S$_2$CNEt$_2$)$_2$(CO)(PhCCOC(O)CCHCH$_2$)] (9c). A solution of **4a** (0.85 g, 1.19 mmol) in CH_2Cl_2 (50 mL) was cooled to −78 °C. Acryloyl chloride (0.0096 mL, 1.19 mmol) was added. After it was warmed to room temperature, the solution was filtered through a layer of silica gel. The volume of the solution was reduced to 5 mL, and an equal volume of hexane was added. Slow reduction of the volume in vacuo resulted in the formation of bright green microcrystals, which were washed with pentane (2 × 5 mL) and dried in vacuo (0.55 g, 68.0%): mp 123–130 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.54–7.58 (m, 2 H), 7.43 (t, J = 7.41 Hz, 2 H), 7.28–7.33 (m, 1 H), (C_6H_5), 6.65 (dd, 1 H, ^3J_t = 17.26, ^2J = 1.31 Hz, CH_2), 6.42 (dd, 1 H, ^3J_c = 10.45 Hz, ^3J_t = 17.26, CH), 6.11 (dd, 1 H, ^3J_c = 10.45 Hz, ^2J = 1.22 Hz, CH_2), 3.59 (m, 8 H, CH_2CH_3), 1.18–1.29 (m, 12 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR δ 237.0 (J_{WC} = 138.4 Hz, CO), 218.1 (J_{WC} = 33.6 Hz, CCO), 211.6, 200.1 (CS_2), 193.2 (J_{WC} = 34.6 Hz, CCO), 161.0 (C=O), 136.7, 134.5, 130.3, 128.7 (C_6H_5), 128.1 (CH), 126.09 (CH_2), 46.3, 45.0, 44.7, 44.4 (CH_2CH_3), 12.8, 12.4, 12.3, 12.2 (CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1920 (s, CO), 1745 (m, C=O). Anal. Calcd for $C_{22}H_{28}N_2O_3S_4W\cdot0.5CH_2Cl_2$: C, 37.40; H, 4.04. Found: C, 36.71; H, 4.07.

[W(S$_2$CNEt$_2$)$_2$(CO)(PhCCOC(O)CHCHCH$_3$)] (9d). The procedure described for **9c** was followed for the reaction of the ketenyl complex **4a** (0.569 g, 0.74 mmol) with crotonyl chloride (0.071 mL, 0.74 mmol). The product was chromatographed on silica gel using CH_2Cl_2 as the eluant. Bright green microcrystals were obtained by cooling a saturated methylene chloride/hexane solution to −8 °C for 24 h (0.44 g, 85.3%): mp 123–130 °C dec; ^{1}H NMR (CD_2Cl_2, 273 K) δ 7.62 (m, J = 6.95 Hz, 2 H), 7.43 (t, J = 7.64 Hz, 2 H), (C_6H_5), 7.36–7.39 (m, 2 H, C_6H_5 and CHMe), 6.17 (d, ^3J = 15.62 Hz, CH), 3.56–3.86 (m, 8 H, CH_2CH_3), 1.20–1.31 (m, 12 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K) δ 237.0 (J_{WC} = 138.3 Hz, CO), 218.1 (J_{WC} = 32.3 Hz, CCO), 211.6, 200.2 (CS_2), 193.0 (J_{WC} = 35.7 Hz, CCO), 161.2 (C=O), 149.7 (CHMe), 137.0, 130.3, 128.6, 128.0 (C_6H_5), 120.9 ($CHCH_3$), 46.3 45.0, 44.7, 44.4 (CH_2CH_3), 18.7, 12.8, 12.4, 12.3, 12.2 (CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1920 (s, CO), 1738 (m, C=O). Anal. Calcd for $C_{23}H_{30}N_2O_3S_4W\cdot CH_2Cl_2$: C, 35.84; H, 4.06. Found: C, 36.98; H, 4.13.

[W(S$_2$CNEt$_2$)$_2$(CO)(PhCCOC(O)CHCHPh)] (9e). A solution of **4a** (0.52 g, 0.69 mmol) was cooled to −78 °C, and *trans*-cinnamoyl chloride (0.26 g, 0.75 mmol) was added. The solution was warmed to room temperature, and the solvent was removed. The product was purified by chromatography on silica gel (19 cm × 2 cm) using methylene chloride as the eluant. The volume of the solution was reduced to 10 mL, and hexane was added until a light cloudiness appeared. A few drops of methylene chloride were added so that the solution became clear once more. Slow cooling to −8 °C afforded bright crystals (0.42 g, 81.8%): mp 126–128 °C dec; ^{1}H NMR (CD_2Cl_2, 277 K) δ 7.96 (d, J = 16 Hz), 7.56–7.85 (m, 4 H), 7.41–7.47 (m, 5 H) (C_6H_5), 7.34–7.28 (m, 1 H, CHPh), 6.76 (d, J = 16 Hz, 1 H, CH), 3.54–3.80 (m, 8 H, CH_2CH_3), 1.71–1.73 (m, 12 H, CH_2CH_3); ^{13}C NMR (CD_2Cl_2, 273 K) δ 237.2 (CO), 218.2 (CCO), 211.6 (quintet, CS_2), 200.1 (quintet, CS_2), 193.3 (t, $^3J_{CH}$ = 5 Hz, CCO), 162.0 (dd, $^2J_{CH}$ = 22.5 Hz, $^3J_{CH}$ = 7.1 Hz, C=O), 148.3 (d, J_{CH} = 157.0 Hz, CH), 137.0 (s), 134.1 (s), 131.3 (d), 130.3 (d), 129.2 (d), 128.7 (d), 128.6 (d), 128.0 (d) (C_6H_5), 116.0 (d, J_{CH} = 164.4 Hz, CH), 46.3, 45.0, 44.7, 44.4 (CH_2CH_3), 12.8, 12.4, 12.3, 12.2 (CH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1920 (s, CO), 1733 (m, C=O). Anal. Calcd for $C_{28}H_{32}O_3N_2S_4W$: C, 44.45; H, 4.23. Found: C, 45.10; H, 4.35.

[W(Et$_2$NCS$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COC(O)CH$_3$)] (9f). Complex **4b** (1.01 g, 1.35 mmol) is dissolved in CH_2Cl_2 (25 mL), and the solution is cooled to −78 °C. $CH_3C(O)Br$ (0.150 mL, 2.02 mmol) is added dropwise, and the mossy green solution turns green as the solution is warmed to room temperature. Stirring is continued for an additional 15 min, followed by removal of solvent and column chromatography. The green band is eluted on silica gel (2 cm × 10 cm) using CH_2Cl_2/hexane (2:1, 200 mL) (yield 0.651 g, 67%). Recrystallization from CH_2Cl_2/hexane affords a green powder: mp 127–130 °C dec; ^{1}H NMR δ 7.65 (d, 2 H, J = 8.36 Hz, C_6H_4), 7.45 (d, 2 H, J = 8.38 Hz, C_6H_4), 3.84–3.54 (m, 8 H, NCH_2CH_3), 2.43 (s, 3 H, $C(O)CH_3$), 1.33 [s, 9 H, $C(CH_3)_3$], 1.57–1.12 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 236.9 (CO), 212.4, 201.1 (CS_2), 192.9 (CCO), 165.8 ($C(O)CH_3$), 151.7, 131.8, 130.5, 125.5 (C_6H_4), 45.9, 44.2 (NCH_2CH_3), 34.4 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 21.1 ($C(O)CH_3$), 12.4 (NCH_2CH_3) (the CCO carbon atom was not located); IR (CH_2Cl_2, cm^{-1}) 1925 (s, CO), 1779 (w, C=O). Anal. Calcd for $C_{25}H_{36}N_2S_4O_3W$: C, 41.44; H, 5.00. Found: C, 42.07; H, 3.81.

[W(S$_2$CNEt$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COC(O)CH$_2$Ph)] (9g). A solution of **4b** is dissolved in CH_2Cl_2 and cooled to −78 °C. A 15% excess of $ClC(O)CH_2Ph$ is added, and the solution changes from mossy green to bright green. The solution is warmed to room temperature, and stirring is continued for an additional 15 min. Solvent is removed in vacuo, and the residue is washed with

hexane. The product is purified by column chromatography using CH_2Cl_2/hexane (2:1), and recrystallization from CH_2Cl_2/hexane affords a green solid (29%): mp 120–124 °C dec; ^1H NMR δ 7.66–7.38 (m, 9 H, C_6H_4, C_6H_5), 4.07 (s, 2 H, CH_2Ph), 3.61–3.75 (m, 8 H, NCH_2CH_3), 1.36 [s, 9 H, $C(CH_3)_3$], 1.21–1.30 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 236.9 (J_{CW} = 137 Hz, CO), 220.1 (CCO), 212.2, 200.9 (Et_2NCS_2), 192.5 (CCO), 166.3 (C=O), 151.7, 132.9, 130.5, 129.5, 128.5, 127.2, 124.9 (C_6H_4, C_6H_5), 45.8, 44.5, 44.1, 43.8 (NCH_2CH_3), 41.2 (CH_2Ph), 34.6 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 12.3 (t, NCH_2CH_3); IR (THF, cm^{-1}) 1931 (s, CO), 1777 (w, C=O). Anal. Calcd for $C_{31}H_{40}N_2S_4O_3W$: C, 46.50; H, 5.03. Found: C, 46.05; H, 4.90.

[W(S$_2$CNEt$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COC(O)CMe$_3$)] (9h). A solution of **4b** is dissolved in CH_2Cl_2 and cooled to −78 °C. Addition of a 15% excess of $ClC(O)CMe_3$ causes the mossy green solution to immediately change to bright green. The reaction mixture is warmed to room temperature, and stirring is continued for an additional 15 min. Solvent is removed in vacuo and the residue washed with hexane (2 × 10 mL). The product is chromatographed on silica gel (2 cm × 10 cm) using CH_2Cl_2/hexane (1:1, 200 mL). Removal of solvent and recrystallization from CH_2Cl_2/hexane gives a green powder (87%): mp 120–125 °C; ^1H NMR δ 7.71 (d, 2 H, J = 8.47 Hz, C_6H_4), 7.45 (d, 2 H, J = 8.46 Hz, C_6H_4), 3.72–3.20 (m, 8 H, NCH_2CH_3), 1.44 (s, 9 H, $C(O)C(CH_3)_3$), 1.33 (s, 9 H, $C(CH_3)_3$), 1.18–1.31 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 236.5 (CO), 221.1 (CCO), 212.3, 201.0, (CS_2), 192.1 (CCO), 173.2 (C=O), 151.8, 132.8, 130.8, 125.0, (C_6H_4), 45.8, 44.5, 44.1, 43.8 (NCH_2CH_3), 39.6 ($C(O)C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 27.1 ($C(O)C(CH_3)_3$), 12.8, 12.3, 12.1 (NCH_2CH_3); IR (THF, cm^{-1}) 1924 (s, CO), 1760 (w, C=O). Anal. Calcd for $C_{28}H_{38}N_2O_3S_4W$: C, 44.09; H, 5.02. Found: C, 43.72; H, 5.60.

[W(S$_2$CNMe$_2$)$_2$(CO)(PhCCOC(O)CMe$_3$)] (9i). This product was prepared from **4c** (0.098 g, 0.135 mmol) and pivaloyl chloride (0.135 mmol) under the same conditions as described for complex **9c**. Green microcrystals were obtained by slow cooling of a saturated CH_2Cl_2/hexane solution to −78 °C. A second powdery crop was obtained from the supernatant (0.072 g, 76.2%): ^1H NMR (273 K) δ 7.71 (m, 2 H), 7.45 (t, 2 H), 7.33 (m, 1 H) (C_6H_5), 3.30 (s, 3 H), 3.23–3.24 (3 s, 9 H) (NCH_3), 1.44 (s, 9 H, CH_3); IR (CH_2Cl_2, cm^{-1}) 1925 (s, CO), 1770 (m, C=O). Anal. Calcd for $C_{20}H_{26}N_2S_4O_3W$: C, 36.70; H, 4.00. Found: C, 36.18; H, 4.05.

[W(C$_6$H$_7$N$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COC(O)CMe$_3$)] (10a). A solution of **2b** (1.04 g, 1.80 mmol) in CH_2Cl_2 (25 mL) is allowed to react with 2.2 equiv of 1-methylpyrrole-2-carboxaldimine in the presence of about 10 pellets of KOH. Upon complete reaction of the starting material, the solution is filtered away from excess KOH and cooled to −78 °C. A 15% excess of $ClC(O)CMe_3$ is added, and the solution is warmed to room temperature and stirred for an additional 15 min. Solvent is removed, and the product is purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1) (yield 0.74 g, 60%): mp 162 °C dec; ^1H NMR δ 8.18, 7.81, 7.48, 6.82, 6.55, 6.38, 6.12, 5.91 ($NC_4H_3CHNCH_3$), 7.45 (s, 2 H, C_6H_4), 7.23 (br, 2 H, C_6H_4), 3.25 (s, 6 H, NCH_3), 1.48 (s, 9 H, $C(O)C(CH_3)_3$), 1.38 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR δ 217.4 (CO), 173.8 ($C(O)C(CH_3)_3$), 160.5, 155.3, 151.4, 143.4, 141.7, 139.4, 136.0, 128.8, 125.1, 116.0, 114.6, 113.9, 112.8 ($NC_4H_3CHNCH_3$, C_6H_4), 50.8, 43.9 (NCH_3), 40.0 ($C(O)C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 27.2 ($C(O)C(CH_3)_3$) (the acetylenic carbon atoms were not located); IR (CH_2Cl_2, cm^{-1}) 1933 (s, CO), 1771 (w, C=O). Anal. Calcd for $C_{30}H_{36}N_4O_3W$: C, 52.64; H, 5.30. Found: C, 51.70; H, 5.19.

[W(C$_6$H$_7$N$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COC(O)CH$_2$Ph)] (10b). A solution of **2b** (1.86 g, 3.21 mmol) is dissolved in CH_2Cl_2 (25 mL), and 2.2 equiv of 1-methylpyrrole-2-carboxaldimine is added in the presence of about 10 pellets of KOH. Upon complete reaction of the starting material, the solution is filtered away from the unreacted KOH and cooled to −78 °C. A 15% excess of $ClC(O)CH_2Ph$ is added, and the solution is warmed to room temperature. Solvent is removed, the residue is washed with hexane, and the product is purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1) (yield 1.93 g, 83%): mp 147 °C; ^1H NMR δ 8.10, 7.74, 7.42, 7.39, 7.37, 7.14, 6.76, 6.49, 6.33, 6.07, 5.86 (17 H, $NC_4H_3CHNCH_3$, C_6H_4, C_6H_5), 3.99 (br, 2 H, CH_2Ph), 3.14 (s, 6 H, NCH_3), 1.32 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR δ 216.6 (CO), 167.0 (C=O), 150.5, 155.4, 151.4, 143.4, 141.7, 139.5, 136.1, 132.9, 129.5, 128.7, 127.5, 125.1, 116.0, 114.7, 112.9 ($NC_4H_3CHNCH_3$, C_6H_4, C_6H_5), 65.8 ($C(O)CH_2Ph$), 50.8, 44.0 (NCH_3), 34.6 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$) (the acetylenic carbon atoms were not located); IR (CH_2Cl_2, cm^{-1}) 1934 (s, CO), 1776 (w, C=O). Anal. Calcd for $C_{33}H_{38}O_3N_4W$: C, 55.17; H, 4.77. Found: C, 53.98; H. 4.57.

[W(C$_6$H$_7$N$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COC(O)C$_6$H$_4$-OMe-4)] (10c). Approximately 10 KOH pellets are added to a stirred solution of **2b** (1.05 g, 1.82 mmol) and 1-methylpyrrole-2-carboxaldimine (0.434 g, 4.02 mmol) in CH_2Cl_2 (25 mL). After 1.5 h the brown-green solution is decanted away from excess KOH and cooled to −78 °C. $ClC(O)C_6H_4$-OMe-4 (0.30 mL, 2.18 mmol) is added, and a green color develops as the solution is warmed to room temperature. Stirring is continued for an additional 15 min. Solvent is removed in vacuo, and the product is purified by column chromatography on silica gel (2 cm × 10 cm) with CH_2Cl_2/hexane (1:1, 200 mL) as eluant. Recrystallization from CH_2Cl_2/hexane affords a green powder (0.96 g, 73%): mp 141 °C; ^1H NMR δ 8.15, 7.78, 7.47, 6.79, 6.51, 6.36, 6.09, 5.89 (8 H, $NC_4H_3CHNCH_3$), 7.43 (d, 2 H, C_6H_4), 7.23 (br, 2 H, C_6H_4), 3.90 (s, 3 H, OCH_3), 3.26 (s, 3 H, NCH_3), 3.18 (br, 3 H, NCH_3), 1.33 (s, 9 H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR δ 230.9 (br, CO), 215.6 (CCO), 188.2 (br, CCO), 164.2 (C=O), 161.8, 160.5, 155.3, 151.1, 143.5, 141.7, 139.5, 136.0, 132.8, 128.6, 125.0, 120.8, 116.0, 114.7, 114.0, 112.8 ($NC_4H_3CHNCH_3$, C_6H_4), 55.5 (OCH_3), 50.9, 44.0 (NCH_3), 34.6 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$); IR (CH_2Cl_2, cm^{-1}) 1933 (s, CO), 1752 (w, C=O). Anal. Calcd for $C_{33}H_{34}N_4O_4W$: C, 53.96; H, 4.67. Found: C, 53.91; H, 4.35.

Reaction of [W(S$_2$CNEt$_2$)$_2$(4-Me$_3$C-C$_6$H$_4$C≡COC(O)-CH$_3$)(CO)] (9f) with Me$_2$NH. Complex **9f** (0.152 g, 0.211 mmol) is dissolved in CH_2Cl_2 (15 mL), and Me_2NH(g) is bubbled through the solution for about 1 min. During this time the deep green reaction solution turns lighter green (IR 2015 w, 1920 m, 1847 s, 1640 s). The reaction mixture is stirred for about 15 min. Then, the solvent is removed in vacuo and the residue is redissolved in CH_2Cl_2. The solution is cooled to −78 °C, and a 15% excess of $ClC(O)CMe_3$ is added. The mixture is warmed to room temperature, and the product is purified by column chromatography on silica gel using CH_2Cl_2/hexane (2:1). ^1H NMR spectroscopy verifies the presence of complex **9h** and [W(Et_2NCS_2)-(Et_2NCS)(CO)($SCHC_6H_4$-CMe_3-4)] in about equal amounts. A small sample of [W(Et_2NCS_2)(Et_2NCS)(CO)($SCHC_6H_4$-CMe_3-4)] was purified by repeated column chromatography: ^1H NMR δ 7.29 (d, 2 H, C_6H_4), 7.09 (d, 2 H, C_6H_4), 5.40 (s, 1 H, SCHR), 4.15–3.85 (m, 8 H, NCH_2), 1.25–1.10 (m, 12 H, NCH_2CH_3), 1.30 (s, 9 H, $C(CH_3)_3$).

Reaction of [W(S$_2$CNEt$_2$)$_2$(4-Me$_3$C-C$_6$H$_4$C≡COC(O)-CH$_2$Ph)(CO)] (9g) with Me$_2$NH. Complex **9g** (0.064 g, 0.080 mmol) is dissolved in CH_2Cl_2 (10 mL), and Me_2NH(g) is bubbled through until a mossy green color develops (~1 min). The flask is sealed under an atmosphere of dimethylamine, and stirring is continued for 5 min. IR spectroscopy shows a 90% conversion to the ynolate derivative. Solvent and excess Me_2NH are removed, and the solution is redissolved in CH_2Cl_2 and cooled to 0 °C. $ClC(O)CMe_3$ (1.2 equiv) is added, and the solution turns green upon warming. The product is found by IR measurements (1921, 1767 cm^{-1}) to be {W(Et_2NCS_2)$_2$(CO)[4-Me_3C-C_6H_4C≡COC(O)^{t}Bu]} (**9h**).

Reaction of [W(S$_2$CNEt$_2$)$_2$(CO)(4-Me$_3$C-C$_6$H$_4$C≡COCH$_3$)] (7) with Me$_2$NH. A small amount of complex **7** is dissolved in CH_2Cl_2 (15 mL), and Me_2NH(g) is bubbled through the solution for ~2 min. The flask is sealed under an atmosphere of dimethylamine. The IR spectrum of the solution showed little change after 14 h.

Reaction of [W(S$_2$CNEt$_2$)$_2$(4-Me$_3$C-C$_6$H$_4$C≡COC(O)-CH$_2$Ph)(CO)] (9g) with NaN[(CH$_3$)$_3$Si]$_2$. Complex **9g** (0.050 g, 0.062 mmol) is dissolved in THF (10 mL), and sodium bis-(trimethylsilyl)amide (0.031 g, 0.169 mmol) is added. The solution changes from green to red-brown. Stirring is continued for 5 min, and IR spectroscopy shows the formation of ketenyl complex **4b** (sodium salt) (1823, 1665 cm^{-1}). The solvent is removed, and the product is redissolved in CH_2Cl_2 (10 mL). After it is cooled to 0 °C, excess $ClC(O)CMe_3$ is added to the solution. The color turns to bright green. Formation of [W(Et_2NCS_2)$_2$(CO){4-$Me_3CC_6H_4C$≡COC(O)CMe_3}] (**9h**; 1924, 1770 cm^{-1}; 50%) was confirmed by IR measurements.

Reaction of $[W(C_6H_7N_2)_2(CO)(4\text{-}Me_3C\text{-}C_6H_4C{\equiv}COC(O)CH_2Ph)]$ (10b) with $NaN[Si(CH_3)_3]_2$. $NaN[Si(CH_3)_3]_2$ (0.029 g, 0.156 mmol) is added to a solution of **10b** (0.066 g, 0.092 mmol) in THF (10 mL). The solution immediately changes from green to brown-orange, and stirring is continued for 10 min. This product is recognized by IR spectroscopy as $[W(C_6H_7N_2)_2(CO)(4\text{-}Me_3CC_6H_4CCO)]^-$ (1821 s, 1660 m cm^{-1}). The reaction mixture is then cooled to −78 °C, and $ClC(O)CMe_3$ (0.017 mL, 0.138 mmol) is added. The solution is warmed to room temperature, and stirring is continued for 10 min. Solvent is removed in vacuo, and the residue is washed with hexane (2 × 10 mL). IR and ^1H NMR spectroscopy confirm the formation of $[W(C_6H_7N_2)_2(CO)(4\text{-}Me_3C\text{-}C_6H_4C{\equiv}COC(O)CMe_3)]$ (**10a**). The product is purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1) (yield 0.033 g, 73%).

Reaction of $[W(C_6H_7N_2)_2(CO)(4\text{-}Me_3C\text{-}C_6H_4C{\equiv}COC(O)C_6H_4\text{-}OMe\text{-}4)]$ (10c) with $NaN[Si(CH_3)_3]_2$. $NaN[Si(CH_3)_3]_2$ (0.020 g, 0.111 mmol) is added to a solution of **10c** (0.046 g, 0.063 mmol) in THF (10 mL). After several minutes the reaction solution turns green-brown, but the IR spectrum shows little change, except for the presence of a small peak at 1816 cm^{-1}. With time the absorption at 1816 cm^{-1} increases in intensity, but after 18 h the reaction is still about only 60% complete.

Reaction of $[W(S_2CNEt_2)_2(4\text{-}Me_3C\text{-}C_6H_4C{\equiv}COC(O)CMe_3)(CO)]$ (9h) with $NaN[Si(CH_3)_3]_2$. Sodium bis(trimethylsilyl)amide (0.020 g, 0.106 mmol) is added to a solution of **9h** (0.030 g, 0.040 mmol) in THF. After 45 min, the reaction was judged to be complete by IR spectroscopy. IR absorptions at 1817 and 1632 cm^{-1} indicate the formation of ketenyl complex **4b**. Addition of excess $ClC(O)CMe_3$ results in the re-formation of the starting material (IR 1929, 1767 cm^{-1}).

Reaction of $[W(C_6H_7N_2)_2(CO)(4\text{-}Me_3C\text{-}C_6H_4C{\equiv}COC(O)CMe_3)]$ (10a) with $NaN[Si(CH_3)_3]_2$. A solution of **10a** (0.077 g, 0.123 mmol) is dissolved in THF (15 mL), and to this is added $NaN[(CH_3)_3Si]_2$ (0.045 g, 0.246 mmol). Within 5 min the solution changes from green to brown-orange. Stirring is continued for an additional 15 min. IR absorptions at 1818 and 1670 cm^{-1} indicate the formation of the η^2-ketenyl complex **5**. Addition of excess $ClC(O)CMe_3$ results in re-formation of the starting material (IR 1938, 1776 cm^{-1}).

$[W(S_2CNEt_2)_2(CO)(4\text{-}Me_3C\text{-}C_6H_4C{\equiv}CNMe_2)]$ (11). Complex **9h** (0.257 g, 0.337 mmol) is dissolved in CH_2Cl_2 (20 mL). Me_2NH(g) is bubbled through, and immediately a lighter green color develops. The flask is sealed under an atmosphere of Me_2NH(g), and stirring is continued for 10 min. Solvent is removed in vacuo, and the product is purified by chromatography on silica gel (2 cm × 15 cm) using CH_2Cl_2/hexane (1:1; 150 mL). The product is recrystallized from CH_2Cl_2/hexane at 0 °C to yield a green powder (0.196 g, 82%): mp 147 °C dec; ^1H NMR δ 7.35 (d, 2 H, J = 8.38 Hz, C_6H_4), 7.11 (d, 2 H, J = 8.39 Hz, C_6H_4), 3.67–3.48 (m, 14 H, NCH_2CH_3, $N(CH_3)_2$), 1.32 (s, 9 H, $C(CH_3)_3$), 1.29–1.20 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 246.7 (CO), 211.9 (*C*CN), 203.9 (*C*CN), 200.5, 199.4 (S_2CNEt_2), 149.0, 142.0, 126.7, 124.4 (C_6H_4), 45.7, 45.4, 44.8, 44.6, 44.3 (NCH_2CH_3, $N(CH_3)_2$), 34.4 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 12.4 (NCH_2CH_3); IR (CH_2Cl_2, cm^{-1}) 1901 (s, CO). Anal. Calcd for $C_{25}H_{39}N_3OS_4W$: C, 42.49; H, 5.52; N, 5.95. Found: C, 40.81; H, 5.72; N, 5.90.

$[W(S_2CNEt_2)(CO)(SC(NEt_2)SCCC_6H_4\text{-}CMe_3\text{-}4)(PMe_3)][O_2CCMe_3]$ (12a). PMe_3 (0.014 mL, 1.37 mmol) is added dropwise to a stirred solution of **9h** (0.875 g, 1.15 mmol) in CH_2Cl_2 (20 mL). The solution changes from bright green to red within 15 min. The solvent is removed in vacuo, and the residue is washed with hexane (2 × 5 mL). Recrystallization from Et_2O/hexane affords a red-orange powder (0.720 g, 75%): mp 95–98 °C dec; ^1H NMR δ 7.45 (d, 2 H, J = 8.36 Hz, C_6H_4), 7.29 (d, 2 H, J = 8.36 Hz, C_6H_4), 3.88–3.00 (m, 8 H, NCH_2CH_3), 1.39 (d, J = 10.0 Hz, $P(CH_3)_3$), 1.35 (s, 9 H, $C(CH_3)_3$), 1.12 (s, 9 H, $OC(O)C(CH_3)_3$), 1.38–1.00 (m, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 224.7 (CO), 215.5 (SCSCC), 207.8 (*C*CS), 202.2, 191.7 (*C*CS and Et_2NCS_2), 182.9 [$O_2CC(CH_3)_3$], 151.7, 135.7, 128.0, 124.9 (C_6H_4), 49.4, 49.0, 45.1, 44.2 (NCH_2CH_3), 39.3 ($O_2CC(CH_3)_3$), 34.6 ($C(CH_3)_3$), 31.4 (br, $C(CH_3)_3$), 27.3 (br, $O_2CC(CH_3)_3$), 16.3 (br, $P(CH_3)_3$), 12.1 (br, NCH_2CH_3); ^{31}P NMR δ −20.7 (J_{PC} = 309 Hz); IR (CH_2Cl_2, cm^{-1}) 1955 (s, CO), 1634 (m, O_2C). Anal. Calcd for $C_{31}H_{42}O_3S_4N_2PW$: C, 44.66; H, 5.08. Found: C, 42.95; H, 6.00. The elemental analysis came out unsatisfactorily; however, little spectroscopic evidence for impurities was found in the ^1H and ^{13}C NMR spectra.

$[W(S_2CNEt_2)(CO)(SC(NEt_2)SCCC_6H_4\text{-}CMe_3\text{-}4)(PEt_3)][O_2CCMe_3]$ (12b). The triethylphosphine analogue was prepared by following the procedure described for **12a**: ^1H NMR δ 7.40 (d, 2 H, J = 7.51 Hz, C_6H_4), 7.24 (d, 2 H, J = 8.14 Hz, C_6H_4), 3.90–2.72 (m, 8 H, NCH_2CH_3), 1.75–0.73 (m, 45 H, $P(CH_3)_3$, $C(CH_3)_3$), $O_2CC(CH_3)_3$), NCH_2CH_3); $^{13}C\{^1H\}$ NMR δ 225.3 (CO), 217.1 (SCSCC), 208.4 (*C*CS), 202.8 (*C*CS), 191.9 (Et_2NCS_2), 182.6 [$O_2CC(CH_3)_3$], 151.1, 135.8, 128.1, 124.8 (C_6H_4), 49.4, 49.0, 44.9, 44.3 (NCH_2CH_3), 39.3 ($O_2CC(CH_3)_3$), 34.6 ($C(CH_3)_3$, 31.1 ($C(CH_3)_3$), 27.5 ($O_2CC(CH_3)_3$), 17.8 (m, $P(CH_2CH_3)_3$), 13.5, 12.4, 12.1, 11.2 (NCH_2CH_3), 7.5 ($P(CH_2CH_3)_3$).

$[W(S_2CNEt_2)(CO)(4\text{-}Me_3C\text{-}C_6H_4CCO)(PMe_3)_2]$ (13). A solution of **4b** (0.923 g, 1.23 mmol) is dissolved in CH_2Cl_2 (25 mL), and an excess of PMe_3 is added dropwise. Stirring is continued for 15 min, and the solution changes from green to purple. The solvent is removed in vacuo. The residue is washed with hexane (2 × 5 mL) and redissolved in THF and the solution filtered over a pad of Celite. Recrystallization from THF/hexane affords a purple microcrystalline solid (0.534 g, 78%): mp 143 °C; ^1H NMR δ 7.66 (d, 2 H, J = 8.31 Hz, C_6H_4), 7.38 (d, 2 H, J = 8.32 Hz, C_6H_4), 3.81–3.74 (q, 2 H, NCH_2CH_3), 3.67–3.60 (q, 2 H, NCH_2CH_3), 1.31–1.17 (m, 33 H, $P(CH_3)_3$, $C(CH_3)_3$, NCH_2CH_3); ^{13}C NMR δ 223.7 (t, J_{CP} = 6.5 Hz, J_{CW} = 148.0 Hz, CO), 207.0, 206.0 (CCO and CS_2), 204.6 (t, *C*CO), 149.7, 139.1, 126.3, 125.7 (C_6H_4), 44.3, 44.0 (NCH_2CH_3), 34.7 (($CH_3)_3$), 31.1 ($C(CH_3)_3$), 16.0 (t, J_{CP} = 30.18 Hz, $P(CH_3)_3$), 12.5, 12.3 (NCH_2CH_3); ^{31}P NMR δ −20.7 (J_{PW} = 266 Hz, $P(CH_3)_3$); IR (CH_2Cl_2, cm^{-1}) 1871 (s, CO), 1700 (w, CCO). Anal. Calcd for $C_{24}H_{37}S_2O_2P_2NW$: C, 42.30; H, 5.47. Found: C, 42.19; H, 6.16.

Reaction of $[Mo(S_2CNEt_2)_2(PhCCOCOPh)(CO)]$ (8) with Carbon Monoxide. A green solution of **8** (0.137 g) in CD_2Cl_2 (2 mL) was placed under 1 atm of CO gas and stirred for 30 min to give a yellow-brown solution. The product, formulated as **14**, was extremely air-sensitive, and both solutions and the solid turned red upon exposure to air: IR (CD_2Cl_2, cm^{-1}) 1946 (s, CO) 1775, 1745 (m, C=O); ^{13}C NMR (CD_2Cl_2, 273 K) δ 237.2 (s) 211.7 (t, $^3J_{CH}$ = 4.8 Hz), 206.6 (pentet, $^3J_{CH}$ = 5.1 Hz), 202.0 (s), 198.1 (pentet, $^3J_{CH}$ = 5.7 Hz), 167.7 (s), 162.0 (t, $^3J_{CH}$ = 4.3 Hz), 136.4 (t, $^2J_{CH}$ = 7.6 Hz), 134.6 (dt, $^1J_{CH}$ = 161.9 Hz, $^2J_{CH}$ = 7.5 Hz), 130.9 (dt, $^1J_{CH}$ = 163.0 Hz, $^2J_{CH}$ = 6.6 Hz), 130.5 (dt, $^1J_{CH}$ = 161.3 Hz, $^2J_{CH}$ = 7.6 Hz), 129.6, 129.6 (dt, $^1J_{CH}$ = 163.2 Hz, $^2J_{CH}$ = 6.5 Hz), 128.9 (dd, $^1J_{CH}$ = 162.8 Hz, $^2J_{CH}$ = 7.7 Hz, 2 *o*-C) 128.5 (t, $^2J_{CH}$ = 7.61 Hz), 46.4 (tq, $^1J_{CH}$ = 139.8 Hz, $^2J_{CH}$ = 4.2 Hz, 1 CH_2), 44.9 (tq, $^1J_{CH}$ = 139.3 Hz, $^2J_{CH}$ = 2.9 Hz, 1 CH_2), 44.6 (tq, $^1J_{CH}$ = 139.3 Hz, $^2J_{CH}$ = 3.9 Hz, 2 CH_2), 12.8 (qt, $^1J_{CH}$ = 128.1 Hz, $^2J_{CH}$ = 3.3 Hz), 12.4 (qt, $^1J_{CH}$ = 127.9 Hz, $^2J_{CH}$ = 3.4 Hz), 12.3 (qt, $^1J_{CH}$ = 127.8 Hz, $^2J_{CH}$ = 3.8 Hz), 12.1 (qt, $^1J_{CH}$ = 128.1 Hz, $^2J_{CH}$ = 3.3 Hz).

Reaction of $[W(S_2CNEt_2)_2(PhCCOCOCHCH_2)(CO)]$ (9c) with Carbon Monoxide. A green solution of $[W(S_2CNEt_2)_2(PhCCOCOCHCH_2)(CO)]$ (0.50 g, 0.73 mmol) in 1:1 CD_2Cl_2/CH_2Cl_2 (4 mL) was placed under 1 atm of CO gas and stirred for 4 h to give a brown solution. The solvent was removed under reduced pressure, and the product was chromatographed on silica gel at ambient temperature, using methylene chloride as the eluent. An orange band remained at the top of the column. The volume of the mossy green eluate was reduced to 5 mL, and hexane (5 mL) was added. The volume was reduced until the solution became turbid. This solution was slowly cooled to −8 °C over 1 h to give a green oil. The supernatant was removed and slowly cooled to −8 °C to give a mossy green, powdery product (0.279 g). This product, formulated as **15**, is extremely air-sensitive, and both solutions and the solid turn brown upon exposure to air: ^1H NMR (CD_2Cl_2) δ 7.74 (d, J = 6.86 Hz, 2 H), 7.53 (t, J = 6.85 Hz, 2 H), 7.45 (d, J = 6.53 Hz, 1 H), 6.58 (dd, J_t = 16.93 Hz, J_g = 1.16 Hz, 1 H), 6.20 (dd, J_c = 10.46 Hz, J_t = 17.04 Hz, 1 H), 6.06 (d, J_c = 9.91 Hz, J_g not resolved, 1 H), 3.57–3.89 (m, 8 H), {1.35 (t, J = 7.11 Hz), 1.20–1.28 (m); 12 H} (the ^1H NMR spectrum (CD_2Cl_2) of the green oil was identical with that of the powdery product, except that the former contained a small amount of hexane and stopcock grease); ^{13}C NMR (CD_2Cl_2, 273 K) δ 236.7 (s with ^{183}W satellites, J_{WC} = 40.8 Hz), 199.5 (pentet, $^3J_{CH}$ = 5.2 Hz), 169.9 (s), 161.2 (ddd, $^2J_{CH}$ = 15.0 Hz, $^3J_{CH}$ = 7.6 Hz, $^3J_{CH}$ = 5.4 Hz), 137.4 (t, $^2J_{CH}$ = 8.0 Hz), 135.1 (ddd, $^1J_{CH}$ = 157.7, 159.1

Hz, $^2J_{CH}$ = 2.5 Hz), 130.5 (dt, $^1J_{CH}$ = 161.5 Hz, $^2J_{CH}$ = 7.1 Hz), 130.1 (dt, $^1J_{CH}$ = 162.6 Hz, $^2J_{CH}$ = 6.7 Hz), 128.9 (dd, $^1J_{CH}$ = 162.8 Hz, $^2J_{CH}$ = 7.53 Hz), 127.5 (d, $^1J_{CH}$ = 164.0 Hz), 46.5 (tq, $^1J_{CH}$ = 139.5 Hz, $^2J_{CH}$ = 3.6 Hz), 45.0 (tq, $^1J_{CH}$ = 140.3 Hz, $^2J_{CH}$ = 3.2 Hz), 44.6 (tq, $^1J_{CH}$ = 139.4 Hz, $^2J_{CH}$ = 3.9 Hz), 44.6 (tq, $^1J_{CH}$ = 139.5 Hz, $^2J_{CH}$ = 4.2 Hz), 12.8 (qt, $^1J_{CH}$ = 128.3 Hz, $^2J_{CH}$ = 2.8 Hz), 12.4 (qt, $^1J_{CH}$ = 128.0 Hz, $^2J_{CH}$ = 2.9 Hz), 12.4 (qt, $^1J_{CH}$ = 127.8 Hz, $^2J_{CH}$ = 2.7 Hz), 12.2 (qt, $^1J_{CH}$ = 128.0 Hz, $^2J_{CH}$ = 3.1 Hz).

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