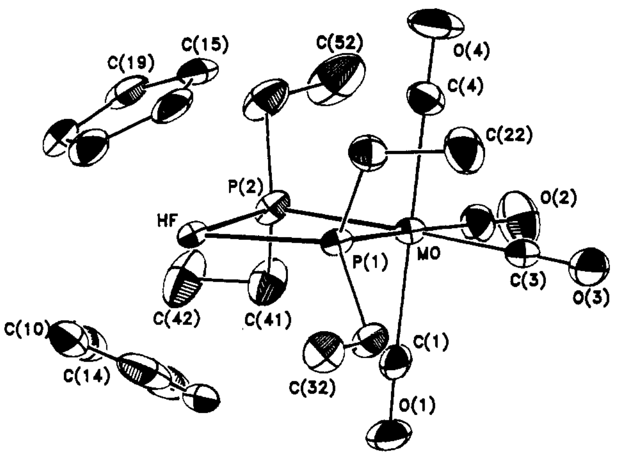

Figure 1. Perspective drawing of $Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4$ (**4**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

the range found[22] (94–97°) for d^0 Cp_2MX_2 complexes and may be compared with P–Hf–P = 98.6 (1)° in $Cp_2Hf(PEt_2)_2$. The bulky Cp_2Hf vertex leads to large Hf–P–C angles to the PEt_2 bridges (ca. 122°). The intermediate[19] Hf–P–Mo angles of 83° result in a Hf···Mo separation of 3.400 (1) Å (cf. Mo–Mo = 3.057 (6) Å in $[Mo(CO)_4(\mu\text{-}PEt_2)]_2$). The influence of the bridge geometry on the observed metal–metal distance is exemplified by comparing the structure of **4** with that of $Cp_2Zr(\mu\text{-}PPh_2)_2W(CO)_4$.[23] As the covalent radii of Zr and Mo are very similar to those of Hf and W, the shorter metal–metal distance (Zr–W = 3.289 (1) Å) observed in the latter case must result primarily from substituting the PEt_2 with bulkier PPh_2 bridges.

Conclusion

The "metal-containing bis(phosphine)" $Cp_2Hf(PEt_2)_2$ binds metal carbonyl fragments to form new heterobimetallic complexes. The spectroscopic and X-ray structural results both suggest that these complexes contain adjacent 16e Hf(IV) and 18e M(0) centers. Reactivity studies on these and related electronically unsaturated heterobimetallics are presently under way.

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Registry No. **1**, 86013-26-5; **2**, 95552-78-6; **3**, 95589-49-4; **4**, 95552-79-7; **5**, 95552-80-0; $Fe(CO)_3(DEPE)$, 95552-81-1; Cp_2HfCl_2, 12116-66-4; $LiPEt_2$, 19093-80-2; $Ni(CO)_4$, 13463-39-3; $Fe_2(CO)_9$, 15321-51-4; $Mo(CO)_4(\eta^4\text{-norbornadiene})$, 12146-37-1; $Fe(CO)_3(\eta^4\text{-benzylideneacetone})$, 38333-35-6.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters, idealized hydrogen atom positions, and observed and calculated structure amplitudes (24 pages). Ordering information is given on any current masthead page.

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Reactions of Cyclopropenes with Molybdenum(II) and Tungsten(II) Carbonyl Complexes: Formation of Coordinated Vinylketene

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Cyclopropene reacts with $Mo(CO)_2(S_2CNR_2)_2$, $Mo(CO)_2(S_2PR_2)_2$, $W(CO)_3(S_2CNR_2)_2$, and $W(CO)_2(PPh_3)(S_2CNR_2)_2$ to yield new complexes that are best formulated as $M(CO)(C_3H_4CO)(BB)_2$ (M = Mo, W). Analogous products form when 1-methylcyclopropene reacts with $W(CO)_3(S_2CNR_2)_2$. Infrared, ^1H NMR, and ^{13}C NMR spectroscopic techniques have been used to probe the mode of attachment of the newly formed vinylketene ligand, C_2H_3RCO (R = H, CH_3), which evidently results from cyclopropene ring opening and CO insertion.

Introduction

For several years we have been interested in the ability of low-valent molybdenum and tungsten dithiolate complexes to bind small molecules. The complexes $Mo(CO)_2(BB)_2$ (BB = S_2CNR_2, S_2PR_2) and $W(CO)_2L(S_2CNR_2)_2$ (L = CO, PPh_3) have been shown to react with acetylenes (including C_2H_2) to yield species of the form $M(CO)(RC_2R)(BB)_2$ (M = Mo, W)[1-4] and $M(RC_2R)_2(BB)_2$ (M = Mo).[2,5,6] NMR, structural, and reactivity data for these systems have been interpreted in terms of the alkynes behaving as formal four- and three-electron donors, respectively; a molecular orbital description[7] of these complexes has been published. Olefins either do not react with the above starting materials or form only weakly associated adducts that readily dissociate.[8]

Cyclopropene has properties intermediate between those of alkenes and alkynes,[9] and with this in mind, we have explored its

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reactivity with $Mo(CO)_2(BB)_2$ compounds. In spite of the abundance of π-bound olefins[10] and acetylenes[11] extant in the organometallic literature, very few well-characterized π-cyclopropene-metal complexes have been reported.[12,13] In addition, cyclopropene has been shown to be an alternative substrate of the molybdenum enzyme nitrogenase, where it is reduced to a 2:1 mixture of propene/cyclopropane both in vitro[14] and in vivo.[15] The formation of this characteristic, reproducible ratio of products has already been used to test the postulated similarity to nitrogenase of the BH_4^--FeMoco[16] and BH_4^--molybdo thiol systems.[17] The potential utility of cyclopropene reduction as a chemical probe of nitrogenase and its models makes its behavior as a ligand important. In this work we describe the reactions of cyclopropenes with several Mo(II) and W(II) dithiolate complexes, present spectral data on the new compounds, and discuss the net reaction of free cyclopropene and coordinated CO to form a coordinated vinylketene ligand.

Experimental Section

Materials and Methods. All manipulations were performed under a dry oxygen-free nitrogen or argon atmosphere by using standard Schlenk techniques unless otherwise noted. Cyclopropene,[9] 1-methylcyclopropene,[19] $Mo(CO)_2(S_2CNEt_2)_2$,[18] $Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$,[18] $W(CO)_3(S_2CNR_2)_2$,[20] and $W(CO)_2(PPh_3)(S_2CNR_2)_2$[20] were prepared as previously reported. Preparation of $W(CO)_2(PPh_3)(S_2CNPh_2)_2$ has not been previously described, but utilization of $HNPh_2$ as the amine for reaction with CS_2 in the presence of base leads to the $^-S_2CNPh_2$ ligand, which displays chemistry similar to that of dialkyldithiocarbamates. Infrared spectra were recorded on a Beckman IR-4250 or a Beckman IR-20A and calibrated with a polystyrene standard. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer at 100 MHz and on a WM Bruker 250 spectrometer at 250 MHz. ^{13}C NMR spectra (62.89 MHz) were recorded on a WM Bruker 250 spectrometer. All chemical shifts are reported as ppm downfield of Me_4Si.

$M(CO)(C_3H_4CO)(BB)_2$ Preparation. Cyclopropene (~0.5 mmol) was transferred by Toepler pumping at −78 °C to a calibrated manometric vacuum system where the amount could be accurately determined. An equivalent amount of $W(CO)_2L(BB)_2$ or $Mo(CO)_2(BB)_2$ was then dissolved in CH_2Cl_2, the solution degassed and frozen at 77 K, and the cyclopropene condensed into the reaction vessel. The reaction mixtures were warmed first to 195 K and then to room temperature. After the reaction was complete, the reaction mixture was again frozen at 77 K, the amount of evolved CO was determined, and then the solution was evaporated to dryness under vacuum. Trituration of the residue with Et_2O (M = W) or hexane (M = Mo) yielded the products as orange solids, which were isolated by filtration, washed with Et_2O, and dried in vacuo. Reaction times appear to be much shorter for the molybdenum (~5 min) than for tungsten (~1 h), although no quantitative studies on the reactions have been carried out. Anal. Calcd for $W(CO)(C_3H_4CO)(S_2CNMe_2)_2$ ($C_{11}H_{16}N_2O_2S_4W$): C, 25.4; H, 3.07; N, 5.38. Found: C, 25.5; H, 3.01; N, 5.19. Calcd for $W(CO)(C_3H_4CO)(S_2CNEt_2)_2$ ($C_{15}H_{24}N_2O_2S_4W$): C, 31.3; H, 4.16; N, 4.86. Found: C, 31.1; H, 4.18; N, 4.74. Calcd for $W(CO)(C_3H_4CO)(S_2CNPh_2)_2$ ($C_{31}H_{24}N_2O_2S_4W$): C, 48.4; H, 3.13; N, 3.65. Found: C, 49.8; H, 3.24; N, 3.30. Due to the high thermal and/or air sensitivity of the Mo complexes, satisfactory elemental analytical data could not be collected.

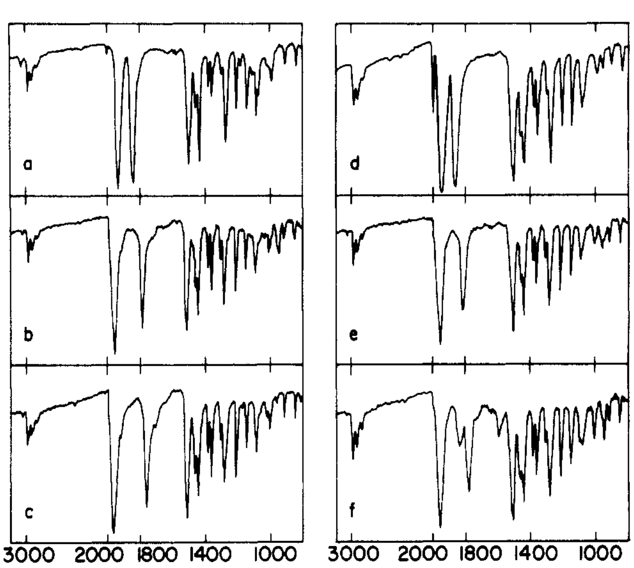

Figure 1. Infrared spectra of complexes of KBr pellets: (a) $W(CO)_2(PPh_3)(S_2CNEt_2)_2$; (b) $W(CO)(C_3H_4CO)(S_2CNEt_2)_2$; (c) $W(CO)(C_4H_6CO)$; (d) $Mo(CO)_2(S_2CNEt_2)_2$; (e) $Mo(CO)(C_3H_4CO)(S_2CNEt_2)_2$; (f) product from the $W(CO)_3(S_2CNEt_2)_2$ + C_3H_4 reaction.

$W(CO)(C_3H_3CH_3CO)(S_2CNR_2)_2$ Preparation. A stream of dry N_2 was used to sweep an excess of 1-methylcyclopropene from the refluxing THF solution in which it was generated through a wash bottle containing 0.5 M H_2SO_4 (to remove NH_3) and then through a $CaSO_4$ drying tube before passing it into a CH_2Cl_2 solution of $W(CO)_3(S_2CNR_2)_2$ chilled in a dry ice/2-propanol bath. The THF reflux is continued for 4–6 h to promote complete reaction of the 3-chloro-2-methylpropene with sodium amide. The CH_2Cl_2 solution of metal reagent and 1-methylcyclopropene was then allowed to warm to 0 °C and was stirred for a few hours. Infrared solution spectra allow one to monitor conversion to the vinylketene complex at this point. The product was purified by Florisil chromatography using a mixed CH_2Cl_2/Et_2O eluant. Yields based on $W(CO)_3(S_2CNR_2)_2$ were greater than 50% after purification. The dialkyldithiocarbamates (R = Me, Et, *i*-Pr) were isolated as bright orange powders, and the pyrrole complex derived from $S_2CNC_4H_4$ was cherry red (the term pyrroledithiocarbamate is inappropriate because it includes the nitrogen twice; pyrrole-*N*-carbodithioate is preferred for naming the $S_2CNC_4H_4$ ligand).

Oxidation of $W(CO)(C_4H_6CO)(S_2CNEt_2)_2$. The complex (0.0694 g; 0.1176 mmol) was oxidized in vacuo by a solution of excess Br_2 (0.10 mL; 1.95 mmol) in CH_2Cl_2 (25 mL) that had previously been rigorously degassed. After 4 h, the reaction mixture was frozen at 77 K and the evolved, noncondensable gas was Toepler pumped to a calibrated manometric system where the amount was accurately determined. The yield was 0.0995 mmol, which corresponded to 0.85 mol of CO/mol of complex.

Results and Discussion

Syntheses. Reactions of cyclopropene with the complexes $Mo(CO)_2(BB)_2$ (BB = $S_2P(i\text{-}Pr)_2$, S_2CNEt_2) proceed smoothly in CH_2Cl_2 solution at room temperature. No CO is evolved, and solid products can be isolated from the reaction mixtures after evaporation of the solvent and trituration of the residues with hexane. As shown in Figure 1, the infrared spectra of these solids contain intense bands at ~1950 and 1820 cm^{-1} (intensity ratio ~3:2, respectively), which are assigned to carbonyl stretching frequencies, and a weak band at ~3050 cm^{-1}, indicative of the presence of C–H groups not present in the starting materials. These spectral data, along with the fact that no CO is evolved in the reaction, are consistent with the solid products having the empirical formula $Mo(CO)_2(C_3H_4)(BB)_2$ (BB = S_2CNEt_2, $S_2P(i\text{-}Pr)_2$). Unfortunately, the high sensitivity of these solids to aerial

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Table I. Infrared ν(CO) Vibrational Frequencies for $M(CO)(C_3H_3RCO)(S_2CNR'_2)_2$ (M = Mo, W) and Related Compounds[a]

complex	ν(CO), cm^{-1}
$Mo(CO)(C_3H_4CO)(S_2CNEt_2)_2$	1960, 1810
$Mo(CO)(C_3H_4CO)(S_2P(Pr\text{-}i)_2)_2$	1945, 1830
$W(CO)(C_3H_4CO)(S_2CNMe_2)_2$	1935, 1780
$W(CO)(C_3H_4CO)(S_2CNEt_2)_2$	1960, 1780
$W(CO)(C_3H_4CO)(S_2CNPh_2)_2$	1947, 1762
$W(CO)(C_3H_3CH_3CO)(S_2CNMe_2)_2$	1938, 1736
$W(CO)(C_3H_3CH_3CO)(S_2CNEt_2)_2$	1942, 1744
$W(CO)(C_3H_3CH_3CO)(S_2CN(Pr\text{-}i)_2)_2$	1942, 1734[b]
$W(CO)(C_3H_3CH_3CO)(S_2CNC_4H_4)_2$	1933, 1778

[a] Recorded in KBr pellets. [b] Recorded in CH_2Cl_2 solution.

oxidation and decomposition has prevented us from obtaining satisfactory elemental analytical or NMR spectral data for the molybdenum complexes.

The rapid uptake of cyclopropene by $Mo(CO)_2(BB)_2$ was reminiscent of the reactivity of these complexes with alkynes, and previous studies of the $M(CO)(C_2R_2)(BB)_2$[3] and $OM(C_2R_2)(BB)_2$[21] (M = Mo, W) systems showed greater stability for the tungsten species. These observations prompted us to synthesize the tungsten analogues of the above molybdenum–cyclopropene species in order to obtain more stable products. The tungsten complexes, $W(CO)_2(PPh_3)(S_2CNR_2)_2$ (R = Me, Et, Ph), were reacted with stoichiometric amounts of cyclopropene in CH_2Cl_2 followed by evaporation of the reaction mixtures to dryness and trituration of the residues with diethyl ether (to remove PPh_3) to yield well-formed orange solids whose elemental analytical data (for R = Me, Et) were again consistent with the empirical formulation $W(CO)_2(C_3H_4)(S_2CNR_2)_2$. For R = Ph, the extremely high solubility of the complex in diethyl ether made complete separation from PPh_3 difficult and the CHN analytical data reflect this problem. As for the above molybdenum systems, no CO was evolved in these reactions and the infrared spectra of the species again contain bands of unequal intensity at ~1950 and 1780 cm^{-1} assigned to carbonyl stretching frequencies (Figure 1). Exact band positions for both Mo and W complexes are given in Table I.

Reactions of the tricarbonyl–tungsten species $W(CO)_3(S_2CNEt_2)_2$ with cyclopropenes were more complex than those of $W(CO)_2(PPh_3)(S_2CNEt_2)_2$. With unsubstituted cyclopropene under the above reaction conditions, a solid product was isolated whose IR spectrum not only contained bands at 1960 and 1780 cm^{-1} due to $W(CO)_2(C_3H_4)(S_2CNEt_2)_2$ but also exhibited medium-intensity bands at 1820 and 1590 cm^{-1} due to an unidentified carbonyl complex (Figure 1). In addition, only ~0.7 equiv of CO was evolved in this reaction rather than the anticipated 1.0 equiv. $W(CO)_3(S_2CNet_2)_2$ was also reacted with 1-methylcyclopropene under somewhat different reaction conditions. In this case, a well-characterized species of empirical formula $W(CO)_2(C_4H_6)(S_2CNEt_2)_2$ was isolated after chromatography of the reaction mixture.

As pointed out above, the infrared spectral, analytical, and gas evolution data are indicative of an empirical formula of $M(CO)_2(C_3H_4)(S_2CNEt_2)_2$ for these products. However, it should be noted that these data are consistent with the complexes containing either two terminal carbonyl ligands or a single terminal carbonyl and a ligand with an organic C=O moiety. In order to differentiate between these possibilities, we oxidized the complex $W(CO)_2(C_4H_6)(S_2CNEt_2)_2$ in vacuo with excess Br_2 and measured the amount of evolved carbon monoxide. This treatment would be expected to liberate terminal carbonyl groups on tungsten, but not CO that was part of a coordinated organic moiety. Only 0.85 equiv of CO was obtained under these conditions, a result which indicates that this complex should be formulated as $W(CO)(C_3H_3CH_3CO)(S_2CNEt_2)_2$, a species containing only one terminal carbonyl ligand. The similarity of the IR spectral properties of the other complexes of empirical formula $M(CO)_2(C_3H_4)(BB)_2$ to those of the tungsten–methylcyclopropene complex (Figure 1) suggests that they should also be formulated in this way. Thus the stronger band at ~1950 cm^{-1} in the infrared spectra of these complexes should be assigned to the terminal carbonyl stretching frequency while the lower energy, weaker band at 1760–1830 cm^{-1} (depending on the metal and ligands) is due to the C=O stretch of the coordinated C_3H_4CO or $C_3H_3CH_3CO$ moiety. NMR data presented in the next section are also consistent with a compound that contains a single terminal CO ligand and, in addition, provide evidence for deducing the nature of the organic, CO-containing ligand.

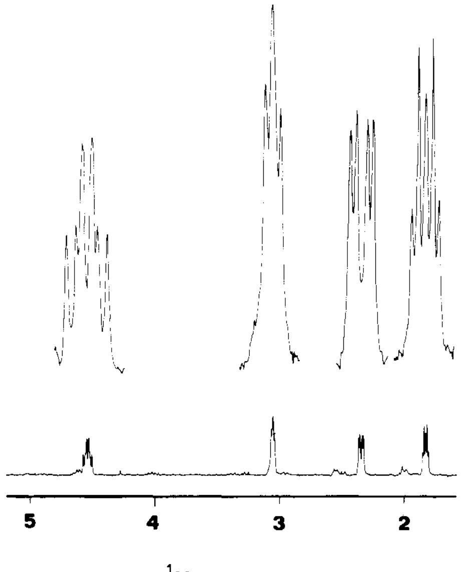

Figure 2. ^1H NMR spectrum of $W(CO)(C_3H_4CO)(S_2CNPh_2)_2$ in C_6D_6 showing expansions of the four proton signals derived from the cyclopropene reagent.

NMR Spectra. The stability of the $W(CO)(C_3H_3R'CO)(S_2CNR_2)_2$ (R' = H, CH_3) complexes allowed us to record ^1H and ^{13}C NMR spectra and provided the data listed in Tables II and III, respectively. A comparison of the data for the parent cyclopropene–metal complexes and the methyl-substituted cyclopropene derivatives suggests that they are analogous. The ^1H NMR spectrum of $W(CO)(C_3H_4CO)(S_2CNMe_2)_2$ exhibits two eight-line doublets of doublets of doublets and one approximate doublet of triplets with each of these three resonances integrating as one proton. The fourth C_3H_4 proton is not observed; presumably it is masked by dithiocarbamate methyl resonances. The corresponding spectrum of the *N,N'*-diphenyldithiocarbamate derivative has an open NMR window above the phenyl resonances and reveals a very similar pattern of C_3H_4 signals with the fourth cyclopropene signal at 3.04 ppm resembling a triplet (Figure 2).

Carbon-13 spectra of dialkyldithiocarbamate–tungsten derivatives proved uninformative. The location of the bound cyclopropene ^{13}C resonances amid the N-bound ^{13}C signals of the ligand complicated definitive spectral analysis. Again $W(CO)(C_3H_4CO)(S_2CNPh_2)_2$ was utilized to provide a more appropriate NMR probe (Figure 3). Three distinct ^{13}C signals were observed between 40 and 77 ppm in the $^{13}C\{^1H\}$ spectrum, and the retention of two CH units and one CH_2 unit in the metal-bound cyclopropene product was confirmed by the $^1J_{^{13}C-H}$ splitting patterns and values of 180 (d), 164 (t), and 179 (d) Hz for the signals at 76.8, 50.8, and 40.4 ppm, respectively, observed in the gated decoupled spectrum (see Table III). The $W(CO)(C_3H_3CH_3CO)(S_2CNC_4H_4)_2$ complex was chosen for ^{13}C NMR studies with ^{13}CO-enriched material.

The ^1H NMR spectrum of $W(CO)_2(C_3H_4)(S_2CNMe_2)_2$ suggested that the four cyclopropene protons were magnetically in-

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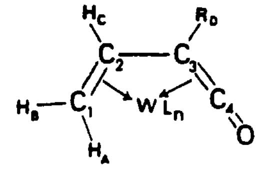
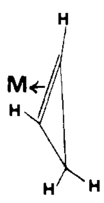
Table II. ^{1}H NMR Data for $W(CO)(C_3H_3RCO)(S_2CNR'_2)_2$ (R = H, CH_3)



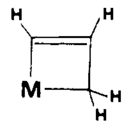
complex	H_A δ (*J*, Hz)	H_B δ (*J*, Hz)	H_C δ (*J*, Hz)	H_D δ (*J*, Hz)	$CH_{3(D)}$, δ	isomeric ratio	solvent
R = H, R'_2 = Me_2	1.94 (dt; 6.3, 2.8, 2.8)	2.36 (ddd; 7.5, 2.8, 0.7)	4.92 (ddd; 7.5, 6.3, 4.2)	(obscured by dithiocarbamate methyl signals)		~1	$CDCl_3$
R = H, R'_2 = Ph_2	1.82 (dt; 6.5, 2.6, 2.6)	2.33 (dd; 7.3, 2.6)	4.52 (ddd; 7.3, 6.5, 4.3)	3.04 (poor t; 4.3, 2.6)		~1	C_6D_6
R = CH_3, R'_2 = Me_2	2.03 (obscured by 2.00 singlet)	2.33 (dd; 7.0, 3.0)	4.75 (≃t; 7.0)		2.00 (s)	0.6	$CDCl_3$
	1.89 (dd; 7.3, 2.7)	2.72 (dd; 6.7, 3.0)	4.43 (≃t; 7.0)		2.13 (s)	0.4	
R = CH_3, R'_2 = Et_2	2.00 (obscured by 2.01 singlet)	2.33 (dd; 6.9, 2.8)	4.74 (≃t; 6.7)		2.01 (s)	0.7	$CDCl_3$
	1.85 (dd; 7.7, 2.8)	2.73 (dd; 6.5, 2.8)	4.43 (≃t; 7.1)		2.12 (s)	0.3	
R = CH_3, R'_2 = Et_2	1.97 (dd; 6.3, 2.8)	2.30 (dd; 6.8, 2.8)	4.68 (≃t; 6.5)		2.03 (s)	0.8	$CDCl_3$
	1.81 (dd; 7.3, 3.0)	2.72 (dd; 6.6, 3.1)	4.48 (≃t; 6.9)		2.12 (s)	0.2	
R = CH_3, R'_2 = C_4H_4	(obscured by methyl signals from 2.2–2.3)	2.35 (dd; 7.2, 3.2)	4.94 (≃t; 6.8)		2.19 (s)	0.6	$CDCl_3$
		2.85 (dd; 6.0, 2.8)	4.78 (≃t; 6.5)		2.33 (s)	0.4	

equivalent. This feature was confirmed by the simple first-order appearance of four distinct single proton resonances in the ^{1}H NMR spectrum of $W(CO)_2(C_3H_4)(S_2CNPh_2)_2$ analogue. The eight-line patterns at 2.3 and 4.9 ppm in the $W(CO)_2(C_3H_4)(S_2CNPh_2)_2$ spectrum each provide three coupling constants and unambiguous chemical shift–coupling constant assignment results.

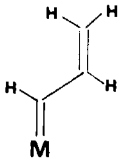
Several possible structures we considered and rejected are presented below. Both the chemical shifts and the coupling constants require a highly unsymmetrical environment for the C_3H_4 fragment and make isomer A unattractive. The two ν(CO) frequencies are too low to be compatible with a metal dicarbonyl derivative formed by either oxidative addition to generate a d^2 metallacyclobutane (B) or by ring opening and rearrangement to produce a π-acid vinylcarbene ligand (C). The lower energy CO stretching frequency is in the range observed for metal-bound ketene ligands,[22] and cyclopropene is known to undergo ring opening and CO insertion with iron carbonyl reagents.[23] Formation of a vinylketene ligand analogous to those found in $(C_3R_4CO)Fe(CO)_3$ complexes suggested itself.



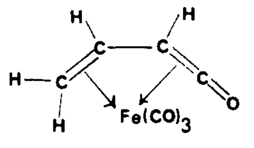
A



B



C



Representative chemical shifts and coupling constants for several vinylketene–iron complexes are included in Table IV for comparison with the $W(CO)(C_3H_3R'CO)(S_2CNR_2)_2$ data reported here. There is a general consistency in the NMR data for these vinylketene complexes even though particular proton assignments in some literature reports are ambiguous.

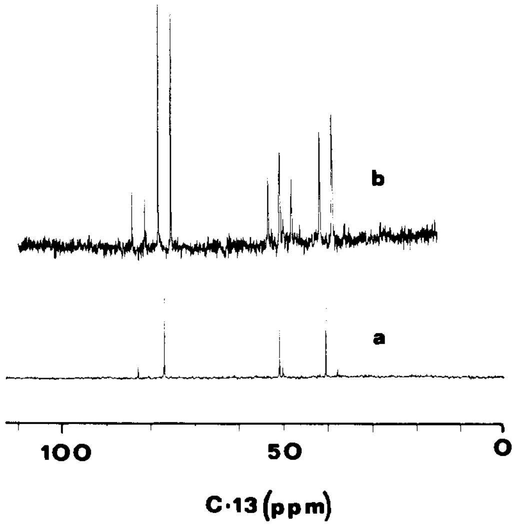
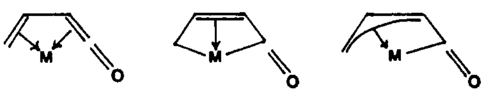


Figure 3. ^{13}C NMR spectra of $W(CO)(C_3H_4CO)(S_2CNPh_2)_2$ in C_6D_6 showing resonances assigned to the carbons of the cyclopropene reagent: (a) $^{13}C\{^1H\}$ NMR spectrum; (b) a coupled spectrum that reveals the $^1J_{C-H}$ coupling constants.

No simple bonding description adequately describes the vinylketene–metal linkage. A resonance form reminiscent of an η^4-butadiene can be drawn but various σ and π combinations may be equally valid representations.



Structures of $(\eta^4\text{-}CH_2C(CO_2Me)C(OMe)CO)Fe(CO)_2(PPh_3)$,[24] $(\eta^4\text{-}CMe_2CHCRCO)Fe(CO)_3$ (R = Me, H),[25,26] and $(\eta^4\text{-}C_3Ph_3HCO)Fe(CO)_3$[27] reflect contributions from all three resonance forms. Green and co-workers have reported the structure of a molybdenum compound that contains an η^4-vinylketene

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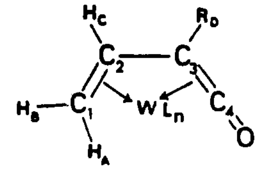
Table III. ^{13}C NMR Data for $W(CO)(C_3H_3RCO)(S_2CNR'_2)_2$ (R = H, CH_3)

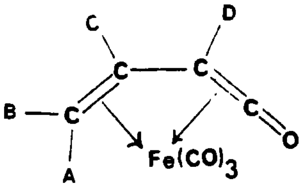


$W(CO)(C_3H_4CO)(S_2CNPh_2)_2$[a]			
δ	$^1J_{CH}$, Hz	isomeric ratio	assgnt
38.4	*b*	0.1	C_3
40.4	179 (d)	0.9	
50.0	*b*	0.1	C_1
50.8	164 (t)	0.9	
76.8	180 (d)	0.9	C_2
82.9	*b*	0.1	
125-135			phenyl carbons
213.2			CO[c]
221.8			S_2CN[c]
225.4			S_2CN[c]
233.0			C_4

$W(CO)(C_3H_3CH_3CO)(S_2CNC_4H_4)_2$[d]			
δ	$^1J_{CH}$, Hz	isomeric ratio	assgnt
8.0	131 (q)	0.6	CH_3
9.7	130 (q)	0.4	
50.1	164 (t)	0.4	C_1
50.2	164 (t)	0.6	
53.1	*b*	0.6	C_3
56.3	*b*	0.4	
79.7	174 (d)	0.6	C_2
88.1	176 (d)	0.4	
115-118			pyrrole carbons
209.1[e]	$^1J_{W-C} = 162$	0.4	W-CO
210.2[e]	$^1J_{W-C} = 159$	0.6	
214.1	*b*	0.6	S_2CN
215.4	*b*	0.4	
221.7	*b*	0.4	S_2CN
224.2	*b*	0.6	
230.4[e]	$J_{W-C} < 10$	0.6	C_4
236.0[e]		0.4	

[a] Spectrum was recorded in benzene-d_6. [b] These signals were too weak to observe coupling in the gated decoupled spectrum. [c] These very weak signals are tentatively assigned by analogy to the ^{13}CO-enriched pyrrole derivative. [d] Spectrum was recorded in chloroform-d_6. [e] These are the only signals observed in the ^{13}C NMR spectrum of material prepared from 50% ^{13}CO-enriched $W(^{13}CO)_3(S_2CNC_4H_4)_2$.

Table IV. ^1H NMR Data for Vinylketene-Iron Complexes[a]

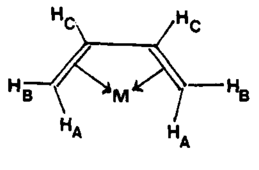


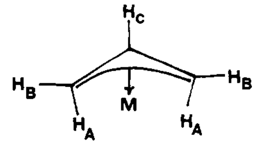
A, B, C, D	H_A	H_B	H_C	H_D	ν_{CO} (ketene)	ref
Me, Me, H, Me			5.62		1785	23a, 27
H, H, Ph, Ph	3.20 ($^2J_{AB} = 1.8$)	1.74 ($^2J_{AB} = 1.8$)			1783	27
Ph, H, Ph, Ph	3.28				1783	27
Me, Me, H, H			5.67 ($^3J_{CD} = 4.5$)	3.26 ($^3J_{CD} = 4.5$)	1760	26
Me, Me, H, H (with PPh_3 replacing one CO)			5.50 ($^3J_{CD} = 4.5$)	1.87 ($J \simeq 4$)	1690	26
H, H, CH_3O, H	1.47 ($^2J_{AB} = 4.7$; $^4J_{AD} = 1$)	2.91 ($^2J_{AB} = 4.7$; $^4J_{BD} = 3$)		3.52 ($^4J_{AD} = 1$; $^4J_{BD} = 3$)	1775	23b

[a] Signals in ppm; coupling constants in Hz.

fragment as part of a complex ligand derived from alkyne insertion into $(\eta^5\text{-}C_5H_5)Mo(C(O)CF_3)(CO)_3$.[28]

The ^1H and ^{13}C NMR assignments summarized in Table V are suggested by comparison with typical metal-bound π-allyl and π-butadiene NMR values. The vinyl fragments of both metal-bound π-C_3H_5[29] and π-C_4H_6[30] typically show increasingly downfield chemical shifts as one passes from H_A (anti) to H_B (syn) to H_C (central). Differentiation of H_C and H_D is possible here since coupling of H_A and H_B to H_C should be large, and even the third coupling constant to H_C, $^3J_{CD}$, is expected to be substantial. This pattern identifies H_C by the three largest coupling constants while the H_D signal is associated with two coupling constants less then 3 Hz in addition to the 4–5-Hz coupling to H_C. Similar reasoning applies to the ^{13}C NMR chemical shift values. The internal carbons of π-allyl and π-butadiene ligands typically





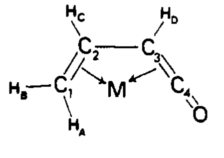


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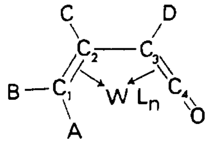
Table V. Summary of NMR Data for $W(CO)(C_3H_3R'CO)(S_2CNR_2)_2$ Complexes[a]



^{1}H NMR Data

H_A	H_B	H_C	H_D
1.8-2.0 $^2J_{AB}$ = 2-3 $^3J_{AC}$ = 6-7 $^4J_{AD}$ = 2-3	2.3-2.9 $^3J_{BA}$ = 2-3 $^3J_{BC}$ = 6-8 $^4J_{BD}$ = 0-1	4.2-4.9 $^3J_{CA}$ = 6-7 $^3J_{CB}$ = 6-8 $^3J_{CD}$ = 4-5	3.0 $^4J_{DA}$ = 2-3 $^4J_{DB}$ = 0-1 J_{DC} = 4-5

^{13}C NMR Data

C_1	C_2	C_3	C_4
50-51 $^1J_{CH}$ = 164	76-88 $^1J_{CH}$ = 174-180	38-56 $^1J_{CH}$ = 179	230-236

[a] Signals in ppm; coupling constants in Hz.

resonate 30–50 ppm below the terminal methylene carbons.[31] Since C_1 and C_4 are unique as a triplet and singlet, respectively, only C_2 and C_3 require differentiation. The signal near 80 ppm is in the range of normal internal carbons for π-C_3H_5 or π-C_4H_6, so we assign it as C_2. The methine signal near 40 ppm is unusually high for an internal CH unit, and we attribute this to the ketene linkage. Alternatively, one can arrive at these same assignments by analogy with the π-allyl fragment present in resonance structure C. The larger $^1J_{CH}$ coupling constants for C_2 and C_3 are also common to internal carbons relative to terminal methylenes in π-bound allyls and dienes.

As an additional probe of CO incorporation into the organic ligand, we synthesized the 1-methylcyclopropene complex from ^{13}CO-enriched $W(CO)_3(S_2CNC_4H_4)_2$. Two $W(^*CO)(C_3H_3CH_3{}^*CO)(S_2CNC_4H_4)_2$ isomers were present in roughly equal amounts,[32] but the level of ^{13}CO enrichment ($\simeq$50%) allowed us to easily resolve $^1H_{^{183}W-^{13}C}$ coupling constants in the carbonyl region. Of the four ^{13}CO signals, the two near 210 ppm were coupled to ^{183}W (14% abundant) with normal values for terminal carbonyl ligands ($\simeq$160 Hz).[34] The other two ^{13}CO signals, located below 230 ppm, showed no resolved coupling to tungsten. We interpret this as reflecting incorporation of one of the reagent carbonyl ligands into the vinylketene ligand in accord with the C_4 ^{13}C NMR assignment.

In summary, we have isolated complexes of the form $W(CO)(C_3H_4CO)(S_2CNR_2)_2$ and $W(CO)(C_3H_3CH_3CO)(S_2CNR_2)_2$ that were generated from reactions of cyclopropenes with tungsten–carbonyl species. These compounds exhibit IR and NMR spectra that are most consistent with the presence of a coordinated vinylketene moiety formed from cyclopropene ring opening and CO insertion. The similarity of the IR spectral data for the extremely labile molybdenum species $Mo(CO)(C_3H_4CO)(BB)_2$ (BB = S_2CNR_2, $S_2P(i\text{-}Pr)_2$ indicate that they are structurally similar to the tungsten analogues.

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Registry No. $Mo(CO)(C_3H_4CO)(S_2CNEt_2)_2$, 95069-43-5; $Mo(CO)(C_3H_4CO)(S_2P(i\text{-}Pr)_2)_2$, 95069-44-6; $W(CO)(C_3H_4CO)(S_2CNMe_2)_2$, 95069-45-7; $W(CO)(C_3H_4CO)(S_2CNEt_2)_2$, 95069-46-8; $W(CO)(C_3H_4CO)(S_2CNPh_2)_2$, 95069-47-9; $W(CO)(C_3H_3CH_3CO)(S_2CNMe_2)_2$, 95098-05-8; $W(CO)(C_3H_3CH_3CO)(S_2CNEt_2)_2$, 95098-06-9; $W(CO)(C_3H_3CH_3CO)(S_2CN(i\text{-}Pr)_2)_2$, 95069-48-0; $W(CO)(C_3H_3CH_3CO)(S_2CNC_4H_4)_2$, 95069-49-1; $Mo(CO)_2(S_2CNEt_2)_2$, 18947-43-8; $Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$, 60965-90-4; $W(CO)_2(PPh_3)(S_2CNMe_2)_2$, 60911-44-6; $W(CO)_2(PPh_3)(S_2CNEt_2)_2$, 60911-45-7; $W(CO)_2(PPh_3)(S_2CNPh_2)_2$, 95069-50-4; $W(CO)_3(S_2CNMe_2)_2$, 72881-01-7; $W(CO)_3(S_2CNEt_2)_2$, 72827-54-4; $W(CO)_3(S_2CN(i\text{-}Pr)_2)_2$, 95069-51-5; $W(CO)_3(S_2CNC_4H_4)_2$, 95069-52-6; cyclopropene, 2781-85-3; 1-methylcyclopropene, 3100-04-7; 3-chloro-2-methylpropene, 563-47-3.

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(32) On the basis of the analogy between coordinated 1,3-butadiene and alkynes,[33] the C_2–C_3 bond of the vinylketene is expected to lie perpendicular to the metal carbonyl axis. Without a structural determination, specific suggestions about isomeric geometries are inappropriate. One can imagine flipping the vinylketene ligand end to end to generate an isomer, or more likely, one could rotate the vinylketene ligand about the C_2–C_3 axis to keep the ketene moiety at the same end as before, but now pointing in a different direction.

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