times required for their ejection (typically a few microseconds). Studies are continuing on other metal-catalyzed polymerization processes further to examine this phenomenon in the gas phase.

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Registry No. Fe^+, 14067-02-8; C_6H_5F, 462-06-6; C_6H_5Br, 108-86-1; C_6H_5I, 591-50-4; $(Fe(C_6H_4)^+)$, 119208-09-2; chlorobenzene, 108-90-7.

Unsaturated Carbene Ligands: (η^2-Vinyl)-, (Vinylcarbene)-, and (η^4-Butadienyl)tungsten Dithiocarbamate Complexes

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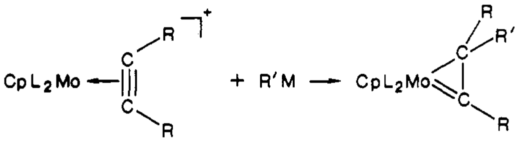
Carbene complexes with unsaturation in the carbene organic substituent have been prepared from $[(S_2CNR_2)_2W(\eta^4\text{-}C_4Ph_4H)][BF_4]$. Addition of one dithiocarbamate ligand to this cationic butadienyl complex results in dechelation of the olefin tail to form a neutral tris(dithiocarbamate) complex containing a vinyl-substituted η^2-vinyl ligand, $(S_2CNR_2)_3W(\eta^2\text{-}CPh{=}CPhCPh{=}CHPh)$. Spectroscopic properties (C_α, 262 ppm) and structural data (W–C_α, 1.94 Å) support formulation of the metal–η^2-vinyl unit as a metallacyclopropene. Protonation of this neutral η^2-vinyl complex produces a cationic complex containing a vinylcarbene ligand, $[(S_2CNR_2)_3W{=}CPhCPh{=}C(Ph)CH_2Ph][BF_4]$. The α-carbon retains its carbene character as evidenced by ^{13}C NMR (257 ppm). Reaction of the cationic η^4-butadienyl complex $[(S_2CNR_2)_2W(\eta^4\text{-}C_4Ph_4H)][BF_4]$ with $Li[Et_3BH]$ produces a terminal sulfide ligand while retaining the η^4-butadienyl ligand in $(S_2CNR_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$. An X-ray structure of the (dithiocarbamato)(butadienyl)tungsten sulfide monomer provides confirmation of the strong bonding between tungsten and both the α-carbon (W–C_α, 1.96 Å) and the terminal sulfide (W–S, 2.10 Å).

Introduction

Organic ligands which can be generically formulated as $\eta^n\text{-}C_nR_{n+1}$ with n = 2, 3 and 4 are an important class of carbene derivatives. Representative complexes containing η^2-vinyl (n = 2), η^3-vinylcarbene (n = 3), and η^4-butadienyl (n = 4) ligands have been prepared during the 1980s. In each case alternative bonding modes are available to the ligand.

Several groups have prepared η^2-vinyl complexes by nucleophilic addition to four-electron alkyne ligands. Green and co-workers have reacted cationic alkyne complexes of the type $[(\pi\text{-}Cp)L_2Mo(RC{\equiv}CR)]^+$ with carbon-based nucleophiles and hydride transfer reagents to form neutral η^2-vinyl complexes $(\pi\text{-}Cp)L_2Mo(\eta^2\text{-}RC{=}CRR')$ (eq 1).[1] Davidson and co-workers have added heteroatom nucleophiles to complexes containing electron-poor hexafluorobutyne ligands to form η^2-vinyl products (eq 2).[2] We have utilized phosphorus-based nucleophiles to convert terminal alkyne ligands in olefin–alkyne complexes to η^2-vinyl ligands (eq 3).[3] In all of these cases a d^4 metal configuration characterizes both the alkyne reagent complex and the η^2-vinyl product monomer.[4]

Vinylcarbene complexes of the type $L_nM(\eta^3\text{-}CR{-}CR{=}CR_2)$ may form from metal carbene–alkyne coupling; a metallacyclobutene formulation is also possible for complexes with this stoichiometry. Cyclopropene is another source of C_3R_4 ligands. Reaction of metal-bound C_3R_4 moieties with carbon monoxide has been postulated as a route to vinylketene ligands of the type $\eta^4\text{-}R_2C{=}CR{-}CR{=}C{=}O$.[5,6]



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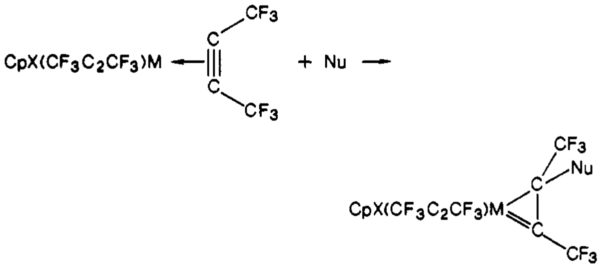

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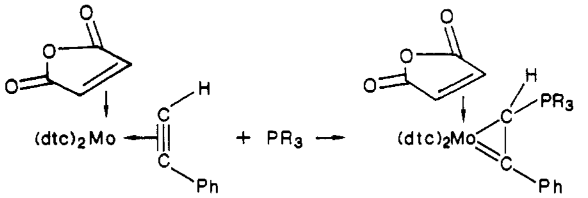

(3)

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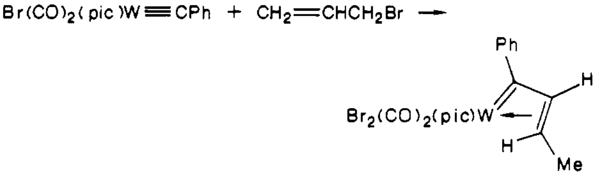
Isolation and structural characterization of vinylcarbene monomers is rare. Mayr and co-workers have prepared an η^3-vinylcarbene complex (eq 4),[7] and the W(η^3-CPhCH=CHMe) unit has W–C distances of 1.98 (2), 2.38 (2), and 2.60 (2) Å. Another example of a tungsten vinylcarbene is provided by (π-Cp)$Cl_3W(C_3H_2Bu^t{}_2)$;[8] no structure is available. More recently Geoffroy has reported formation of a vinylcarbene complex from the reaction of a transient benzylidene complex, $Cp(CO)_2W{=}CHAr^+$, with diphenylacetylene (eq 5).[9]



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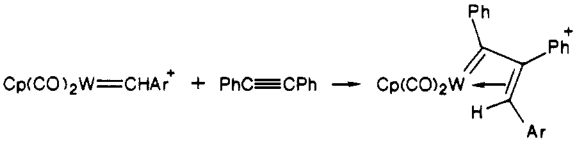
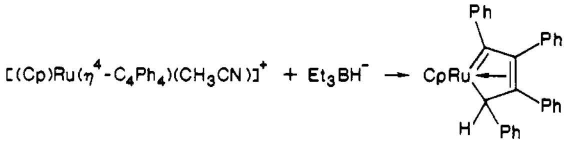


(5)

Hydride addition to a cationic ruthenium cyclobutadiene complex produced an η^4-butadienyl ligand in the (π-Cp)Ru(η^4-C_4Ph_4H) product (eq 6).[10] We have previously prepared η^4-butadienyl complexes by acid addition to bis(alkyne) precursors (eq 7).[11] We now report reactions of these cationic bis(dithiocarbamato)(η^4-butadienyl)tungsten complexes which involve retention of the η^4-butadienyl ligand, conversion of the η^4-C_4R_5 unit to an η^2-vinyl (generically η^2-C_2R_3), and further reaction of the η^2-vinyl product to form a cationic vinylcarbene complex.



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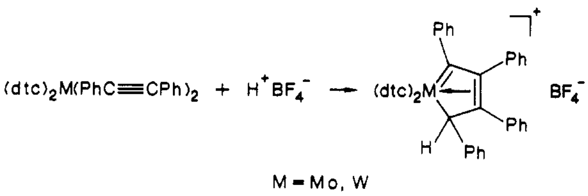

(7)

Experimental Section

Materials and Methods. All manipulations were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Methylene chloride was distilled from P_2O_5. Tetrahydrofuran was distilled from sodium benzophenone. Other solvents were purged with N_2 prior to use. Reagents were used as obtained from commercial sources. Literature methods were used to prepare $(S_2CNR_2)_2W(PhC_2Ph)_2$ (R = Me, Et) and $[(S_2CNR_2)_2W(C_4Ph_4H)][BF_4]$ (R = Me, Et).[11]

Infrared spectra were recorded on a Beckman IR 4250 spectrometer and calibrated with a polystyrene standard. ^{1}H and ^{13}C NMR were recorded on a Bruker AC 200 or Varian XL400 instrument. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN.

Syntheses. $(S_2CNR_2)_3W(\eta^2\text{-}C_4Ph_4H)$ (R = Me, Et). A stoichiometric amount of $Na(S_2CNEt_2)\cdot 3H_2O$ (0.50 g, 2.2 mmol) was added to a solution of $[(S_2CNEt_2)_2W(\eta^4\text{-}C_4Ph_4H)][BF_4]$ (2.0 g, 2.2 mmol) in 30 mL of CH_2Cl_2. The dark red reaction solution was stirred for 10 min under N_2 and then filtered. The solvent was removed under vacuum, and the solid residue that remained was chromatographed on alumina by using toluene as the eluent. A dark red band was collected, most of the toluene was evaporated, and hexanes were added before the solution was placed in the refrigerator overnight. The dark red crystals that formed were isolated by filtration, washed with hexanes, and dried in vacuo (1.9 g, 90% yield). The solid is stable in air for brief exposures, but solutions of the product are moderately air-sensitive. ^{1}H NMR (CD_2Cl_2): δ 7.81 (d, Ph), 7.25 (t, Ph), 7.08 (s, Ph) 7.0 (br m, Ph), 6.87 (t, Ph), 6.72 (m, Ph), 6.63 (t, Ph), 6.56 (d, Ph), 6.47 (t, Ph), 6.26 (d, Ph), 5.67 (s, 1 H, $=C\mathit{H}Ph$), 2.9–3.8 (m, 12 H, Et $C\mathit{H}_2$'s), 1.19, 1.15, 1.10, 0.98, 0.87, 0.81 (each a t, 18 H total, Et $C\mathit{H}_3$'s). ^{13}C NMR (CD_2Cl_2): δ 260.6 (s, $^1J_{WC}$ = 64 Hz, $W{=}\mathit{C}Ph$–), 209.2, 201.3, 200.8 ($S_2\mathit{C}N$), 150.8 to 122.9 (C_6H_5 and C=C), 62.1 (C_β of η^2-CPh—CPhCPh=CHPh), 45.3, 44.0, 43.9, 43.6, 43.0, 42.8 ($\mathit{C}H_2CH_3$), 12.9, 12.5, 12.4 ($CH_2\mathit{C}H_3$). Anal. Calcd for $W_1C_{43}H_{51}N_3S_6$: C, 52.40; H, 5.20; N, 4.26; S, 19.50; W, 18.67. Found: C, 51.62; H, 5.61; N, 3.88; S, 18.92; W, 17.90. Preparation of dark red crystals of $(S_2CNMe_2)_3W(\eta^2\text{-}C_4Ph_4H)$ was accomplished by an analogous method (80% yield). ^{1}H NMR (CD_2Cl_2): δ 8.09 (d, Ph), 7.36 (t, Ph), 7.17 (s, Ph), 7.09 (m, Ph), 6.75–6.55 (m, Ph), 6.15 (d, Ph), 5.57 (s, 1 H, $=C\mathit{H}Ph$), 3.26, 3.18, 3.01, 2.92, 2.75, 2.55 (each a s, 18 H, $C\mathit{H}_3$). ^{13}C NMR (CD_2Cl_2): δ 262.2 (C_α), 209.7, 201.7 ($S_2\mathit{C}N$), 150.7, 148.8, 145.9, 144.1, 139.9 (4 C_{ipso} + C–Ph), 122–132 (Ph + C olefin), 62.3 (η^2-CPhCPhCPh=CHPh), 40.2, 39.0, 38.2, 38.1, 37.6, 37.2 ($\mathit{C}H_3$). Anal. Calcd for $W_1C_{37}H_{39}N_3S_6$: C, 49.28; H, 4.33, N, 4.66; S, 21.3; W, 20.41. Found: C, 48.96; H, 4.65; N, 4.33; S, 20.64; W, 20.98. The molybdenum derivatives $(R_2NCS_2)_3Mo(\eta^2\text{-}CPhCPhCPh{=}CHPh)$ were also prepared by addition of NaS_2CNR_2 to the cationic molybdenum precursors. $(S_2CNMe_2)_3Mo(\eta^2\text{-}C_4Ph_4H)$: ^{1}H NMR ($CD_2Cl_2$) δ 8.20 (d, Ph), 7.43 (t, Ph), 7.26–6.62 (m, Ph), 6.26 (d, Ph), 5.68 (s, 1 H, $=C\mathit{H}Ph$), 3.38, 3.29, 3.12, 3.02, 2.85, 2.64 (each a s, 18 H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 278.9 (C_α), 208.1, 202.2, 202.1 ($S_2\mathit{C}N$), 146.6, 146.2, 144.9, 141.3, 138.9 (C_{ipso} + C–Ph), 131.3–123.1 (Ph + C olefin), 64.0 (C_β), 40.1, 38.9, 37.9, 37.8, 37.3, 37.0 ($\mathit{C}H_3$). Anal. Calcd for $Mo_1C_{37}H_{39}N_3S_6$: C, 54.62; H, 4.80;, N, 5.17. Found: C, 54.88; H, 4.88; N, 4.57. $(Et_2NCS_2)_3Mo(\eta^2\text{-}C_4Ph_4H)$: ^{1}H NMR ($CD_2Cl_2$) δ 8.18 (d, Ph), 7.39 (t, Ph), 7.22–6.64 (m, Ph), 6.38 (d, Ph), 5.89 (s, 1 H, $=C\mathit{H}Ph$), 3.96–3.08 (m, 12 H, Et $C\mathit{H}_2$'s), 1.26, 1.23, 1.22, 1.10, 1.02, 0.93 (each a t, 18 H, Et $C\mathit{H}_3$'s); ^{13}C NMR (CD_2Cl_2) δ 277.1 (C_α), 207.5, 201.2, 200.9 ($S_2\mathit{C}N$), 147.0, 146.3, 144.8, 141.1, 139.0 (C_{ipso} + C–Ph), 131.0–122.8 (Ph + C olefin), 62.8 (C_β), 45.1, 43.8, 43.5, 43.3, 42.6, 42.5 ($\mathit{C}H_2CH_3$), 12.69, 12.47, 12.36, 12.3 ($CH_2\mathit{C}H_3$). Anal. Calcd for $Mo_1C_{43}H_{51}N_3S_6$: C, 57.53, H, 5.69; N, 4.68; S, 21.41; Mo, 10.70. Found: C, 55.76; H, 5.68; N, 4.46; S, 21.35; Mo, 10.43.

$[(S_2CNEt_2)_3W(CPhCPh{=}CPhCH_2Ph)][BF_4]$. A solution of $(S_2CNEt_2)_3W(\eta^2\text{-}C_4Ph_4H)$ (2.0 g, 2.0 mmol) in 10 mL of CH_2Cl_2 was cooled to 0 °C in an ice water bath, and a stoichiometric amount of $HBF_4\cdot Me_2O$ was added. The solution color changed from deep red to dark green within minutes. After 10 min of stirring the reaction solution was transferred to a flask containing 100 mL of Et_2O. A green solid precipitated immediately. The green solid was isolated by filtration and dried in vacuo (1.96 g, 90%). Recrystallization from CH_2Cl_2/Et_2O produced beautiful deep forest green crystals. ^{1}H NMR (CD_2Cl_2): δ 7.88 (d, Ph), 7.5–6.9 (m, Ph), 6.44 (d, Ph), 4.06 (s, 2 H, $C\mathit{H}_2Ph$), 3.7–3.4 (m, 12 H, Et CH_2's), 1.3–1.1 (m, 18 H, Et CH_3's). ^{13}C NMR (CD_2Cl_2): δ 256.7 (C_α), 202.3, 196.8 ($S_2\mathit{C}N$), 142.4, 141.3, 140.7, 137.6, 133.7, 132.2, 130–126 (Ph), 46.5 ($\mathit{C}H_2Ph$), 46.0, 45.4, 44.9, 44.0 ($\mathit{C}H_2CH_3$), 12.8, 12.6, 12.4, 12.3 ($CH_2\mathit{C}H_3$). Anal. Calcd for $W_1C_{43}H_{52}N_3S_6B_1F_4$: C, 48.10; H, 4.85; N, 3.98; S, 17.90; W, 17.14. Found: C, 48.27; H, 5.26; N, 3.59; S, 17.83; W, 17.00. Preparation of the green dimethyldithiocarbamato analogue was accomplished

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(6) For a recent example of carbon monoxide insertion into a vinylcarbene complex, with numerous references, see: Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368.

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by a similar protonation reaction (80% yield). **[$(S_2CNMe_2)_3$W(CPhCPh=CPhCH$_2$Ph)][BF$_4$]**: ^{1}H NMR (CD_2Cl_2) δ 7.81 (d, C_6H_5), 7.57 (t, C_6H_5), 7.29 (t, C_6H_5), 7.21–6.82 (m, C_6H_5), 6.24 (d, C_6H_5), 3.88 (s, 2 H, CH_2Ph), 3.27, 3.21, 3.17, 2.99 (18 H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 257.0 (s, C_α) 202.9, 196.6 (S_2CN), 143.0–126.0 (Ph), 47.5 (t, $^1J_{CH}$ = 129 Hz, CH_2Ph), 40.4, 39.4, 39.3, 37.9 (q, $^1J_{CH}$ = 140 Hz, CH_3). Anal. Calcd for $W_1C_{38}H_{42}N_3S_6B_1F_4Cl_2$: C, 42.47; H, 3.91; N, 3.91. Found: C, 41.54; H, 3.81; N, 3.87.

$(S_2CNEt_2)(\eta^4$-$C_4Ph_4H)$W=S. A stoichiometric amount of Li[Et_3BH] (2.2 mL) was added to a solution of [$(S_2CNEt_2)_2$W(η^4-C_4Ph_4H)][BF$_4$] (2.00 g, 2.2 mmol) in 20 mL of THF. The solution color was red-orange after it had stirred for 20 min. The solution was filtered, and the solvent was evaporated. The residue was chromatographed on alumina with toluene as an eluent. The orange band that eluted was collected, and the solvent was evaporated. Proton NMR of the red-orange oil indicated that the material was a 4:1 mixture of $(S_2CNEt_2)(\eta^4$-$C_4Ph_4H)$W=S and $(S_2CNEt_2)_3W(\eta^2$-$C_4Ph_4H)$. Careful recrystallization from CH_2Cl_2/hexanes yielded pure $(S_2CNEt_2)(\eta^4$-$C_4Ph_4H)$W=S (0.8 g, 50%). ^{1}H NMR (CD_2Cl_2): δ 7.42 (d, Ph), 7.22 (t, Ph), 7.1–6.8 (m, Ph), 6.55 (d, Ph), 4.09 (s, C*H*Ph, 14% ^{183}W, d, J_{WH} = 15 Hz), 3.7–3.6, 3.4 (m, 4 H, CH_2CH_3), 1.23, 1.12 (t, 3 H each, CH_2CH_3). ^{13}C NMR (CD_2Cl_2): δ 267.5 (s, =CPh), 203.4 (S_2CNEt_2), 144.8, 141.0, 138.6, 135.6, 132.5, 131.5, 130.4, 129.4, 128.1, 127.65, 127.63, 127.47, 127.25, 126.87, 125.35 (C_6H_5), 123.4, 111.8 (s, = CPhCPhCPhCHPh), 59.84 (d, $^1J_{CH}$ = 142 Hz, $^1J_{WC}$ = 38 Hz, CHPh), 46.35, 44.58 (t, $^1J_{CH}$ = 140 Hz, CH_2), 12.83, 12.67 (q, $^1J_{CH}$ = 130 Hz, CH_3). IR (KBr): ν (W=S) 520 cm^{-1}. Anal. Calcd for $W_1C_{35}H_{35}N_1S_3Cl_4$: C, 47.15; H, 3.93; N, 1.57; S, 10.78; W, 20.64. Found: C, 47.52; H, 6.11; N, 1.49; S, 11.45; W, 21.14.

Collection of Diffraction Data. A dark red prism of $(Me_2NCS_2)_3W(\eta^2$-PhCCPhCPh=CHPh) of dimensions 0.60 × 0.30 × 0.10 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[12] Twenty-five centered reflections found in the region 15.0 < θ < 17.0 and refined by least-squares calculations indicated a monoclinic cell. The cell parameters are listed in Table I. A red-orange prism of $(Et_2NCS_2)(\eta^4$-$C_4Ph_4H)$W=S of dimensions 0.40 × 0.10 × 0.10 mm was mounted in the same way, and twenty-five reflections with 10.0 < θ < 13.0 were used to define the unit cell as listed in Table I.

Diffraction data were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table I. Three reflections chosen as intensity standards were monitored every 3 h and showed no significant (<1.5%) decay. The crystal was checked for orientation every 300 reflections and was recentered if necessary. Psi scans with nine reflections having 80° < χ < 90° were collected, and an empirical absorption correction was applied (the corrections ranged from 0.82 to 1.00 for the η^2-vinyl complex and from 0.96 to 1.00 for the sulfide). Only data with $I > 3\sigma(I)$ were used in structure solution and refinement.[13] The data were corrected for Lorentz-polarization effects during the final stages of data reduction.

Solution and Refinement of the Structures. Solution of both structures was straightforward from applications of the heavy-atom method. Space group $P2_1/c$ was confirmed in both cases, and the position of the tungsten atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

Least-squares refinement[14] of the 47 non-hydrogen atoms of the η^2-vinyl molecule and a molecule of acetonitrile, fixing the acetonitrile and varying all but the phenyl carbons anisotropically, produced unweighted and weighted residuals of 4.7% and 4.6%,[15] respectively. Hydrogen atom positions were calculated by using a C–H distance of 0.95 Å and an isotropic thermal parameter of 6.0 Å^2. Further refinement resulted in residuals of R = 4.3% and R_w = 3.9%.[16] The final difference Fourier map had no peak greater than 0.43 e/Å^3 for $(Me_2NCS_2)_3W(\eta^2$-$C_4Ph_4H)$.

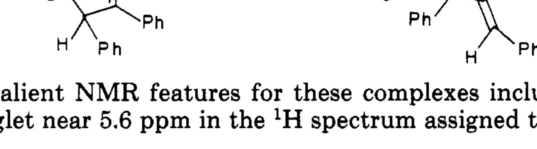
Table I. Crystallographic Data Collection Parameters

	$(Me_2NCS_2)_3$W-(η^2-C_4Ph_4H)	(Et_2NCS_2)-(η^4-C_4Ph_4H)W=S
	Crystal Data	
mol formula	$WS_6N_4C_{39}H_{42}$	$WCl_4S_3NC_{35}H_{35}$
fw, g/mol	943.03	891.53
cryst dimens, mm	0.60 × 0.30 × 0.10	0.40 × 0.10 × 0.10
space group	$P2_1/c$	$P2_1/c$
cell parameters		
a, Å	10.839 (3)	11.094 (4)
b, Å	18.907 (3)	12.892 (5)
c, Å	20.298 (7)	25.704 (8)
β, deg	101.99 (3)	95.30 (3)
V, Å^3	4068.8	3660.8
Z	4	4
d(calcd), g/cm^3	1.539	1.618
	Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	Zr filter	Zr filter
linear abs coeff, cm^{-1}	33.4	38.2
scan type	$\omega/1.33\theta$	ω/θ
bckgd	25% of full scan width on both sides	25% of full scan width on both sides
θ limits	2° < θ < 25°	2° < θ < 25°
quadrant collected	$\pm h,+k,+l$	$\pm h,+k,+l$
total no. of reflctns	7129	6429
data with $I > 3\sigma(I)$	4491	2772
R	4.3%	6.0%
R_w	3.9%	4.4%
GOF	2.20	1.80
no. of parameters	316	223
largest parameter shift	0.39	0.03

For the $(Et_2NCS)(\eta^4$-$C_4Ph_4W)$W=S structure, two molecules of methylene chloride per asymmetric unit were located, with one of the molecules having a threefold disorder. Least-squares refinement of the 47 non-hydrogen atoms of the molecule, fixing the methylene chlorides and varying all but the phenyl carbons anisotropically, produced unweighted and weighted residuals of 6.4% and 5.2%, respectively. Hydrogen atom positions were calculated by using C–H distances of 0.95 Å and an isotropic thermal parameter of 6.0 Å^2. Further refinement resulted in residuals of R = 6.0% and R_w = 4.4%. The final difference Fourier map showed two peaks with intensities of 0.86 and 0.72 e/Å^3 in the proximity of tungsten, with the next largest peak having an intensity of 0.52 e/Å^3.

Results

η^2-Vinyl Complexes. Cationic η^4-butadienyl tungsten complexes, [W(η^4-C_4Ph_4H)(S_2CNR_2)$_2$][BF$_4$] (R = Me, Et), react with free dithiocarbamate ($R_2NCS_2^-$ = dtc) to form vinyl-substituted η^2-vinyl complexes, $(R_2NCS_2)_3W(\eta^2$-CPh=CPhCPh=CHPh), in high yield (eq 8). These neutral products were purified by chromatography on alumina followed by recrystallization from methylene chloride/hexane.



(8)

Salient NMR features for these complexes include a singlet near 5.6 ppm in the ^{1}H spectrum assigned to the

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[12] Programs used during solution and refinement were from the Enraf-Nonius structure determination package.

[13] $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (pI)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and p = 0.01 is a correction factor.

[14] The function minimized was $\sum w(|F_o| - |F_c|)^2$.

[15] $R_{\text{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

[16] Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

Table II. Atomic Positions for $(Me_2NCS_2)_3W(\eta^2\text{-}C_4Ph_4H)$

	x	*y*	*z*
W	0.33270 (4)	0.33549 (2)	0.38783 (2)
S(1)	0.4527 (2)	0.3416 (2)	0.2944 (1)
S(2)	0.4934 (2)	0.4354 (1)	0.4039 (1)
S(3)	0.2999 (2)	0.2207 (1)	0.3204 (1)
S(4)	0.2080 (2)	0.2464 (1)	0.4373 (1)
S(5)	0.3664 (2)	0.3641 (1)	0.5112 (1)
S(6)	0.5260 (2)	0.2699 (1)	0.4562 (1)
N(1)	0.6355 (7)	0.4386 (4)	0.3107 (4)
N(2)	0.1574 (8)	0.1257 (4)	0.3691 (4)
N(3)	0.5654 (8)	0.2990 (4)	0.5878 (4)
N(4)	0.628 (1)	0.4592 (7)	0.0758 (6)
C(1)	0.5402 (8)	0.4098 (5)	0.3337 (4)
C(2)	0.7100 (9)	0.4955 (6)	0.3451 (6)
C(3)	0.672 (1)	0.4147 (6)	0.2493 (5)
C(4)	0.2125 (8)	0.1883 (5)	0.3740 (4)
C(5)	0.157 (1)	0.0807 (6)	0.3120 (6)
C(6)	0.082 (1)	0.1027 (6)	0.4150 (6)
C(7)	0.4943 (9)	0.3096 (5)	0.5262 (5)
C(8)	0.540 (1)	0.3349 (8)	0.6445 (6)
C(9)	0.672 (1)	0.2543 (6)	0.6007 (6)
C(10)	0.2048 (7)	0.4104 (5)	0.3741 (4)
C(11)	0.1488 (7)	0.3713 (4)	0.3155 (4)
C(12)	0.1612 (7)	0.4016 (5)	0.2483 (4)
C(13)	0.2336 (8)	0.4613 (5)	0.2468 (4)
C(14)	0.1692 (7)	0.4798 (4)	0.3953 (4)
C(15)	0.0609 (8)	0.5140 (5)	0.3600 (4)
C(16)	0.021 (1)	0.5790 (6)	0.3786 (5)
C(17)	0.091 (1)	0.6127 (6)	0.4334 (5)
C(18)	0.2028 (9)	0.5831 (6)	0.4687 (5)
C(19)	0.2427 (9)	0.5174 (5)	0.4496 (5)
C(20)	0.0322 (7)	0.3277 (5)	0.3175 (4)
C(21)	−0.0074 (8)	0.2712 (5)	0.2746 (4)
C(22)	−0.1102 (9)	0.2302 (5)	0.2816 (5)
C(23)	−0.180 (1)	0.2469 (6)	0.3296 (5)
C(24)	−0.1433 (9)	0.3028 (5)	0.3721 (5)
C(25)	−0.0380 (9)	0.3436 (5)	0.3663 (4)
C(26)	0.0931 (8)	0.3692 (5)	0.1839 (4)
C(27)	−0.0304 (8)	0.3871 (5)	0.1541 (4)
C(28)	−0.086 (1)	0.3586 (5)	0.0913 (5)
C(29)	−0.021 (1)	0.3126 (6)	0.0614 (5)
C(30)	0.097 (1)	0.2916 (6)	0.0902 (5)
C(31)	0.1586 (8)	0.3207 (5)	0.1511 (4)
C(32)	0.2663 (8)	0.5008 (5)	0.1907 (4)
C(33)	0.3705 (9)	0.5457 (5)	0.2068 (5)
C(34)	0.406 (1)	0.5884 (6)	0.1584 (5)
C(35)	0.340 (1)	0.5874 (6)	0.0943 (5)
C(36)	0.237 (1)	0.5452 (6)	0.0765 (5)
C(37)	0.2002 (8)	0.4997 (5)	0.1233 (4)
C(38)	0.530 (1)	0.4277 (8)	0.0635 (7)
C(39)	0.409 (1)	0.3954 (8)	0.0385 (7)

Table III. Selected Bond Distances (Å) for $(Me_2NCS_2)_3W(\eta^2\text{-}C_4Ph_4H)$

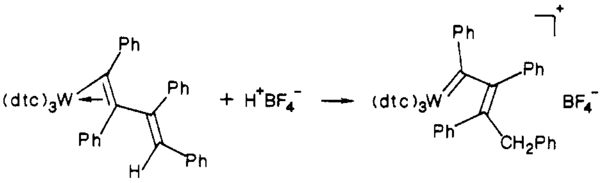
W–S(1)	2.515 (2)	S(5)–C(7)	1.704 (7)
W–S(2)	2.544 (2)	S(6)–C(7)	1.702 (7)
W–S(3)	2.549 (2)	N(1)–C(1)	1.336 (7)
W–S(4)	2.497 (2)	N(2)–C(4)	1.319 (8)
W–S(5)	2.514 (2)	N(3)–C(7)	1.341 (7)
W–S(6)	2.579 (2)	C(10)–C(11)	1.433 (7)
W–C(10)	1.935 (6)	C(10)–C(14)	1.473 (8)
W–C(11)	2.319 (6)	C(11)–C(12)	1.512 (7)
S(1)–C(1)	1.699 (7)	C(11)–C(20)	1.515 (7)
S(2)–C(1)	1.680 (7)	C(12)–C(13)	1.378 (8)
S(3)–C(4)	1.699 (7)	C(12)–C(26)	1.493 (8)
S(4)–C(4)	1.699 (6)	C(13)–C(32)	1.467 (8)

vinyl proton of the unchelated olefin and a low field singlet near 260 ppm in ^{13}C spectra assigned to C_α of the η^2-vinyl ligand. A single-crystal X-ray structure confirmed the existence of three chelating dithiocarbamate ligands and an η^2-vinyl ligand. Atomic positions, selected bond lengths, and selected angles are listed in Tables II through IV, respectively. Important bond distances in the WC_2 unit are $W\text{–}C_\alpha$ 1.935 (6) Å, $W\text{–}C_\beta = 2.319$ (6) Å, and $C_\alpha\text{–}C_\beta =$ 1.433 (7) Å.

Table IV. Selected Bond Angles (deg) for $(Me_2NCS_2)_3W(\eta^2\text{-}C_4Ph_4H)$

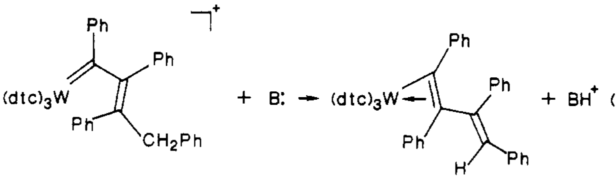
S(1)–W–S(2)	67.38 (6)	S(4)–W–C(11)	89.2 (2)
S(1)–W–S(3)	70.77 (6)	S(5)–W–S(6)	68.49 (5)
S(1)–W–S(4)	137.92 (6)	S(5)–W–C(10)	86.5 (2)
S(1)–W–S(5)	138.66 (6)	S(5)–W–C(11)	119.7 (2)
S(1)–W–S(6)	86.48 (6)	S(6)–W–C(10)	153.3 (2)
S(1)–W–C(10)	108.1 (2)	S(6)–W–C(11)	167.9 (2)
S(1)–W–C(11)	91.2 (1)	C(10)–W–C(11)	38.0 (2)
S(2)–W–S(3)	135.72 (6)	W–C(10)–C(11)	85.6 (4)
S(2)–W–S(4)	149.57 (6)	W–C(10)–C(14)	147.8 (4)
S(2)–W–S(5)	76.04 (6)	C(11)–C(10)–C(14)	126.4 (5)
S(2)–W–S(6)	80.22 (6)	W–C(11)–C(10)	56.3 (3)
S(2)–W–C(10)	85.0 (2)	W–C(11)–C(12)	117.2 (4)
S(2)–W–C(11)	109.8 (2)	W–C(11)–C(20)	115.8 (4)
S(3)–W–S(4)	67.40 (5)	C(10)–C(11)–C(12)	116.4 (5)
S(3)–W–S(5)	133.85 (6)	C(10)–C(11)–C(20)	119.5 (5)
S(3)–W–S(6)	83.51 (6)	C(12)–C(11)–C(20)	117.5 (5)
S(3)–W–C(10)	122.0 (2)	C(11)–C(12)–C(13)	119.2 (5)
S(3)–W–C(11)	84.5 (2)	C(11)–C(12)–C(26)	120.9 (5)
S(4)–W–S(5)	73.89 (6)	C(11)–C(12)–C(26)	120.9 (5)
S(4)–W–S(6)	84.60 (6)	C(13)–C(12)–C(26)	119.8 (6)
S(4)–W–C(10)	97.6 (2)	C(12)–C(13)–C(32)	131.7 (6)

Vinylcarbene. The vinyl-substituted η^2-vinyl complexes react with acid at the free terminal olefin carbon to form vinylcarbene products (eq 9). Structural details of these vinylcarbene complexes are not known, but elemental analyses and ^1H and ^{13}C NMR data define the stoichiometry and carbene character of the $C_4Ph_4H_2$ ligand, respectively.



(9)

The protonation reaction appears to be rapid at 0 °C as judged by the color of the methylene chloride solution which changed from deep red to dark green as tetrafluoroboric acid was added. Recrystallization from CH_2Cl_2/Et_2O yielded dark green crystals of the simple proton addition product in 90% yield. Addition of base to the green cation regenerates the neutral η^2-vinyl reagent (base = pyridine or dithiocarbamate, eq 10).



(10)

Informative NMR features include a singlet at 4.06 ppm that integrates for two protons in the ^1H NMR spectrum and a low-field ^{13}C singlet at 257 ppm which is assigned as the α-carbon of the vinylcarbene ligand. In addition to the methylene ^{13}C signals due to the six ethyl groups of the three dithiocarbamate ligands, a ^{13}C triplet at 46.5 ppm has been assigned as the benzyl methylene group on the vinyl substituent. This ^{13}C signal was correlated with the 4.06 ppm ^1H signal by a heteronuclear 2D NMR experiment. In addition this methylene exhibits slightly smaller $^1J_{CH}$ coupling constants than those of the six ethyl groups (126 Hz for CH_2Ph cf. 140 Hz for NCH_2CH_3). No unique signals were evident for C_β or C_γ of the carbene vinyl group; presumably these resonances appear among the phenyl carbons.

η^4-Butadienyl Sulfide Complexes. Addition of 1 equiv of $Li[Et_3BH]$ to η^4-butadienyl complexes formed a neutral sulfide butadienyl complex, $(dtc)(\eta^4\text{-}C_4Ph_4H)W{=}S$,

Table V. Atomic Positions for $(Et_2NCS_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$

	x	y	z
W	0.48849 (7)	0.37606 (6)	0.28687 (3)
S(1)	0.3521 (4)	0.5198 (3)	0.2975 (2)
S(2)	0.4882 (4)	0.4217 (3)	0.3818 (2)
S(3)	0.6403 (4)	0.4310 (4)	0.2520 (2)
N	0.344 (1)	0.5833 (9)	0.3954 (4)
C(1)	0.388 (1)	0.303 (1)	0.2323 (5)
C(2)	0.324 (1)	0.248 (1)	0.2709 (5)
C(3)	0.390 (1)	0.208 (1)	0.3162 (5)
C(4)	0.519 (1)	0.212 (1)	0.3167 (5)
C(5)	0.371 (1)	0.291 (1)	0.1768 (5)
C(6)	0.384 (1)	0.372 (1)	0.1436 (5)
C(7)	0.377 (1)	0.362 (1)	0.0907 (5)
C(8)	0.358 (1)	0.266 (1)	0.0680 (6)
C(9)	0.343 (1)	0.183 (1)	0.0999 (6)
C(10)	0.347 (1)	0.196 (1)	0.1530 (6)
C(11)	0.189 (1)	0.241 (1)	0.2612 (6)
C(12)	0.123 (1)	0.154 (1)	0.2712 (6)
C(13)	−0.004 (1)	0.147 (1)	0.2641 (5)
C(14)	−0.063 (1)	0.233 (1)	0.2452 (6)
C(15)	−0.006 (1)	0.324 (1)	0.2343 (6)
C(16)	0.120 (1)	0.326 (1)	0.2419 (6)
C(17)	0.324 (1)	0.178 (1)	0.3609 (5)
C(18)	0.348 (1)	0.081 (1)	0.3810 (6)
C(19)	0.288 (2)	0.048 (1)	0.4235 (7)
C(20)	0.212 (1)	0.115 (2)	0.4458 (6)
C(21)	0.184 (1)	0.210 (1)	0.4256 (6)
C(22)	0.246 (1)	0.241 (1)	0.3838 (5)
C(23)	0.611 (1)	0.187 (1)	0.3628 (5)
C(24)	0.590 (1)	0.195 (1)	0.4145 (6)
C(25)	0.683 (1)	0.170 (1)	0.4550 (6)
C(26)	0.786 (1)	0.137 (1)	0.4394 (6)
C(27)	0.813 (1)	0.127 (2)	0.3893 (6)
C(28)	0.723 (1)	0.153 (1)	0.3503 (6)
C(29)	0.387 (1)	0.519 (1)	0.3639 (5)
C(30)	0.256 (1)	0.664 (1)	0.3780 (6)
C(31)	0.314 (2)	0.765 (1)	0.3663 (7)
C(32)	0.378 (1)	0.580 (1)	0.4514 (6)
C(33)	0.296 (2)	0.517 (2)	0.4795 (8)
	Disordered CH_2Cl_2		
Cl(1)	0.0219	0.2114	0.0453
Cl(2)	−0.0262	0.4009	0.0944
Cl(3)	0.890	0.400	0.4282
Cl(4)	0.992	0.494	0.3431
Cl(5)	1.050	0.466	0.366
Cl(6)	0.968	0.420	0.439
Cl(7)	0.914	0.518	0.337
Cl(8)	0.815	0.411	0.396
C(34)	0.062	0.285	0.1013
C(35)	0.892	0.407	0.360
C(36)	0.940	0.359	0.372

reflecting net replacement of one dithiocarbamate ligand by a sulfido ligand (eq 11). A small amount of dithiocarbamate addition to the butadienyl cation was also evident. The crude reaction mixture was chromatographed on alumina with toluene as an eluent. The orange band that eluted was collected and stripped to an oil that contained approximately a 4:1 ratio of $W{=}S(Ph_4C_4H)(S_2CNEt_2)$ and $(S_2CNEt_2)_3W(Ph_4C_4H)$. Slow recrystallization from CH_2Cl_2/hexanes produced pure $(S_2CNEt_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$ in an overall yield of 50%.

$$(\eta^4\text{-}C_4Ph_4H)(Et_2NCS_2)_2W + LiEt_3BH \rightarrow (\eta^4\text{-}C_4Ph_4H)(Et_2NCS_2)W{=}S \quad (11)$$

Distinctive spectroscopic data for this sulfide derivative included a strong infrared absorption at 520 cm^{-1} assigned to the terminal tungsten sulfide stretching mode, a proton NMR singlet at 4.10 ppm with small sidebands indicating coupling to tungsten ($^2J_{WH}$ = 16 Hz), and a low-field ^{13}C NMR signal for the carbene-like α-carbon of the butadienyl ligand at 267.5 ppm.

An X-ray structural determination confirmed the identity of this product. Atomic positions are listed in Table V. Selected bond distances and angles are included in Tables VI and VII, respectively. Important distances are W=S, 2.103 (4) Å, W–C(1), 1.96 (1) Å, W–C(2), 2.47 (1) Å, W–C(3), 2.58 (1) Å, and W–C(4), 2.26 (1) Å. Distances from C(1) to C(4) around the butadienyl carbon skeleton are 1.46 (2), 1.42 (2), and 1.44 (2) Å, respectively. Bonding to the bidentate dithiocarbamate ligand is somewhat unsymmetrical: W–S(1), 2.424 (4) Å; W–S(2), 2.510 (3) Å.

Table VI. Selected Bond Distances (Å) for $(Et_2NCS_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$

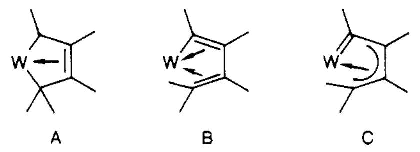
W–S(1)	2.424 (4)	N–C(30)	1.47 (1)
W–S(2)	2.510 (3)	N–C(32)	1.45 (2)
W–S(3)	2.103 (4)	C(1)–C(2)	1.46 (2)
W–C(1)	1.96 (1)	C(1)–C(5)	1.43 (1)
W–C(2)	2.47 (1)	C(2)–C(3)	1.42 (2)
W–C(3)	2.58 (1)	C(2)–C(11)	1.50 (2)
W–C(4)	2.26 (1)	C(3)–C(4)	1.44 (2)
S(1)–C(29)	1.72 (1)	C(3)–C(17)	1.47 (2)
S(2)–C(29)	1.72 (1)	C(4)–C(23)	1.52 (1)
N–C(29)	1.28 (1)		

Table VII. Selected Bond Angles (deg) for $(Et_2NCS_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$

S(1)–W–S(2)	69.7 (1)	C(3)–W–C(4)	33.8 (4)
S(1)–W–S(3)	108.9 (1)	W–C(1)–C(2)	91.8 (8)
S(1)–W–C(1)	97.5 (3)	W–C(1)–C(5)	142 (1)
S(1)–W–C(2)	94.0 (3)	C(2)–C(1)–C(5)	127 (1)
S(1)–W–C(3)	109.0 (3)	W–C(2)–C(1)	52.2 (6)
S(1)–W–C(4)	138.8 (3)	W–C(2)–C(3)	77.9 (8)
S(2)–W–S(3)	114.1 (1)	W–C(2)–C(11)	141.4 (9)
S(2)–W–C(1)	139.4 (4)	C(1)–C(2)–C(3)	119 (1)
S(2)–W–C(2)	104.6 (3)	C(1)–C(2)–C(11)	117 (1)
S(2)–W–C(3)	82.8 (3)	C(3)–C(2)–C(11)	123 (1)
S(2)–W–C(4)	84.5 (3)	W–C(3)–C(2)	69.7 (7)
S(3)–W–C(1)	106.5 (4)	W–C(3)–C(4)	60.9 (6)
S(3)–W–C(2)	139.8 (3)	W–C(3)–C(17)	134.7 (9)
S(3)–W–C(3)	142.0 (3)	C(2)–C(3)–C(4)	116 (1)
S(3)–W–C(4)	110.9 (3)	C(2)–C(3)–C(17)	119 (1)
C(1)–W–C(2)	36.0 (4)	C(4)–C(3)–C(17)	125 (1)
C(1)–W–C(3)	64.6 (4)	W–C(4)–C(3)	85.3 (7)
C(1)–W–C(4)	81.3 (5)	W–C(4)–C(23)	122.2 (8)
C(2)–W–C(3)	32.5 (3)	C(3)–C(4)–C(23)	126 (1)
C(2)–W–C(4)	61.2 (4)		

Discussion

η^2-Vinyl Formation. Protonation of neutral bis(alkyne)bis(dithiocarbamato)tungsten(II) complexes produces η^4-butadienyl ligands. Resonance form A is an acceptable description of this ligand, but other resonances forms are also viable. If one counts the butadienyl ligand as monoanionic, granting that other less common oxidation state formalisms are possible, the ligand protonation effectively oxidizes the metal to tungsten(IV) to form a d^2 monomer.



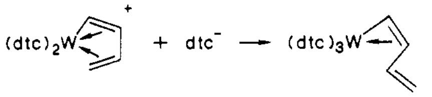
The $[(dtc)_2W(\eta^4\text{-}C_4Ph_4H)]^+$ (dtc = R_2NCS_2) cation counts only 16 electrons at tungsten even with C_β–C_γ bound to the metal. Indeed the cation is electrophilic and rapidly adds a third dithiocarbamate ligand to yield a neutral η^2-vinyl product. The net result is displacement of the olefin tail of the η^4-butadienyl ligand (resonance form B) by the chelating dithiocarbamate. This η^2-vinyl product counts 18 electrons at tungsten, and, again counting the organic unit as a monoanion, a d^2 W(IV) formalism applies. Although we are not aware of other d^2 η^2-vinyl complexes, the molecular orbital correspondence between 4-electron alkyne ligands and η^2-vinyl ligands[17] is com-

Table VIII. Structural Parameters for Mo and W η^2-Vinyl Complexes

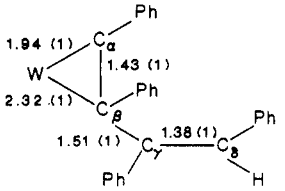
complex	M–C$_\alpha$, Å	M–C$_\beta$, Å	C$_\alpha$–C$_\beta$, Å	ref
$\mathrm{CpMo[P(OMe)_3]_2(\eta^2\text{-}CPhCHPh)}$	1.95	2.30	1.43	*a*
$\mathrm{CpMo[P(OMe)_3]_2(\eta^2\text{-}CBu^tCHPh)}$	1.94	2.29	1.44	1
$\mathrm{CpMo[P(OMe)_3]_2(\eta^2\text{-}CMeCPh_2)}$	1.96	2.25	1.46	1
$\mathrm{(\eta^5\text{-}C_9H_7)Mo[P(OMe)_3]_2(\eta^2\text{-}CSiMe_3CH_2)}$	1.96	2.26	1.44	*b*
$\mathrm{CpMoCl(CF_3C{\equiv}CCF_3)[\eta^2\text{-}CF_3CC(CF_3)(PEt_3)]}$	1.92	2.29	1.43	2
$\mathrm{CpMoCl(CF_3C{\equiv}CCF_3)[\eta^2\text{-}CF_3CC(CF_3)(PEt_3)]}$	1.91	2.32	1.42	2
$\mathrm{CpW(CO)_2[\eta^2\text{-}CF_3CC(CF_3)(C(O)SMe)]}$	1.96	2.19	1.44	*c*
$\mathrm{CpW(CF_3C{\equiv}CCF_3)(SC_6H_4Me)[\eta^2\text{-}CF_3CC(CF_3)(PEt_3)]}$	1.91	2.33	1.45	*d*
$\mathrm{CpW(CF_3C{\equiv}CCF_3)[\eta^3\text{-}CF_3CC(CF_3)(SPr^i)]}$	1.91	2.18	1.42	*e*
$\mathrm{CpW(CF_3C{\equiv}CCF_3)Cl[\eta^2\text{-}CF_3CC(CF_3)(CNBu^t)]}$	1.89	2.30	1.41	*d*
$\mathrm{CpMo(CF_3C{\equiv}CCF_3)[\eta^3\text{-}CF_3CC(CF_3)(NC_5H_4S)]}$	1.91	2.12	1.39	*f*
$\mathrm{(dtc)_3W(\eta^2\text{-}CPh{=}CPh{-}CPh{=}CHPh)}$	1.94	2.32	1.43	this work

[a] Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267. [b] Allen, S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 826. [c] Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2167. [d] Davidson, J. L.; Vasapollo, G.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. [e] Carlton, L.; Davidson, J. L.; Miller, J. C.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1984**, 11. [f] Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlovic-Muir, L.; Muri, K. W. *J. Chem. Soc., Chem. Commun.* **1981**, 1059.

patible with isolation of monomeric d^2 and d^4 η^2-vinyl products to date.



As in the d^4 η^2-vinyl monomers, there is multiple metal–carbon bond character evident to C$_\alpha$ in both spectral and structural parameters. The geometry of the W–C$_\alpha$–C$_\beta$ triangle is the most important feature of the structure.



The 1.94 Å distance for W–C$_\alpha$ is in the double bond range, and the 2.32 Å distance for W–C$_\beta$ is toward the long end of the single bond range.[18] The 1.43, 1.51, and 1.38 Å distances along the C$_\alpha$–C$_\beta$–C$_\gamma$–C$_\delta$ chain show that the π bond of the pendant vinyl group is localized. Data in Table VIII indicate that these η^2-vinyl structural parameters are comparable to geometries of related d^4 η^2-vinyl complexes.

The overall molecular geometry is roughly that of a distorted pentagonal bipyramid with the η^2-vinyl and S(6) occupying the axial positions (Figure 1). Two dithiocarbamates lie nearly within the equatorial plane (S(1)–S(2) and S(3)–S(4)) while atom S(5) lies near the equatorial plane but is tied to the axial S(6). Comparison with (dtc)$_3$M(NO)[19] is instructive. Replacement of the linear NO, a formal 3-electron donor, with η^2-vinyl, also a formal 3-electron donor as a neutral fragment, leaves the basic geometry intact. Metal sulfur distances are bracketed between 2.50 and 2.58 Å with the W–S(6) distance of 2.58 Å significantly longer than the remaining five values. This presumably reflects the trans influence of the η^2-vinyl, particularly the strong bonding of the W–C$_\alpha$ link. Each of the six dithiocarbamate alkyl groups is distinct at room temperature in both ^{1}H and ^{13}C NMR spectra, so no fluxional process is evident in solution.

The conceptual utility of assigning the η^2-vinyl to a single coordination site is that one can build from standard seven-coordinate molecular orbital descriptions to rationalize the η^2-vinyl orientation. In a pentagonal bipyramid there are seven σ^* orbitals which stem from the nine available metal valence orbitals.[20] The two remaining metal orbitals are approximately nonbonding with respect to the σ framework. For a diamagnetic d^2 configuration one of the two d$_\pi$ orbitals, d$_{xz}$ or d$_{yz}$, will be filled, and one will be vacant. Here the anionic η^2-vinyl ligand brings a filled π-donor orbital (the carbon 2p of C$_\alpha$) and a vacant π-acceptor orbital (the π^* of C$_\alpha$–C$_\beta$) in addition to the σ-donor role fulfilled by the C$_\alpha$–C$_\beta$ π bond. The most important complementary metal–ligand π interaction in the coordination sphere is with the sulfur atom trans to the η^2-vinyl, S(6). With the assumption that the W–C$_\alpha$ bond dominates the π interaction, then d$_{yz}$ will be vacant in order to overlap constructively with the filled C$_\alpha$ 2p orbital. It follows that d$_{xz}$ will be filled in order to form a bond by overlap with the C$_\alpha$–C$_\beta$ π^* combination (Figure 2). The π-donor orbital on S(6) lies perpendicular to the plane of the S(5)–S(6) dithiocarbamate ligand, and in order for it to encounter a vacant d$_\pi$ orbital the η^2-vinyl must lie in the same plane as the S(5)–S(6) dithiocarbamate.

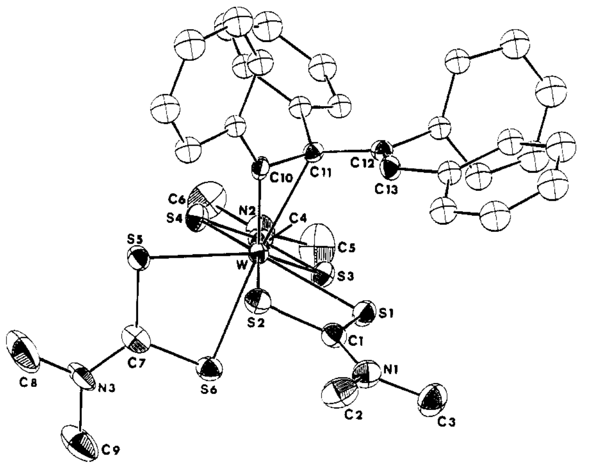


Figure 1. An ORTEP drawing of (Me$_2$NCS$_2$)$_3$W(η^2-CPh=CPhCPh=CHPh).

Vinylcarbene Formation. The neutral tris(dithiocarbamato)(η^2-vinyl)tungsten complex is electron-rich due to the three chelating anionic sulfur donors and the unsaturation in both the free and bound vinyl moieties of the organic ligand. Indeed this complex cleanly adds a single proton to form a cationic product. Several options seem reasonable for the site of protonation: C$_\alpha$ to form buta-

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(17) Brower, D. C.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics*, **1986**, *5*, 94.

(18) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

(19) Brennan, T. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 283.

(20) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511.

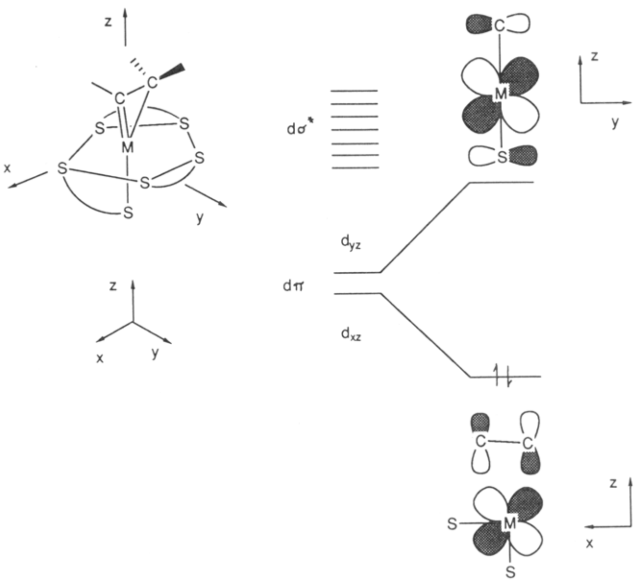
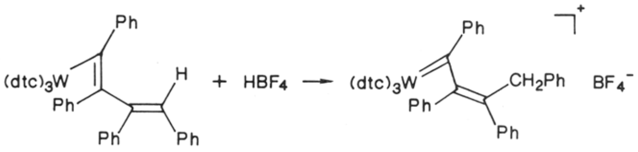
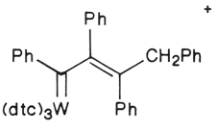


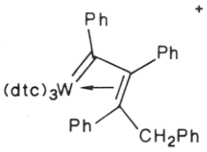
Figure 2. A qualitative molecular orbital scheme rationalizing the d_π orbital splitting pattern.

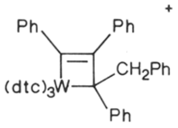
diene, a dithiocarbamate S, the metal center. The presence of a two-proton singlet in the ^{1}H NMR for the cationic product, in addition to phenyl and dithiocarbamate resonances, indicated equivalence of the two key protons on the NMR time scale. Only after correlation of the δ 4.06 ^{1}H signal with a carbon-13 resonance at 46.5 ppm which appeared as a triplet in the gated decoupled ^{13}C NMR spectrum were we confident of the presence of a methylene group due to protonation of the terminal olefin carbon.



We do not know if the vinylcarbene is bound in an η^3 or an η^1 fashion. The carbon-13 signals of the two vinyl carbons are not observed outside of the phenyl carbon range; they probably lie between 125 and 132 ppm. For Mayr's η^3-vinylcarbene the vinyl carbons resonate at 123 and 91 ppm[7] while Schrock's η^1-vinylcarbene exhibits ^{13}C vinyl resonances at 187 and 104 ppm.[8] The C_α chemical shift of 257 ppm indicates that a metallacyclobutene formulation (F) is inappropriate relative to carbene formulations (D and E).


D


E


F

The equivalence of the two methylene protons and two of the three dithiocarbamate ligands on the NMR time scale at room temperature suggested that a fluxional process might be responsible for the effective mirror symmetry; most static geometries would create diastereotopic methylene protons. Indeed the ^{1}H NMR at −90 °C consists of six separate signals for the dithiocarbamate alkyl groups and an AB pattern for the benzyl protons (J_{AB} = 14 Hz). Low-temperature line broadening and a coalescence temperature of −45 °C for the benzyl protons indicated a barrier of 10.5 kcal/mol for the rearrangement. The barrier could reflect dechelation of the olefin tail and swinging it to the other side prior to recoordinating, or it could reflect the barrier to rotation of the plane of the carbene ligand with the olefin never bound to the metal.

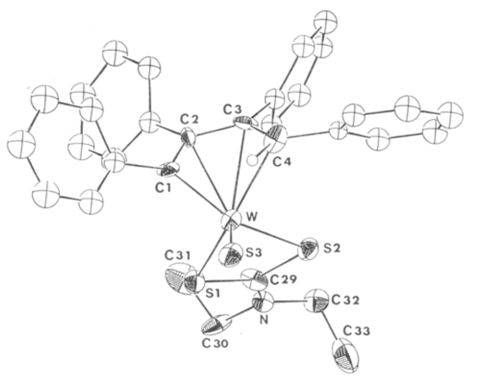
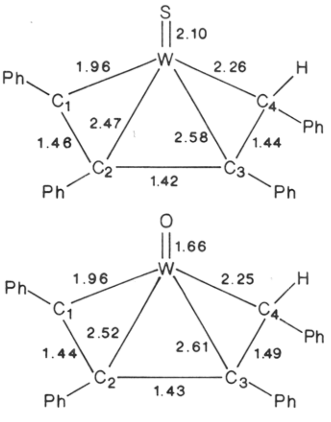


Figure 3. An ORTEP drawing of $(Et_2NCS_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$.

η^4-Butadienyl Retention. In an effort to reduce the butadienyl ligand we added $LiEt_3BH$ to $[(dtc)_2W(\eta^4\text{-}C_4Ph_4H)][BF_4]$. After workup the major product was identified as $(dtc)(\eta^4\text{-}C_4Ph_4H)W{=}S$, a sulfide analogue of the oxo derivative prepared previously.[11] We have no mechanistic information, but a dithiocarbamate ligand must be the source of sulfide in this reaction.

Spectral data for $(dtc)(\eta^4\text{-}C_4Ph_4H)W{=}S$ is reminiscent of the $(dtc)(\eta^4\text{-}C_4Ph_4H)W{=}O$ isomer which was structurally characterized (^{1}H δ 4.09, J_{WH} = 15 Hz for the sulfide cf. ^{1}H δ 4.05, J_{WH} = 21 Hz for the oxo analogue).

The two structures are congruent in molecular geometries as expected (see Figure 3). The tungsten η^4-butadienyl distances (in Å) are reproduced graphically below.



Delocalization of the ring π system is evident in the carbon–carbon bond lengths. The difference in W–S bond lengths to the dithiocarbamate sulfurs reflects the higher trans influence of the carbene like C(1) (trans to S(2) with W–S(2) 2.51 Å) compared to C(4) (trans to S(1) with W–S(1) 2.42 Å).

The overall geometry is that of a square pyramide if C(3) and C(4) are neglected in defining the tungsten coordination sphere, or a distorted octahedron can be visualized with the site trans to the terminal sulfide occupied by the olefinic C(2)–C(3) bond. The W–C(2) and W–C(3) distances of 2.47 and 2.58 Å are beyond normal single bond lengths. Curtis has recently argued that the folding of C_β and C_γ toward molybdenum in a metallacyclopentatriene, $CpClMo(C_4Ph_4)$, reflects relief of antibonding interactions rather than constructive overlap between the metal and these β-carbons which lie 2.35 and 2.36 Å from the metal center.[21] The 1.96 Å W–C_α bond length here is repre-

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[21] Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218.

sentative of tungsten–carbon double bonds.

Summary. Three aspects of these results deserve mention here. First, the formation of carbene complexes has been achieved by acidification of a bis(alkyne) precursor. Plausible routes to metal carbenes to form active catalysts are sometimes elusive, but from this work it is clear that simple protonation of unsaturated organic ligands can lead to carbene complexes. Second, interconversion of butadienyl, η^2-vinyl, and vinylcarbene ligands has been easily accomplished with only ligand addition reactions and acidification. Third, the ability of these unsaturated carbene ligands to provide additional electron density to the metal from the organic π system as evident in the ground-state properties of these molecules will no doubt be important in stabilizing electron-deficient intermediates along reaction coordinates containing related C_nR_{n+1} ligands.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research.

Supplementary Material Available: ORTEP drawings showing complete atomic numbering and tables of anisotropic temperature factors, isotropic temperatures factors, complete bond distances and angles, calculated hydrogen positions, and planes and dihedral angles for $(Me_2NCS_2)_3W(\eta^2\text{-}C_4Ph_4H)$ and $(Et_2NCS_2)(\eta^4\text{-}C_4Ph_4H)W{=}S$ (16 pages); listings of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of the Thermal Rearrangement of Some (Chloromethyl)silanes

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Kinetics have been measured for the gas-phase pyrolysis of a series of eight aryl-substituted (chloromethyl)silanes in a stirred flow reactor. These compounds undergo unimolecular rearrangements involving chloro migration to form chlorosilanes with concomitant migration of a group from silicon to carbon; the ease of migration is H > Ar > Me. The kinetic results indicate that the rearrangements are probably concerted in the gas phase.

Introduction

There have been two recent gas-phase kinetic studies of the thermal isomerization of (chloromethyl)dimethylsilane.[1,2] Both studies found that the main reaction was a clean unimolecular isomerization to form trimethylchlorosilane, accompanied by a minor radical chain sequence; the latter could be suppressed by added propene,[1] or by choice of pyrolysis conditions (eq 1).[2] The unimo-

$$(CH_3)_2Si(CH_2Cl)H \xrightarrow{\Delta} \underset{\text{major}}{(CH_3)_3SiCl} \tag{1}$$

lecular isomerization, involving migration of chlorine from carbon to silicon and migration of hydrogen from silicon to carbon, is an example of a dyotropic rearrangement. This was originally envisaged by Reetz as a fully concerted process with a doubly bridged transition state,[3] but Bassindale, Brook, et al. concluded from their studies of the thermal rearrangement of a number of α-substituted silanes that α-halo and α-acetoxy silanes followed a stepwise mechanism.[4] They suggested that the first step for α-halo silanes was the formation of a three-center transition state in which the halogen atom bridged between carbon and silicon giving an "inverse ylid" with a $\delta-$ charge on silicon and a $\delta+$ charge on carbon. Subsequently, rapid migration of a group attached to silicon took place. A similar mechanism for α-acetoxy silanes may operate.[4,5] We now report kinetic studies designed to probe both the extent to which rearrangement of (chloromethyl)silanes may be concerted in the gas phase and the charge distribution in the transition state.

Results

We have pyrolyzed and studied the kinetics of eight aryl-substituted (chloromethyl)silanes, $ArMeSi(CH_2Cl)Y$ (Ar equals X–Ph with X = H, *p*-F, *p*-Me, and *m*-CF_3 and Y = H and Me). Kinetic measurements were made in a stirred flow (SFR) apparatus with analysis by gas chromatography; products were identified by pyrolyses in a similar SFR apparatus attached to a GC/mass spectrometer (HP5995C). Both types of apparatus and the procedure for measuring kinetics have been fully described.[6,7]

The main reaction of the four compounds with Y = H was formation of a chlorosilane, with migration of chlorine from carbon to silicon and migration of hydrogen from silicon to carbon, in a manner analogous to the pyrolysis of (chloromethyl)dimethylsilane (eq 2).[1,2] Migration of

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[†] The University.

[‡] University of Colorado at Denver.

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[2] Davidson, I. M. T.; Ijadi-Maghsoodi, S. *Organometallics* **1986**, *5*, 2086.

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