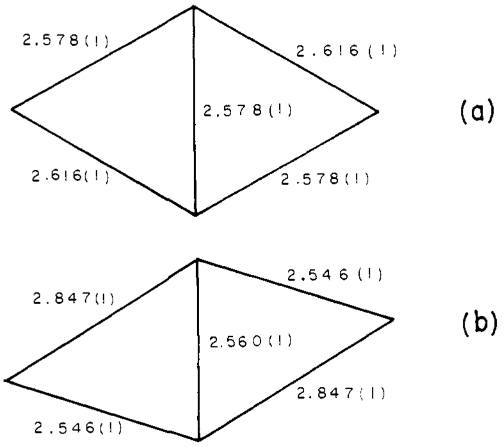

Figure 7. The Mo–Mo distances in the two Mo_4 clusters found in Torardi and McCarley's $Ba_{1.13}Mo_8O_{16}$.

for Mo–Mo bonding according to the formula given. Torardi and McCarley propose to consider one of the clusters a 10-electron species and the other an 8.26-electron species. On the basis of our work we would not necessarily disagree with this, but would only remark that perhaps the slight distortion of the more symmetrical cluster implies that it has slightly less than 10 electrons, with the other one having slightly more than 8.26 electrons. However, we do not at all insist on this notion since the very small distortion in the first one, even though it has the correct form for a Jahn–Teller distortion, may well have some other cause.

The preliminary values of the Mo–O bond lengths available to us when this manuscript was written[14,15] were not of sufficient precision or apparent accuracy to warrant a consideration of the possible role of Mo–O π bonding in the deformation process. Professor R. E. McCarley has subsequently informed us that the final values, which have esd's of 0.006 Å, lead him to conclude that the distortion from the 10-electron to the 8-electron cluster structure is probably aided by an increase in the strength of two Mo–O π bonds that tends to offset the decrease in the strength of the two opposite Mo–Mo bonds that become elongated. The two Mo–O bond lengths in question change from 2.022 (6) Å to 1.894 (6) Å on going from the undistorted to the distorted cluster. We are entirely in agreement with this suggestion.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. $W_4(OC_2H_5)_{16}$, 78166-59-3.

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Electrophilic Attack on a Metal Alkynyl by Carbon Disulfide: Preparation and Structure of $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$, a Cationic Vinylidene Complex

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Abstract: The electron-rich metal alkynyl complex $[Fe(C{\equiv}CMe)(dppe)(Cp)]$ ($Fp'C{\equiv}CMe$, I) undergoes (2 + 2) cycloaddition with carbon disulfide to form $[Fe(\overline{C{=}CMeC(S)S})(dppe)(Cp)]$ (II) containing a 2*H*-thiete-2-thione functional group. This CS_2 adduct is subsequently alkylated by iodomethane to yield $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$ (III), a cationic vinylidene complex. The products were investigated by spectroscopic means and, in the case of III, by an X-ray crystal structure analysis: space $P2_1/c$, $a = 11.625$ (3) Å, $b = 20.609$ (4) Å, $c = 15.490$ (2) Å, $\beta = 103.25$ (2)°, $V = 3612.4$ Å^3, $Z = 4$, $\rho(\text{calcd}) = 1.487$ g·cm^{-3}. Refinement on 2552 reflections with $F^2 \geq 3\sigma(F^2)$ yielded the final discrepency indices $R = 0.058$ and $R_w = 0.070$. The substituted vinylidene ligand of complex III is bonded to the iron atom by a very short Fe–C bond, 1.74 (2) Å, and the Fe–C1–C2 bond angle is nearly linear, 176 (1)°. Spectroscopic and structural evidence suggest that 2-(dithiocarbomethoxy)propenylidene is a very large strong π-acid ligand.

Electron-rich transition-metal alkynyl complexes react with protic acids or alkylating agents to form cationic metal vinylidene complexes.[1] This behavior is attributed to a buildup of electron density on the alkynyl β-carbon atom by back-bonding from filled metal orbitals, resulting in nucleophilic character at that carbon atom. A few instances of additions of more complex electrophiles[2] to metal alkynyls have been reported, involving addition of tetracyanoethylene or hexafluoroacetone to $[Fe(C{\equiv}CPh)(CO)_2(Cp)]$, $[Fe(C{\equiv}CPh)(CO)(PPh_3)(Cp)]$,[3] and $[Ru(C{\equiv}CPh)(PPh_3)_2(Cp)]$.[4]

Carbon disulfide is an unsaturated electrophile with an extensive organic and organometallic chemistry.[5] Typically, CS_2 reacts with metal alkyls or hydrides by insertion, forming dithio-

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carboxylate or dithioformate complexes. A new mode of reactivity of CS_2 with an electron-rich metal alkynyl complex is reported here, along with the structural characterization of the metal vinylidene complex formed by methylation of the resulting CS_2 adduct.

Experimental Section

General Procedures and Starting Materials. All operations involving the handling of organometallic complexes in solution were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Solvents were distilled from appropriate drying and deoxygenating agents and stored under nitrogen. Carbon disulfide was purified by passage through activated alumina and trap-to-trap distillation. $[Fe(C{\equiv}CMe)(dppe)(Cp)]$ $(Fp'C_2Me)$[6] was prepared by the published method.[7] Other reagents were used as received from commercial sources.

^1H NMR spectra were obtained on a Hitachi Perkin-Elmer R22 spectrometer (90 MHz) or a JEOL FX60Q spectrometer (59.75 MHz, FT mode). ^{13}C NMR spectra were obtained on a JEOL FX60Q spectrometer (15 MHz, FT mode) and are referenced to internal Me_4Si (positive shifts are downfield). Infrared spectra were obtained on a Perkin-Elmer 457A spectrometer with a polystyrene reference. UV/visible spectra were obtained on a Cary 17 spectrophotometer. Mass spectra were obtained on a CEC 21-110 spectrometer (high resolution). Melting points were determined on samples sealed in evacuated capillaries and are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

Preparation of $[Fe(\overline{C{=}CMeC(S)S})(dppe)(Cp)]$ (II). One gram (1.79 mmol) of $Fp'C_2Me$ was placed in a 35-mL flask, and 20 mL of ethyl ether and 1 mL of CS_2 were added by cannula. The mixture was magnetically stirred for 6 h at room temperature. The resulting deep purple microcrystalline precipitate was filtered, washed with ether and pentane, and dried in vacuo. The reaction is virtually quantitative (ca. 1.1 g; mp >130 °C slow dec, 161–163 °C). Recrystallization from most solvent systems produces solvates of varying stoichiometry.

Anal. Calcd for $Fp'C_2Me{\cdot}CS_2{\cdot}{}^1/_2CH_2Cl_2$ $(C_{35.5}H_{31}ClFeP_2S_2)$ from CH_2Cl_2/hexane: C, 62.50; H, 5.48; P, 9.10; S, 9.42. Found: C, 62.91; H, 5.41; P, 9.34; S, 8.69. Anal. Calcd for $Fp'C_2Me{\cdot}CS_2{\cdot}C_6H_6$ $(C_{41}H_{38}FeP_2S_2)$ from benzene/heptane/CS_2: C, 69.10; H, 5.37; P, 8.69, S, 8.92. Found: C, 68.24; H, 5.45; P, 8.60; S, 8.92. IR (Kel-F and Nujol mulls): 3045 (w), 2955 (w), 2930 (w), 1585 (w), 1480 (w), 1455 (w), 1436 (w, sh) 1275 (vs, br), 1180 (m), 1120 (w), 1095 (m), 1065 (w, br), 1015 (m), 1000 (w), 980 (w), 865 (w), 842 (m), 828 (m), 790 (w), 747 (m), 723 (w), 700 (s), 657 (s), 618 (w), 530 (s), 490 (m), 442 (m) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, freshly prepared): δ 8.0–7.0 (m, 20 H, Ph), 4.45 (s, 5 H, Cp), 3.2–2.3 (br m, 4 H, PCH_2), 0.90 (s, 3 H, CH_3). ^1H NMR (59.75 MHz, $(CD_3)_2CO$, FT): δ 7.76, 7.40 (m, Ph), 4.49 (s, Cp), 3.00 (d, J_{PH} = 9.8 Hz, PCH_2), 0.99 (s, CH_3). UV/vis (MeCN): λ_{max} = 564 nm (ϵ = 9420), 402 (8810), intense UV absorption.

Thermal Decomposition of $Fp'C_2Me{\cdot}CS_2$ (II). $Fp'C_2Me{\cdot}CS_2$ (0.110 g, 0.173 mmol), 30 mL of benzene, and 5 mL of heptane were heated to reflux in a stream of nitrogen for 20 min with magnetic stirring. About 5 mL of solvent remained. This was filtered while hot and slowly reduced in volume in a stream of nitrogen while the mixture was cooled. The resulting red solid was characterized as pure $Fp'C_2Me$ by ^1H NMR and IR ($\nu(C{\equiv}C)$ = 2100 cm^{-1}) spectra.

Preparation of $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$ (III). $Fp'C_2Me{\cdot}CS_2$ (0.64 g, 1.01 mmol) was dissolved in 20 mL of CH_2Cl_2, and 0.10 mL (0.23 g, 1.6 mmol) of iodomethane was added by syringe. The color changed from deep red-purple to deep yellow within ca. 15 min. After 3 h of stirring, the volatiles were removed in vacuo. The yellow-brown residue was dissolved in a warm mixture of methanol (10 mL), dichloromethane (4 mL), and a few drops of iodomethane and the mixture was filtered. Slow reduction in volume and subsequent cooling to −15 °C produced deep yellow-brown crystals (0.52 g, 0.65 mmol, 64% yield) which were washed with methanol/ethyl ether (1/1) and ethyl ether and dried in vacuo (mp 171–177 °C dec).

Anal. Calcd for $C_{37}H_{39}FeIOP_2S_2$: C, 54.96; H, 4.86; P, 7.66; S, 7.93. Found: C, 54.88; H, 4.86; P, 7.44; S, 7.63. IR (Kel-F and Nujol mulls): 3338 (s), 3100 (w), 3078 (w), 3023 (w), 2930 (w), 2905 (m), 1975 (vw), 1900 (vw), 1825 (vw), 1675 (w), 1550 (vs), 1485 (m), 1438 (s), 1425 (m), 1400 (w), 1383 (w), 1359 (m, sh), 1313 (w), 1190 (s), 1140 (w), 1095 (m), 1079 (m), 1030 (m), 1021 (s), 1010 (s), 967 (w), 921 (w), 890 (w), 865 (m), 832 (w), 815 (m), 755 (m), 749 (m), 730 (w), 722 (m), 700 (s), 680 (m), 660 (w), 611 (w), 540 (s), 530 (m). 497 (m), 445 (w), 402 (w) cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 7.8–6.9 (m, 20 H, Ph), 5.37 (t, $^3J_{PH}$ = 0.8 Hz, 5 H, Cp), 3.40 (s, 3 H, CH_3OH), 3.10 (d, $^2J_{PH}$ = 13.0 Hz, 4 H, PCH_2), 2.18 (s, 3 H, SCH_3), 1.45 (br s, 3 H, CH_3). ^{13}C NMR (15 MHz, $CDCl_3$): δ_c 364.5 (t, $^2J_{PC}$ = 32.2 Hz, C_α), 218.2 (t, $^3J_{PC}$ = 2.9 Hz, C=S), 144.7 (s, C_β), 136.2–128.3 (m, Ph), 90.2 (s, Cp), 49.7 (s, CH_3OH), 27.9 (t, $^1J_{PC}$ = 22.7 Hz, PCH_2), 18.2 (s, SCH_3), 13.4 (s, CH_3). UV/vis (CH_3CN): δ_{max} = 368 nm (ϵ = 6700), 415 (4900), intense UV absorption.

Table I. Crystal Parameters at 25 °C for the X-ray Diffraction Study of $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$

space group	$P2_1/c$
a	11.625 (3) Å
b	20.609 (4) Å
c	15.490 (2) Å
β	103.25 (2)°
V	3612.4 Å^3
Z	4
mol wt	808.57
ρ(calcd)	1.487 g·cm^{-3}

Table II. Bond Distances (Å) with Errors for $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$

Fe–P1	2.217 (4)	CB1–CB2	1.56 (2)
Fe–P2	2.231 (4)	C11–C12	1.38 (2)
Fe–C1	1.74 (2)	C12–C13	1.41 (2)
Fe–CP1	2.13 (1)	C13–C14	1.37 (2)
Fe–CP2	2.11 (1)	C14–C15	1.35 (2)
Fe–CP3	2.15 (1)	C15–C16	1.45 (2)
Fe–CP4	2.15 (1)	C16–C11	1.42 (2)
Fe–CP5	2.13 (2)	C21–C22	1.38 (2)
P1–CB1	1.85 (1)	C22–C23	1.45 (2)
P1–C11	1.83 (1)	C23–C24	1.36 (2)
P1–C21	1.80 (1)	C24–C25	1.38 (2)
P2–CB2	1.86 (1)	C25–C26	1.46 (2)
P2–C31	1.82 (1)	C26–C21	1.45 (2)
P2–C41	1.80 (1)	C31–C32	1.42 (2)
S1–C4	1.73 (2)	C32–C33	1.42 (2)
S1–C5	1.31 (2)	C33–C34	1.38 (2)
S2–C4	1.66 (2)	C34–C35	1.40 (2)
C1–C2	1.31 (2)	C35–C36	1.38 (2)
C2–C3	1.55 (2)	C36–C31	1.41 (2)
C2–C4	1.48 (2)	C41–C42	1.42 (2)
CP1–CP2	1.40 (2)	C42–C43	1.46 (2)
CP2–CP3	1.47 (2)	C43–C44	1.37 (2)
CP3–CP4	1.42 (2)	C44–C45	1.33 (2)
CP4–CP5	1.42 (2)	C45–C46	1.46 (2)
CP5–CP1	1.48 (2)	C46–C41	1.40 (2)
		O–CM	1.51 (2)

Crystal Preparation and Data Collection for $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$ (III). Single crystals were obtained by recrystallization from dichloromethane/methanol. A crystal of approximate dimensions 0.10 mm × 0.15 mm × 0.40 mm was coated with epoxy and mounted on a glass fiber, nearly aligned along the long axis of the crystal. All diffraction measurements were performed by using an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. The unit cell was initially determined from 25 randomly located reflections and subsequently refined from 25 high-angle reflections by using the CAD-4 center, index, and least-squares routines. Crystal data are listed in Table I.

Data with $F^2 \geq 3\sigma(F^2)$ were used in the solution and refinement of the structure. The value of the P factor used in calculating $\sigma(F^2)$ was 0.02. Three standard reflections monitored during data collection showed only random fluctuations in intensity. The calculated linear absorption coefficient was 15.21 cm^{-1}. An empirical absorption correction (CAMEL) based on scans of 12 reflections taken at 15° increments on θ was applied.[8]

Solution and Refinement of the Structure. All calculations were performed on an IBM 370 computer system using local versions of Ibers' NUCLS least-squares program (based on the Busing-Levy ORFLS), Zalkin's FORDAP Fourier program, the Busing-Levy ORFFE error function program, the absorption correction program CAMEL, and Johnson's ORTEP thermal

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[6] Abbreviations used: Cp = (η^5-C_5H_5); dppe = 1,2-bis(diphenylphosphino)ethane; Fp' = [Fe(dppe)(Cp)].

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Table III. Selected Bond Angles (Deg) with Errors for [Fe(C$_2$MeCS$_2$Me)(dppe)(Cp)]I·MeOH

P1–Fe–P2	86.2 (1)	P1–C11–C12	124 (1)
P1–Fe–C1	85.6 (4)	P1–C11–C16	115.7 (9)
P2–Fe–C1	95.8 (4)	C16–C11–C12	120 (1)
Fe–P1–CB1	105.4 (4)	C11–C12–C13	120 (1)
Fe–P1–C11	121.5 (4)	C12–C13–C14	122 (1)
Fe–P1–C21	116.9 (4)	C13–C14–C15	120 (1)
CB1–P1–C11	101.4 (6)	C14–C15–C16	121 (1)
CB1–P1–C21	105.8 (6)	C15–C16–C11	117 (1)
C11–P1–C21	103.8 (6)	P1–C21–C22	118 (1)
Fe–P2–CB2	108.8 (5)	P1–C21–C26	120 (1)
Fe–P2–C31	117.7 (4)	C26–C21–C22	122 (1)
Fe–P2–C41	115.6 (5)	C21–C22–C23	119 (1)
CB2–P23–C31	104.4 (7)	C22–C23–C24	120 (1)
CB2–P2–C41	107.7 (6)	C23–C24–C25	122 (1)
C31–P2–C41	101.7 (6)	C24–C25–C26	122 (1)
C4–S1–C5	107.8 (9)	C25–C26–C21	116 (1)
Fe–C1–C2	176 (1)	P2–C31–C32	120 (1)
C1–C2–C3	122 (1)	P2–C31–C36	121 (1)
C1–C2–C4	120 (1)	C36–C31–C32	119 (1)
C3–C2–C4	118 (1)	C31–C32–C33	120 (1)
C2–C4–S1	115 (1)	C32–C33–C34	120 (1)
C2–C4–S2	124 (1)	C33–C34–C35	119 (1)
S1–C4–S2	121 (1)	C34–C35–C36	122 (1)
CP5–CP1–CP2	108 (1)	C35–C36–C31	119 (1)
CP1–CP2–CP3	109 (1)	P2–C41–C42	119 (1)
CP2–CP3–CP4	107 (1)	P2–C41–C46	121 (1)
CP3–CP4–CP5	110 (2)	C46–C41–C42	120 (1)
CP4–CP5–CP1	107 (2)	C41–C42–C43	119 (1)
P1–CB1–CB2	105.6 (9)	C43–C44–C45	125 (2)
P2–CB2–CB1	108.0 (9)	C44–C45–C46	118 (1)
		C45–C46–C41	120 (2)

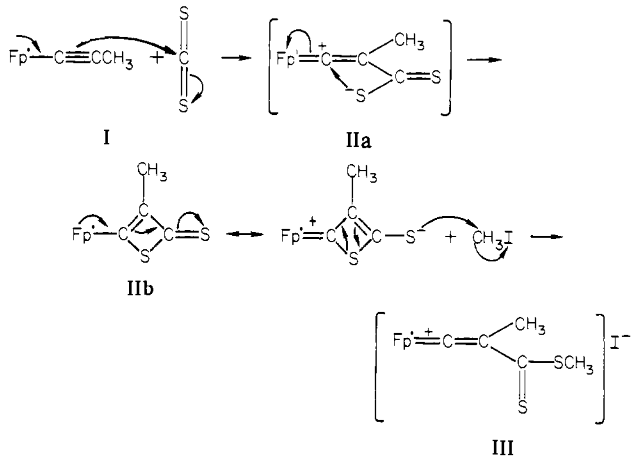
ellipsoid plotting program. Anomalous dispersion corrections were included for the scattering of I, Fe, S, and P atoms. Least-square refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F_o)^2$. The positions of the iron and iodine atoms were determined from a Patterson map, and other atom positions were obtained by successive difference Fourier techniques. Full-matrix least-squares refinements usng anisotropic temperature factors for all atoms except the carbon atoms of the four phenyl rings, which were isotropic, converged to the final residuals $R = 0.058$ and $R_w = 0.070$. The largest residual peak in the final difference Fourier synthesis was 0.8 e·Å^{-3}, corresponding in position to a "ripple" on the iodine atom. Seventeen of the expected thirty-nine hydrogen atoms could be located in the final difference Fourier, but these were not included in the refinement. The largest shift of a positional parameter on the final cycle was 0.017 Å (shift/error = 1.30); the largest shift of a temperature factor was 0.000 15 (shift/error = 1.27). Final positional and thermal parameters are listed in Table II. Bond distances and angles with errors obtained on the final cycle of refinement are listed in Table II and III. Tables of experimental parameters for data collection (Table V), positional and thermal parameters (Table VI), least-squares planes (Table VII), and observed and calculated structure factors (Table VIII) are available as supplementary material.

Results

Preparation of the Complexes. The electron-rich alkynyl complex Fp′C≡CMe (I) reacts quantitatively with carbon disulfide, in neat or ethyl ether solution, to form a 1:1 adduct (II). This CS$_2$ adduct is an air-stable, deep red-purple solid, poorly soluble in most polar and nonpolar solvents. It is appreciably soluble in dichloromethane and chloroform, but gradual decomposition to uncharacterized products occurs in these solvents. The adduct II gradually dissolves in refluxing benzene/heptane to give a red-brown soltuion from which Fp′C≡CMe (I) can be recovered in 80% yield. Similarly, attempts to obtain a mass spectrum of Fp′C$_2$Me·CS$_2$ (II) result in a spectrum of its alkynyl precursor (I) (M$^+$ calcd *m*/*e* 558.1247, found, *m*/*e* 558.1265). Thus, CS$_2$ addition is thermally reversible in both solution and the solid state.

The CS$_2$ adduct II reacts with electrophiles, e.g., iodomethane, tetrafluoroboric acid, and [W(CO)$_5$(py)] (py = pyridine). Only the iodomethane adduct has been fully characterized. This methylated complex (III) is a deep yellow, air-stable solid which readily crystallizes as 1:1 methanol solvate. The iodide counterion of III can be exchanged by using aqueous NH$_4$BF$_4$ or NH$_4$PF$_6$ in ethanol or methanol.

Scheme I



Fp′ = (C$_5$H$_5$)(dppe)Fe

Spectroscopic Properties of the Complexes. The complex Fp′C$_2$Me·CS$_2$ (II) may be formulated in either an open (IIa) or a closed (IIb) form (see Scheme I). The open form (IIa) is expected to resemble a dithiocarboxylate or, better, PEt$_3$·CS$_2$ which has been structurally characterized as a phosphonium dithiocarboxylate zwitterion.[9] On the other hand, the closed form (IIb) is a *β*-dithiolactone (2*H*-thiete-2-thione) which should show properties consistent with the presence of a thiocarbonyl moiety. A strong infrared absorption at 1275 cm^{-1} is at a slightly higher frequency than that of most thiones and thioesters (1190–1250 cm^{-1}),[10] but much higher than the dithiocarboxylate absorption of Me$_3$P·CS$_2$ (1044 cm^{-1}).[11] This elevated thiocarbonyl vibration frequency may be attributed to ring strain in the four-membered *β*-dithiolactone ring (cf., Me$_2$=CCH$_2$SC=S with infrared absorptions at 1235 and 1160 cm^{-1}).[12] An absorption at 1585 cm^{-1} in the IR spectrum of II is attributed to *ν*(C=C) for the cycloalkene moiety, lowered by ring strain and by conjugation with the thiocarbonyl group.[13] The electronic absorption spectrum of II resembles that of *α*-dithiopyrone (S=CSCH=CHCH=CH, λ_{max} = 436, 587 nm vs. 402, 564 nm for II).[14] No previous report of a 2*H*-thiete-2-thione has been found in the literature for comparison.[15] The ^{1}H NMR spectrum of II lends further support to the closed formulation IIb. The position of the cyclopentadienyl resonance (*δ* 4.45) is nearer to that of an uncharged [Fe(dppe)(Cp)] complex (cf. *δ* 4.28 for I)[7] than to that of a cationic complex (cf. *δ* 5.08 for [Fe(CO)(dppe)(Cp)][PF$_6$]).[16] All satisfactory Lewis structures for the open form IIa place a positive charge on the iron atom, whereas the closed form IIb has contributing resonance forms with the iron center both charged and uncharged (Scheme I). Thus, the intermediate position of the C$_5$H$_5$ resonance lends support to the closed form IIb. The low solubility of Fp′C$_2$Me·CS$_2$ in most organic solvents precludes ^{13}C NMR spectra. Overall, spectroscopic evidence favors closed formulation IIb for Fp′C$_2$Me·CS$_2$,

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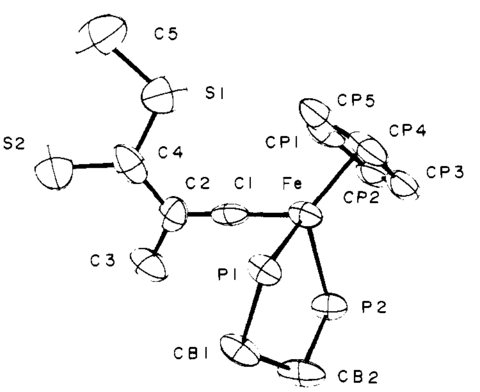

Figure 1. An ORTEP diagram of the central coordination sphere of the $[Fe(C_2MeCS_2Me)(dppe)(Cp)]^+$ cation showing 50% probability ellipsoids. The phenyl groups have been omitted for clarity.

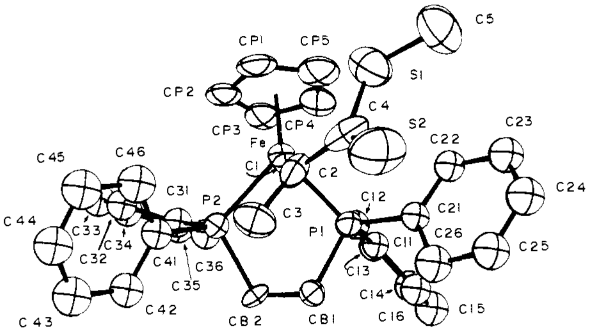

Figure 2. An ORTEP diagram of the $[Fe(CS_2MeCS_2Me)(dppe)(Cp)]^+$ cation showing 50% probability ellipsoids. Phenyl groups are included and the orientation of the vinylidene ligand is emphasized.

although IIa or a dimeric or polymeric form cannot be ruled out. We have thus far been unable to obtain crystals of II suitable for a definite X-ray diffraction study.

Spectroscopic measurements on $Fp'C_2Me{\cdot}CS_2{\cdot}MeI{\cdot}MeOH$ (III) support an "open" methyl(dithiocarbomethoxy)vinylidene formulation in solution, consistent with its solid-state structure (vide infra). The ^{13}C NMR spectrum defines an "alkylidene" carbon (δ_C 364.5)[17] and a thiocarbonyl carbon (δ_C 218.2).[18] A strong infrared absorption at 1190 cm^{-1} may be assigned to the thiocarbonyl stretch,[10] and a medium intensity band at 1550 cm^{-1} is assigned to the vinylidene C═C stretch, lowered from the usual frequency range at 1600–1700 cm^{-1} (cf. 1675 cm^{-1} for $[Fe(C{=}CMe_2)(dppe)(Cp)]^+$)[1a] by the strongly electron-withdrawing dithioester substituent. The electronic absorption spectrum of III (415, 368 nm) is typical of a dithioester.[19] The low field positions of the cyclopentadienyl resonances in the proton and carbon NMR spectra of III (δ_H 5.37, δ_C 90.2) indicate that the 2-(dithiocarbomethoxy)propenylidene ($C{=}CMeCS_2Me$) ligand is the most strongly electron-withdrawing ligand we have encountered in a [Fe(dppe)Cp)] complex, even more so than propenylidene ($C{=}CHMe$) or neopentylidene ($CHCMe_3$) ligands (δ_H(Cp) 5.30 and 5.28, δ_C(Cp) 89.5 and 87.6, respectively).[1a,20]

Description of the Structure of $[Fe(C_2MeCS_2Me)(dppe)(Cp)]I{\cdot}MeOH$ (III). The molecular structure of the organometallic cation of compound III is illustrated in Figures 1 and 2. Figure 1 emphasizes the central coordination sphere of the iron atom, which contains a nearly symmetrically bonded η^5-cyclopentadienyl ring, the phosphorus atoms of a chelating 1,2-bis(diphenylphosphino)ethane ligand, and the carbon atom (C1) of a 2-(dithiocarbomethoxy)propenylidene ligand which is the feature of primary interest. The iron–carbon bond has a formal bond order of 2, and its shortness (1.74 (2) Å) supports this view. The carbon–carbon double bond of the vinylidene ligand is 1.31 (2) Å long, typical of an allene $C(sp^2)$—C(sp) bond (cf. 1.31 Å for $CH_2{=}C{=}CH_2$).[21] The iron–vinylidene linkage is very nearly linear (Fe—C1—C2 = 176 (1)°). The angles at C2 range from 118° to 122°, consistent with sp^2 hydridization at that carbon atom. The vinylidene ligand is virtually planar (see Table VII); the atoms Fe, C1, C2, C3, and C4 all lie within 0.05 Å of an idealized plane. The pseudomirror plane of the [(Cp)Fe(dppe)] moiety, defined by the iron atom, carbon atom C1, and the centroid of the cyclopentadienyl ring (CPO), forms a dihedral angle of 130.3° with the vinylidene plane, contrasting with the predicted value of 90° for a model system[22] (see Discussion).

The vinylidene moiety is substituted at C2 with a dithiocarbomethoxy group. Overall, this group bears a strong structural resemblance to the osmium-bonded dithiocarbomethoxy group in the complex $[OsH(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2]$ (IV).[23] The carbon-sulfur double bond in complex III is 1.66 (2) Å long, compared to 1.648 (4) Å in the osmium complex IV,[23] 1.611 Å in the thioformaldehyde,[24a] and 1.652 (2) Å in ethylene trithiocarbonate ($S{=}\overline{CSCH_2CH_2S}$).[24b] The $C(sp^2)$—S single bond in the dithioester group of III (C4—S1 = 1.73 (2) Å) is short enough to reflect some double-bond character (cf. 1.724 (5) Å in complex IV[23] and 1.732 Å (av) in ethylene trithiocarbonate).[24b] The methyl—sulfur bond in III (S1—C5 = 1.83 (2) Å) has a typical $C(sp^3)$—S bond length (cf. 1.800 (7) Å in II[23] and 1.80–1.82 Å in thioalkanes).[24c–g] Within the dithioester group, the angle between the vinylic carbon and the thiocarbonyl sulfur is rather acute (C2—C4—S2 = 115 (1)°), whereas the angle between the vinylic carbon and the methylated sulfur is rather obtuse (C2—C4—S1 = 124 (1)°) relative to a typical $C(sp^2)$ bond angle of 120°. The methyl group on S1 is cis to the thiocarbonyl sulfur atom S2 in complex III, just as it is in osmium complex IV. This methyl group lies in the dithiocarbomethoxy plane, which forms a dihedral angle of 17.9° with the principal plane of the vinylidene ligand (Fe—C1—C2—C3—C4), allowing effective overlap between the π orbitals of the vinylidene group and the dithiocarbomethoxy group.

Other aspects of the geometry of cation III are typical of those found in other $[Fe(dppe)(Cp)]$[7,25] complexes. The cyclopentadienyl ligand is planar with an average C–C bond length of 1.44 (2) Å, an average bond angle of 108 (1)° within the ring, and an average Fe-C bond length of 2.13 (1) Å. The carbon atom C1 of the vinylidene ligand lies between CP1 and CP5 of the cyclopentadienyl ligand (nonbonding distances of 2.78 (2) and 2.97 (2) Å, respectively). The iron-phosphorus bond distances (2.217 (4), 2.231 (4), average 2.224 (4) Å) are slightly longer than the Fe-P bonds in other $[(Cp)Fe(dppe)L]^{n+}$ complexes (L = MeCN, n = 1, Fe-P(av) = 2.200 (1) Å;[25a] L = CO, n = 1, 2.210 (1) Å;[25a] L = MgBr·2THF, n = 0, 2.107 (1) Å[25c]). This may be due to the cationic charge on III combined with the strongly electron-withdrawing character of the 2-(dithiocarbomethoxy)propenylidene ligand, leading to a weakening of the Fe-P bonds. The chelate ring of the dppe ligand adopts a "folded

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Table IV. Properties of Structurally Characterized Vinylidene Complexes

	d(M=C), A	d(C=C), A	$M-C_\alpha-C_\beta$, deg	ν(C=C), cm^{-1}	$\delta_c(C_\alpha)$
$[Fe(C{=}CMeCS_2Me)(dppe)(Cp)]I\cdot MeOH$	1.74 (2)	1.31 (2)	176 (1)	1550	364.5
$[Mn(C{=}CHPh)(CO)_2(Cp)]^a$	1.68 (2)	1.34 (3)	174 (2)	1592	379.5
$[MoCl\{C{=}C(CN)_2\}\{P(OMe)_3\}_2(Cp)]^b$	1.833 (6)	1.378 (8)	166.6 (4)	ca. 1420	
$[Os(C{=}CCH{=}CHMeCH{=}CH)(CO)_2(PPh_3)_2]^c$	1.90 (1)	1.33 (1)	169 (3)	1609, 1649	

[a] Reference 32. [b] Reference 33. [c] Reference 34.

envelope" conformation with the iron atom, two phosphorus atoms, and carbon atom CB2 coplanar, and carbon atom CB1 in the "flap" of the envelope. Torsional angles in the chelate ring are 2.5 (5), 28.8 (10), -50.7 (10), 52.5 (9), and -27.7 (5)° about the bonds Fe-P2, P2-CB2, CB2-CB1, CB1-P1, and P1-Fe, respectively (see ref 25a for comparison with several other dppe complexes). The phenyl groups of the dppe ligand are planar with an average C-C distance of 1.40 Å and an average angle of 120 (1)° within the rings.

Besides the $[Fe(C_2MeCS_2Me)(dppe)(Cp)]^+$ cation, the unit cell of III also contains an iodide ion and a methanol of crystallization. The methanol oxygen atom is located 3.36 Å from cyclopentadienyl carbon atom CP3, and 3.46 Å from the iodide ion. The iodide ion also lies 3.93 Å from phenyl carbon atom C16. The closest intermolecular contact between iron cations is found between atoms C35 and CP2 of adjacent cations, 3.41 Å apart.

Discussion

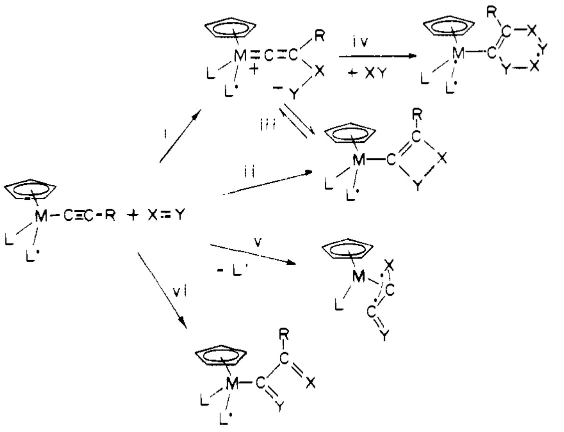
To the best of our knowledge, no reactions of metal alkynyls nor the chemically related ynamines with carbon disulfide have previously been reported.[15] Enamines ($R_2NCH{=}CH_2$) react with carbon disulfide in a 2:1 molar ratio to form α-dithiopyrones with elimination of 1 mol of R_2NH,[26] but simple (2 + 2) cycloaddition is not observed.

Several pathways have now been established for reactions of metal alkynyls with unsaturated electrophiles (Scheme II). Zwitterion formation (i) followed by either reversible or irreversible ring closure (iii) or addition of a second electrophile (iv) have all been observed in various reactions of tetracyanoethylene (TCNE) or hexafluoroacetone with $[Fe(C{\equiv}CPh)(CO)_2(Cp)]$ or $[Fe(C{\equiv}CPh)(CO)(PPh_3)(Cp)]$.[3] Cleavage of the electrophile TCNE occurs when it is added to $[Ru(C{\equiv}CPh)(PPh_3)_2(Cp)]$ (path vi) or $[Ru(C{\equiv}CPh)(CO)(PPh_3)(Cp)]$ (path vii).[4] The present reaction of $Fp'C{\equiv}CCH_3$ (I) with CS_2 appears to follow pathway ii, i.e., (2 + 2) cycloaddition without an observable zwitterionic intermediate.

Attempts to react iron alkyne (I) with CO_2 and COS have been uniformly unsuccessful, probably owing to the lower electrophilicity of these molecules. Additional studies of the reactivity of metal alkynes toward isocyanates and isothiocyanates may shed more light on the nature of cycloadduct II.

The methylation of CS_2 adduct II must proceed with ring opening, since the structurally characterized product III contains an acyclic 2-(dithiocarbomethoxy)propenylidene ligand. There are two reasonable mechanisms for the formation of III from II. (1) Selective methylation of an open, zwitterionic form of the CS_2 adduct (IIa) may occur. The concentration of the open form IIa in equilibrium with the closed form IIb would have to be quite low, however, since it is not detected by ^1H NMR in solutions of II. Nonetheless, the thermal reversibility of CS_2 addition to I suggests its presence. (2) Methylation of the thione moiety of closed form IIb may occur with subsequent or simultaneous ring opening. It is well established that the sulfur atom of a thione is a nucleophilic site,[27] and the thione moiety in IIb should be particularly electron-rich due to conjugation with the highly donating alkenyl-iron substituent. A related sequence of reaction occurs when the phosphorus ylide $Ph_3P{=}C{=}C(OEt)_2$ reacts with CS_2 to form $Ph_3P{=}C{-}C(OEt)_2SC{=}S$, subsequent methylation of which yields a ring-opened product.[28] A mechanism for the formation of II and III which is consistent with our observations is presented in Scheme I.

Scheme II



Some features of the structure of cation III are worthy of comment. The bond between the iron atom and the vinylidene ligand is much shorter (1.74 (2) Å) than the sum of the iron and carbon covalent radii (ca. 2.02 Å).[29] Comparatively, the Fe-C(acyl) bond in $[Fe(COPh)(dppe)(Cp)]$ is 1.93 Å long,[25b] and the formally double Fe-C bond in the cycloheptatrienylidene complex $[Fe(\eta^1\text{-}C_7H_6)(CO)_2(Cp)][PF_6]$ is 1.979 (3) Å long.[30] The only comparably short Fe-C bonds occur in anionic metal carbonyls such as $[FeH(CO)_4]^-$ (mean Fe-C = 1.74 Å)[31] in which back-bonding from the formally anionic iron atom should be very strong. It appears that the donor ability of the dppe ligand and the acceptor ability of the dithioester substituent counteract the expected bond-lengthening effect of the cationic charge on III, leading to very effective iron-to-vinylidene back-bonding.

Short metal-carbon bonds have been found in three other structurally investigated vinylidene complexes (see Table IV). The vinylidene C=C bond in complex III is the shortest found in a vinylidene complex, and the Fe—C—C angle is the closest to linearity among these.[37]

One of the more interesting features of the structure of cation III is the orientation of the vinylidene ligand with respect to the [Fe(dppe)(Cp)] pseudomirror plane (Table VII). Whereas extended Hückel calculations by Hoffmann and co-workers on the model system $[Fe(C{=}CH_2)(CO)_2(Cp)]^+$ predict that the vi-

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nylidene plane should bisect the [$Fe(CO)_2(Cp)$] symmetry plane (dihedral angle of 90°),[22] the observed dihedral angle in cation III is 130.3°. This orientation may be governed by both electronic and steric factors. Sterically, there are close intramolecular approaches between the methylated sulfur S1 and cyclopentadienyl carbon CP5 (3.31 Å) and phenyl carbon C22 (3.54 Å), between methyl carbon C3 and phenyl carbons C46 (3.47 Å) and C41 (3.67 Å), and between thione carbon C4 and phenyl carbon C21 (3.69 Å). Since these distances are close to the sums of the appropriate van der Waals radii (S, 1.85 Å; methyl, 2.0 Å, half-thickness of phenyl ring, 1.70 Å),[35] the vinylidene group may be "tilted" by steric contacts. On the other hand, Figure 2 emphasizes that the longer iron—phosphorus bond (Fe—P2) is nearly parallel to the plane of the vinylidene ligand, while the shorter iron—phosphorus bond (Fe—P1) is nearly perpendicular to it. The electron-withdrawing dithiocarbomethoxy group lies "trans" to the Fe—P2 bond across the vinylidene linkage. A similar orientation has been reported for the phenylvinylidene ligand in [Mn(C=CHPh)-$(CO)_2(Cp)$], in which the carbonyl ligand with a longer Mn—C bond lies nearly in the phenylvinylidene plane and is "trans" to the phenyl group, whereas the carbonyl with the shorter Mn—C bond lies perpendicular to the vinylidene plane.[32] Since there is no evidence for steric crowding in the manganese system, there may be an electronic component to the "unexpected" orientations of the vinylidene planes in both the manganese complex and III. Perhaps effects of ligand asymmetry, similar to those described by Hoffmann and co-workers for other [(Cp)MLL′] complexes, account for these orientations.[36] Further structural studies on metallacumulenes relevant to this problem are in progress.[37]

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Registry No. I, 68866-84-2; II, 79792-47-5; III, 79792-49-7; CS_2, 75-15-0; ICH_3, 74-88-4.

Supplementary Material Available: Experimental parameters for data collection (Table V), positional and thermal parameters (Table VI), least-squares planes (Table VII), and observed and calculated structure factors (Table VIII) for the structure of III (21 pages). Ordering information is given on any current masthead page.

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Cyclometalation of Dialkylbis(triethylphosphine)platinum(II) Complexes: Formation of *Pt*,*Pt*-Bis(triethylphosphine)platinacycloalkanes[1]

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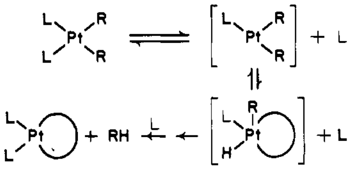
Abstract: The thermal decompositions of three analogues of bis(triethylphosphine)dineopentylplatinum(II) ($L_2Pt[CH_2C(CH_3)_3]_2$ (**1**))—$L_2Pt[CH_2C(CH_3)_2CH_2CH_3]_2$ (**3**), $L_2Pt[CH_2C(CH_3)_2CH_2CH_2CH_3]_2$ (**5**), and $L_2Pt[CH_2C(CH_3)_2CH_2C(CH_3)_3]_2$ (**7**)—have been examined. Compounds **3** and **7** decompose more rapidly than **1** by a factor of ca. 10^4 to give as products *Pt*,*Pt*-bis(triethylphosphine)-3,3-dimethylplatinacyclohexane (**4**) and *Pt*,*Pt*-bis(triethylphosphine)-3,3,5,5-tetramethylplatinacyclohexane (**8**), respectively, and 1 equiv of the corresponding alkane. Compound **5** decomposes at a rate ca. 50 times faster than **1** to yield *Pt*,*Pt*-bis(triethylphosphine)-2,4,4-trimethylplatinacyclopentane (**6a**), -3-methyl-3-*n*-propylplatinacyclobutane (**6b**), and -3,3-dimethylplatinacyclohexane (**6c**). The conversion of **3** to **4** and **5** to **6a** proceeds by dissociation of triethylphosphine, intramolecular oxidative addition of a δ carbon-hydrogen bond of one the alkyl groups to platinum, and reductive elimination of alkane. The decomposition of $L_2Pt[CH_2CH_2C(CH_3)_3]_2$ (**11**) proceeds by β-hydride elimination rather than cleavage of a carbon-hydrogen bond and formation of platinacycloalkane. The difference in the free energies of activation for reactions which form four- and five-membered platinacycloalkanes is small ($\Delta\Delta G^{\ddagger} \simeq 4$ kcal mol^{-1}); that for reactions which form four- and six-membered rings is smaller ($\Delta\Delta G^{\ddagger} \simeq 0$ kcal mol^{-1}). We identify these values of $\Delta\Delta G^{\ddagger}$ with estimates of the strain energies of these rings, assuming the strain energy of the platinacyclohexane is small. The important conclusion from these studies is that the strain energy of the platinacyclobutane studied here is small (<5 kcal mol^{-1}).

Homogeneous reactions which break unactivated aliphatic C–H bonds by oxidative addition to transition metals provide mechanistic information which is useful in understanding catalytic reactions of hydrocarbons.[4] Well-defined stoichiometric reactions which cleave C–H bonds include a group of facile intramolecular cyclizations involving a coordinated ligand.[5] Most reported

Scheme I. Mechanism of Formation of Metalacycloalkanes by Cyclometalation



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(2) Chevron Fellow, 1980-1982.

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