phenylphosphonium)cyclopentadienylidene product (**4**). One can envision two means of ylide formation: (a) the diazo ligand may attack the nickel-phosphine complex to form the "phosphazine" (**1**) which decomposes in the presence of the metal to the ylide (**4**) or (b) the nickel-diazo complex decomposes to form a carbene species $(PPh_3)_2Ni{=}C_5H_4$ which preferentially attacks triphenylphosphine rather than diethyl maleate to form **4**.

The reaction chemistry of diazocyclopentadienes coordinated to Ni(0) is thus very different from that observed for diazomethane or diazofluorene Ni systems. Perhaps the ability of the cyclopentadienyl carbene species $:C_5H_4$ to stabilize electron density on the "carbenoid" carbon atom by delocalization into a C_5 aromatic system is one reason for the differing reaction chemistry. Such stabilization would tend to diminish the carbenoid character of the C(1) carbon atom and thus inhibit its reaction as a carbene with olefins to produce cyclopropane products. In fact the stabilization of the carbene by aromatization would tend to make the C(1) carbon atom more positive in character and thus facilitate its reaction with electron-donor species, such as triphenylphosphine, to give ylide products.

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Registry No. I, 73531-57-4; II, 73531-58-5; III, 73531-59-6; IV, 73531-60-9; V, 73531-62-1; VI, 73531-63-2; VII, 73531-64-3; VIII, 73531-65-4; $Ni(C_2H_4)(PPh_3)_2$, 23777-40-4; $Ni(COD)_2$, 1295-35-8; $Ru(CO)_2(C_2H_4)(PPh_3)_2$, 35795-47-2; $[Ru(CO)_2(N_2Ph)(PPh_3)_2][PF_6]$, 56389-71-0; $RuH_2(CO)_2(PPh_3)_2$, 21029-29-8; $Ru(CO)_2(PPh_3)_3$, 35880-54-7; $Ni(t\text{-}BuNC)_2$, 29564-99-6; $Ni(N_2C_5Cl_4)(PPh_3)_2$, 73531-66-5; $Ni(N_2C_5H_4)(PPh_3)_2$, 73531-67-6; $Ph_3PC_5H_4$, 29473-30-1; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; diethyl maleate, 141-05-9.

Supplementary Material Available: Table VI, the idealized positions of the hydrogen atoms, Table VII, the root-mean-square amplitudes of vibration, and the listing of observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination du CNRS associé l'Université Paul Sabatier, 31400 Toulouse, France, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Electrophilic Addition of a Proton to 1,2-Bis(carbomethoxy)acetylene Inserted into the Iron-Iron Bond of $[(\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2]_2$. X-ray Structure at -162 °C of the Reaction Product, a Chelated 1,2-Bis(carbomethoxy)ethylene Complex, $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$

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The synthesis and structure from IR and NMR data of the complex $((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCCOOCH_3)$ are described, and its reactivity toward H^+ is studied. Protonation gives a chelated (C,O) 1,2-bis(carbomethoxy)ethylene complex in which the added proton is cis to the carbon-bonded iron atom. The structure of the product has been established by a crystal structure determination of $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$. In this complex each iron atom is octahedrally coordinated to two bridging sulfur atoms of the methylthiolato groups, two phosphine ligands trans to the sulfur atoms, one carbonyl group, and a vinylic carbon atom for one iron atom and an oxygen atom of the α-carbonyl ester group for the other. The compound crystallizes with 4 formula units in the monoclinic space group $C_{2h}^5\text{-}P2_1/c$ in a cell of dimensions $a = 10.716$ (4) Å, $b = 30.227$ (11) Å, $c = 16.346$ (5) Å, and $\beta = 102.75$ (1)°. On the basis of 5856 unique reflections, the structure was refined by full-matrix least-squares techniques to conventional indices (on F) of $R = 0.050$ and $R_w = 0.057$. The Fe-Fe separation of 3.452 (1) Å and the dihedral angle around the sulfur atoms of 157.8° lead to the widest spacing thus far found for this type of dinuclear, sulfur-bridged iron complex.

Introduction

The reaction of alkynes with transition-metal hydrides to give alkene complexes is well-known and has been extensively studied.[2] It has also been found that protonation of mononuclear alkyne complexes of platinum, palladium,[3,4] and osmium[5] gives alkene complexes.

We have shown recently[6] that photochemical activation induces the insertion of an alkyne into the iron-iron bond of $[(\mu\text{-}A)Fe(CO)_3]_2$ complexes ($A = SCH_3$, SC_6H_5, $P(CH_3)_2$), and it was of interest to determine if the double σ-bonded alkynes in these complexes have the same type of reactivity as do alkynes in mononuclear complexes. If protonation occurs, we expected the product to be a σ-π alkene complex, as has been encountered in the reaction of methyl vinyl sulfide with Fe_3CO_{12}[7] and in the reaction of ethylene with $H_2Os_3CO_{10}$.[8,9] We thus undertook a study of the protonation of $(\mu\text{-}SCH_3)_2Fe_2(CO)_{6-n}(P(CH_3)_3)_n(CH_3COOCCCOOCH_3)$

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complexes and determined the X-ray structure of the product for $n = 4$.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer. Proton NMR spectra were obtained on a Varian A60A spectrometer. The solvent was CH_2Cl_2 with Me_4Si as the internal standard. Positive values indicate low-field chemical shifts. $[(\mu\text{-}SCH_3)Fe(CO)_3]_2$ was purchased from Pressure Chemical Co. and $CH_3COOCCCOOCH_3$ from Fluka. $[(\mu\text{-}SCH_3)Fe(CO)_3]_2(CH_3COOCCCOOCH_3)$ was prepared by the published method.[6]

All reactions were carried out under a pure dinitrogen atmosphere by using Schlenk tubes and vacuum line procedures.

Preparation of $[(\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2]_2(CH_3COOCCCOOCH_3)$ (1). $[(\mu\text{-}SCH_3)Fe(CO)_3]_2(CH_3COOCCCOOCH_3)$ (400 mg) was dissolved in benzene, and 0.4 mL of $P(CH_3)_3$ (slight excess) was introduced. The solution was refluxed for 16 h. Benzene was evaporated under vacuum, and the residue was dissolved in a minimum of pentane and filtered. Crystallization gave 0.245 mg of orange crystals (yield ~45%). Mp 162 °C dec. Anal. Calcd for $C_{22}H_{48}Fe_2O_6P_4S_2$: C, 37.28; H, 6.78; P, 17.51. Found: C, 37.45; H, 6.73; P, 17.22. IR: 1909 (s), 1896 (m) cm^{-1} [ν(CO), hexadecane solution]; 1660 [ν(CO) of $O{=}COCH_3$]; 1460 cm^{-1} [ν(C=C)] (KBr pellets). ^1H NMR: δ 1.16 (broad signal, $J_{PH} \approx 8$ Hz), 2.30 (SCH_3), 3.63 (OCH_3).

Preparation of $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)]X$ Where X = PF_6 (2) and $B(C_6H_5)_4$ (3). An excess of CF_3COOH was added to a CH_2Cl_2 solution of **1**. The red solution turned brown immediately. The solution was next evaporated to dryness and the residue dissolved in methanol. To this solution was added a slight excess of a water solution of NH_4PF_6. A precipitate immediately appeared which was filtered and dried. Recrystallization from a CH_2Cl_2/ether medium gave orange crystals of **2** in quantitative yield. Mp 95 °C dec. Anal. Calcd for $C_{22}H_{49}F_6Fe_2O_6P_5S_2$: C, 30.91; H, 5.73; P, 18.15; F, 13.14. Found: C, 30.76; H, 5.56; P, 17.75; F, 13.43. IR: 1938 (s), 1930 (sh) cm^{-1} [ν(CO), CH_2Cl_2 solution]; 1700, 1590, 1540 cm^{-1} [ν(CO) of $COOCH_3$ and ν(C=C) (see text) KBr pellets]. ^1H NMR: δ 6.15 (1 H, vinyl proton), 3.96 (3 H, OCH_3), 2.35 (6 H, SCH_3), 1.37 ($J_{PH} = 9.2$ Hz, 18 H, $P(CH_3)_3$), 1.30 ($J_{PH} = 8.2$ Hz, 18 H, $P(CH_3)_3$). Crystals more suitable for crystallographic studies were obtained as the $B(C_6H_5)_4$ salt, **3**. The compound was prepared in the same way, with $NaBPh_4$ (Ph = C_6H_5) in slight excess being added to the methanol solution to give immediately an orange precipitate which was then recrystallized from CH_2Cl_2. Mp 151 °C for $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][BPh_4]$, **3**.

X-ray Study. Preliminary photographic data for compound **3** revealed monoclinic symmetry. Systematic extinctions ($0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$) are consistent with space group C_{2h}^5-$P2_1/c$. All constants were obtained as previously described[10] by least-squares refinement of the setting angles of 12 hand-centered reflections which had been chosen from diverse regions of reciprocal space with $24° \le 2\theta(\text{Mo}) \le 26°$. These cell constants and other pertinent data are shown in Table I. The density of 1.25 g cm^{-3}, observed at room temperature by flotation in $ZnCl_2$ aqueous solution, may be compared with that of 1.323 g/cm^3 calculated for 4 formula units in the low-temperature cell. Intensity data were collected at −162 °C on a computer-controlled Picker four-circle diffractometer. A total of 8082 intensities was recorded out to $2\theta(\text{Mo}) = 46.5°$. The data were processed as previously described[11] by using a value of p of 0.04. The 5856 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. An absorption correction was applied to the data.[12]

Table I. Summary of Crystal Data and Intensity Collection

compound	$[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$
formula	$C_{46}H_{69}BFe_2P_4O_6S_2$
fw	1028.6
a(at −162 °C)	10.716 (4) Å
b	30.227 (11) Å
c	16.346 (5) Å
β	102.75 (1)°
V	5164.3 $Å^3$
Z	4
density (calcd for −162 °C)	1.323 g cm^{-3}
density (measd in $ZnCl_2$(aq))	1.25 (2) g cm^{-3}
space group	$C_{2h}^5 - P2_1/c$
cryst dimens	0.144 × 0.289 × 0.317 mm
boundary faces of the prism	{001}, $\{12\bar{1}\}$
temp	−162 °C
radiation	Mo Kα (λ(Mo Kα_1) = 0.7093 Å) from monochromator
linear abs coeff	7.91 cm^{-1}
transmission factors	0.795–0.902
receiving aperture	4.0 × 4.5 mm; 30 cm from crystal
takeoff angle	2.7°
scan speed	2° in 2θ/min
scan range	0.75 ° below Kα_1 to 0.75° above Kα_2
bkgd counts	10 s
2θ limits	2.8–46.5°
final no. of variables	382
unique data used	5856 ($F_o^2 > 3\sigma(F_o^2)$)
quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weight	$w = 4F_o^2/\sigma^2(F_o^2)$
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.050
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2)^{1/2}$	0.057
std error in an observn of unit wt	1.54 e

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques.[12] Values of the atomic scattering factors[13] and the anomalous terms[14] were from the usual sources. The effects of anomalous dispersion for the Fe, S, and P atoms were included in F_c.[15] The phenyl rings of the BPh_4 anions were treated as rigid groups[16] with a C–C distance of 1.392 Å and a C–H distance of 0.95 Å. Refinement of an isotropic model converged to values of R and R_w of 0.08 and 0.11, respectively.

A difference Fourier map clearly revealed the positions of all the 49 H atoms. Their contribution to F_c was then calculated and used for the final cycles of refinement which included anisotropic thermal parameters for all nonhydrogen atoms except the C atoms of the phenyl rings. In the calculation of the fixed contribution of the H atoms, an isotropic thermal parameter assigned to each H atom was 1 $Å^2$ greater than that of the atom to which it is attached.

The final values of R and R_w are 0.050 and 0.057. An analysis of $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ as a function of $\lvert F_o\rvert$, setting angles, and Miller indices shows no trends. A final difference Fourier map shows some peaks of the order of 0.6 (2) e/$Å^3$ associated with the benzene rings. These peaks are approximately 11% of the heights of typical light-atom peaks on earlier Fourier maps. Thus the final difference Fourier map is essentially featureless.

In Table II we present the atomic parameters of the nongroup atoms together with their standard deviations as derived from the inverse matrix. Group parameters appear in Table III. In Table IV we present the positions of the 49 H atoms of the complex cation.[17] Table V lists the root-mean-square amplitudes of vibration for those atoms refined anisotropically.[17] A listing of $10\lvert F_o\rvert$ vs. $10\lvert F_c\rvert$ is available.[17]

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Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
FE(1)	0.00580(6)	0.42687(2)	0.33266(4)	34.2(7)	3.42(8)	13.1(3)	0.2(2)	4.9(3)	-0.4(1)
FE(2)	0.05588(6)	0.31595(2)	0.37860(4)	29.2(7)	3.61(8)	11.2(3)	0.0(2)	5.7(3)	0.6(1)
S(1)	0.1514(1)	0.38219(4)	0.42435(7)	37.(1)	4.0(1)	12.1(5)	-0.6(3)	3.1(6)	0.1(2)
S(2)	-0.1159(1)	0.36357(4)	0.32067(7)	32.(1)	3.8(1)	16.4(5)	0.5(3)	7.7(6)	0.4(2)
P(1)	-0.1437(1)	0.46471(4)	0.24078(8)	41.(1)	4.1(2)	20.0(6)	1.7(3)	3.8(7)	0.4(2)
P(2)	0.1603(1)	0.47832(4)	0.33805(8)	43.(1)	4.2(2)	17.0(6)	-2.2(4)	3.7(7)	0.1(2)
P(3)	-0.0379(1)	0.25744(4)	0.30700(8)	32.(1)	3.6(1)	13.1(5)	-0.6(3)	6.3(6)	0.4(2)
P(4)	0.2254(1)	0.27756(4)	0.45319(8)	31.(1)	4.7(1)	14.3(5)	1.0(3)	5.2(6)	1.7(2)
O(1)	-0.0914(4)	0.4642(1)	0.4671(2)	104.(5)	9.1(5)	28.(2)	5.(1)	27.(3)	-5.0(8)
O(2)	-0.0677(3)	0.3013(1)	0.5180(2)	47.(4)	8.9(5)	17.(2)	0.(1)	14.(2)	2.6(7)
O(3)	0.2758(3)	0.3676(1)	0.1578(2)	59.(4)	6.7(5)	23.(2)	4.(1)	20.(2)	5.4(7)
O(4)	0.0448(3)	0.39827(10)	0.2271(2)	37.(3)	3.2(4)	15.(1)	1.6(9)	7.(2)	-0.5(6)
O(5)	0.0262(3)	0.3384(1)	0.1448(2)	46.(3)	5.1(4)	13.(1)	1.4(9)	4.(2)	-0.9(6)
O(6)	0.4297(3)	0.3183(1)	0.2042(2)	45.(4)	11.1(5)	24.(2)	7.(1)	20.(2)	5.0(8)
C(1)	-0.0502(5)	0.4495(2)	0.4134(3)	46.(5)	4.4(6)	23.(2)	-2.(1)	1.(3)	-1.1(10)
C(2)	-0.0195(5)	0.3059(2)	0.4627(3)	34.(5)	4.8(6)	19.(2)	-2.(1)	0.(3)	-0.6(9)
C(3)	0.1441(4)	0.3304(1)	0.2627(3)	35.(5)	2.8(5)	12.(2)	-2.(1)	6.(2)	0.0(8)
C(4)	0.0719(4)	0.3594(2)	0.2171(3)	26.(5)	5.4(6)	16.(2)	-2.(1)	12.(3)	-1.0(9)
C(5)	-0.0359(5)	0.3663(2)	0.0750(3)	76.(6)	7.7(7)	9.(2)	5.(2)	-4.(3)	1.3(10)
C(6)	0.2620(4)	0.3202(2)	0.2734(3)	38.(5)	5.1(6)	12.(2)	1.(1)	8.(3)	0.8(9)
C(7)	0.3183(4)	0.3387(2)	0.2059(3)	33.(5)	5.4(6)	15.(2)	-4.(1)	9.(3)	-2.4(10)
C(8)	0.4924(5)	0.3337(2)	0.1401(4)	60.(6)	15.3(10)	30.(3)	2.(2)	27.(3)	4.(1)
C(9)	0.1331(5)	0.3429(2)	0.5306(3)	60.(6)	7.1(7)	11.(2)	-2.(2)	3.(3)	-1.6(9)
C(10)	-0.2303(5)	0.3665(2)	0.3871(3)	41.(5)	6.6(7)	30.(3)	3.(1)	17.(3)	3.(1)
C(11)	-0.0949(5)	0.4570(2)	0.1494(3)	62.(6)	6.7(7)	19.(2)	1.(2)	3.(3)	2.2(10)
C(12)	-0.2149(5)	0.5120(2)	0.2818(4)	78.(7)	6.4(7)	37.(3)	8.(2)	14.(4)	1.(1)
C(13)	-0.2472(5)	0.4343(2)	0.1902(3)	48.(6)	7.1(7)	33.(3)	2.(2)	-9.(3)	3.(1)
C(14)	0.2571(6)	0.4670(2)	0.2523(4)	74.(7)	11.9(9)	35.(3)	-16.(2)	31.(4)	-5.(1)
C(15)	0.2804(5)	0.4802(2)	0.4349(3)	50.(5)	5.4(6)	29.(3)	-5.(2)	0.(3)	1.(1)
C(16)	0.1234(5)	0.5370(2)	0.3246(3)	69.(6)	4.8(6)	32.(3)	-6.(2)	-8.(3)	4.(1)
C(17)	-0.0707(4)	0.2105(2)	0.3686(3)	32.(5)	4.8(6)	18.(2)	-1.(1)	5.(3)	0.9(9)
C(18)	-0.1942(5)	0.2680(2)	0.2409(3)	47.(5)	4.8(6)	19.(2)	-4.(1)	5.(3)	-0.8(9)
C(19)	0.0383(5)	0.2320(2)	0.2297(3)	60.(6)	5.1(6)	18.(2)	-1.(1)	15.(3)	-2.2(9)
C(20)	0.2848(5)	0.2277(2)	0.4118(3)	37.(5)	5.2(6)	28.(2)	2.(1)	11.(3)	1.5(10)
C(21)	0.3721(5)	0.3091(2)	0.4913(3)	40.(5)	5.9(6)	19.(2)	1.(1)	1.(3)	0.1(9)
C(22)	0.2038(5)	0.2556(2)	0.5535(3)	48.(5)	9.6(7)	20.(2)	5.(2)	7.(3)	5.(1)
B	0.4608(5)	0.6208(2)	0.1703(3)	41.(6)	3.8(6)	13.(2)	4.(2)	9.(3)	1.9(10)

ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS EXP -(B11H^2 +B22K^2 +B33L^2 +2B12HK+2B13HL+2B23KL) . THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS x 10^4 .

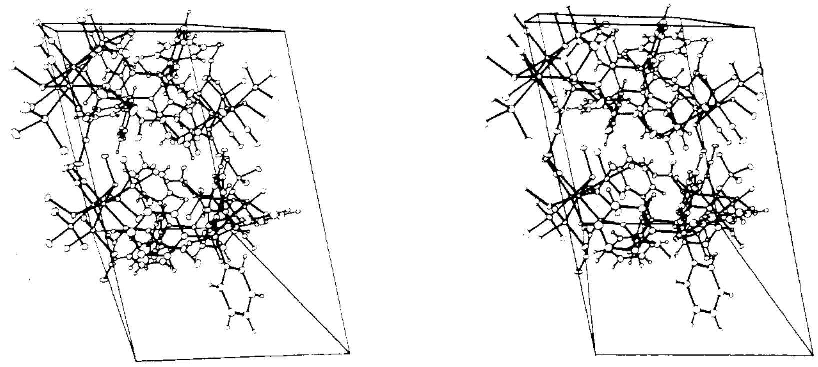

Figure 1. Stereoscopic view of a unit cell of $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$. The z axis is horizontal from left to right, the x axis is perpendicular from bottom to top, and the y axis comes out of the paper. The vibrational ellipsoids are drawn at the 30% level. Hydrogen atoms of the complex cation are omitted.

Results and Discussion

Syntheses and Reactions. The substitution of carbonyl groups in $[(\mu\text{-}SCH_3)Fe(CO)_3]_2(CH_3COOCCCOOCH_3)$ by trimethylphosphine ligands is facile, four CO groups being displaced in benzene under reflux to give in good yield $[(\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3]_2(CH_3COOCCCOOCH_3)$, **1**. This compound shows two infrared-active bands in the ν(CO) stretching region and a band of moderate intensity at 1460 cm^{-1} which we attribute to the ν(C=C) stretching vibration. The ν(C=C) band in the unsubstituted complex is at 1516 cm^{-1}.[6] This shift in frequency of 56 cm^{-1} to lower energy is the expected result of the substitution of four CO groups by trimethylphosphine ligands. The ^{1}H NMR spectrum of **1** shows a broad signal for the $P(CH_3)_3$ groups and one signal for the SCH_3 and OCH_3 groups. These results strongly suggest that the molecule has C_{2v} symmetry with the phosphine ligands trans to the SCH_3 thiolato bridges and with the SCH_3 groups in a syn conformation.

Protonation of the $P(CH_3)_3$-substituted complexes by trifluoroacetic acid occurs readily for both the tri- and tetrasubstituted derivatives, but only the tetrasubstituted product has been fully characterized as hexafluorophosphate or tetraphenylborate salts. The $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)]^+$ cations, associated with either PF_6^- or BPh_4^- anions, show two infrared-active bands in the ν(CO) stretching region which are shifted 29 cm^{-1} to higher frequencies relative to **1**. This increase in frequency is much lower than that generally observed after protonation of a metal center, i.e., about 80–100 cm^{-1}.[18] Thus, the proton is not bonded to an iron atom. In the PF_6^- salt one band of medium intensity is observed at 1700 cm^{-1} which we attribute to the ν(CO) band of the ester group. Two other bands of equal medium intensity are observed at 1590 and 1540 cm^{-1}. Their assignment is less certain as in this region bands associated with either an ester carbonyl group coordinated to a metal atom[19,20] or a ν(C=C) vibration of alkene CH$_3$COOC=CH-

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Table III. Derived Parameters for the Rigid Group Atoms of $[((\mu\text{-SCH}_3)\text{Fe(CO)(P(CH}_3)_3)_2)_2(\text{CH}_3\text{COOCCHCOOCH}_3)][\text{B(C}_6\text{H}_5)_4]$

ATOM	X	Y	Z	B(Å^2)	ATOM	X	Y	Z	B(Å^2)
C(23)	0.4144(3)	0.66948(7)	0.1237(2)	1.58(9)	C(35)	0.4403(3)	0.61801(10)	0.2693(1)	1.53(9)
C(24)	0.3507(3)	0.67103(7)	0.0398(2)	1.78(9)	C(36)	0.5036(3)	0.58492(9)	0.3216(2)	2.00(9)
C(25)	0.3203(3)	0.71165(9)	0.0003(1)	2.06(9)	C(37)	0.4815(3)	0.57973(9)	0.4018(2)	2.5(1)
C(26)	0.3536(3)	0.75074(7)	0.0449(2)	1.93(9)	C(38)	0.3961(3)	0.6076(1)	0.4297(1)	2.5(1)
C(27)	0.4174(3)	0.74919(7)	0.1288(2)	1.74(9)	C(39)	0.3329(3)	0.64072(9)	0.3773(2)	2.4(1)
C(28)	0.4477(3)	0.70856(9)	0.1682(1)	1.74(9)	C(40)	0.3550(3)	0.64591(9)	0.2971(2)	1.88(9)
H(24)	0.3280(4)	0.64436(9)	0.0094(2)	2.8	H(36)	0.5618(4)	0.5659(1)	0.3026(3)	3.0
H(25)	0.2768(4)	0.7127(1)	-0.0570(1)	2.8	H(37)	0.5246(4)	0.5571(1)	0.4376(2)	3.5
H(26)	0.3329(4)	0.77847(8)	0.0179(2)	2.9	H(38)	0.3811(4)	0.6041(1)	0.4844(2)	3.5
H(27)	0.4401(4)	0.77586(9)	0.1591(2)	2.8	H(39)	0.2747(4)	0.6598(1)	0.3963(3)	3.4
H(28)	0.4912(4)	0.7075(1)	0.2255(1)	2.8	H(40)	0.3119(4)	0.6685(1)	0.2613(2)	2.9
C(29)	0.3715(2)	0.57842(8)	0.1227(2)	1.72(9)	C(41)	0.6145(2)	0.6169(1)	0.1632(2)	1.76(9)
C(30)	0.4254(2)	0.53870(10)	0.1046(2)	2.24(10)	C(42)	0.7145(3)	0.6251(1)	0.2318(1)	2.08(10)
C(31)	0.3468(3)	0.50332(8)	0.0722(2)	2.7(1)	C(43)	0.8405(2)	0.6231(1)	0.2228(2)	2.5(1)
C(32)	0.2145(3)	0.50766(8)	0.0577(2)	2.5(1)	C(44)	0.8665(2)	0.6128(1)	0.1452(2)	3.0(1)
C(33)	0.1606(2)	0.54738(10)	0.0757(2)	2.20(10)	C(45)	0.7665(3)	0.6045(1)	0.0767(2)	2.8(1)
C(34)	0.2391(3)	0.58276(8)	0.1082(2)	1.98(9)	C(46)	0.6405(2)	0.6065(1)	0.0857(2)	2.13(10)
H(30)	0.5157(2)	0.5357(1)	0.1145(3)	3.3	H(42)	0.6968(4)	0.6322(2)	0.2847(2)	3.1
H(31)	0.3836(4)	0.47619(10)	0.0599(3)	3.7	H(43)	0.9088(3)	0.6288(2)	0.2695(2)	3.5
H(32)	0.1609(3)	0.4835(1)	0.0356(3)	3.5	H(44)	0.9526(2)	0.6114(2)	0.1391(3)	4.0
H(33)	0.0703(2)	0.5503(1)	0.0659(3)	3.2	H(45)	0.7842(4)	0.5974(2)	0.0237(2)	3.8
H(34)	0.2024(4)	0.60989(9)	0.1205(3)	3.0	H(46)	0.5722(3)	0.6009(2)	0.0389(2)	3.1

RIGID GROUP PARAMETERS

GROUP	X_C	Y_C	Z_C	DELTA	EPSILON	ETA
PHI(1)	0.3840(2)	0.71011(7)	0.0843(1)	-2.484(2)	-2.302(2)	-0.772(3)
PHI(2)	0.2930(2)	0.54304(7)	0.0902(1)	-0.113(2)	-2.818(2)	-0.058(2)
PHI(3)	0.4182(2)	0.61282(7)	0.3495(1)	0.356(4)	2.109(2)	-1.171(4)
PHI(4)	0.7405(2)	0.61481(6)	0.1542(1)	1.650(2)	2.959(2)	1.329(2)

X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY. S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

$COOCH_3$ σ bonded to a metal[21,22] are expected. The fact that the band at 1700 cm^{-1} has about the same intensity as these two bands suggests that one of these is a ν(CO) stretching vibration of a coordinated ester group. The ^1H NMR spectrum shows two triplets for the $P(CH_3)_3$ resonance in a 1/1 ratio and one signal for the SCH_3 resonance. Furthermore, there are two signals in the OCH_3 region and one broad signal in the vinyl proton region.

These spectroscopic results strongly suggest that protonation of **1** gives an alkene complex. But is coordination through the oxygen atom of one of the ester groups, and what is the disposition of the added hydrogen atom relative to the carbon-bound iron atom? Since these questions could not be answered from the spectroscopic study, an X-ray study of the BPh_4 salt, **3**, was carried out.

Description of the Structure. The crystal structure of **3** consists of the packing of four discrete $[((\mu\text{-SCH}_3)\text{Fe(CO)(P(CH}_3)_3)_2)_2(\text{CH}_3\text{COOCCHCOOCH}_3)]^+$ cations and four discrete BPh_4^- anions, as shown in Figure 1. Figure 2 shows a perspective view of the complex cation along with the labeling scheme. Figure 3 is a stereoscopic view of this cation. Bond distances and angles of interest are given in Tables VI and VII.

In the dinuclear cation the two iron atoms are each octahedrally coordinated to two bridging sulfur atoms of the methylthiolato group, two phosphine ligands trans to the sulfur atoms, and one carbonyl group. The sixth position of atom

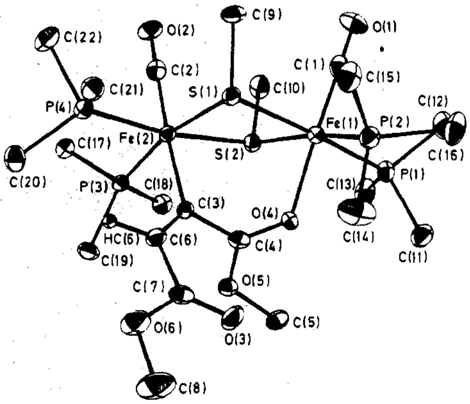

Figure 2. Perspective representation of the $[((\mu\text{-SCH}_3)\text{Fe(CO)(P(CH}_3)_3)_2)_2(\text{CH}_3\text{COOCCHCOOCH}_3)]^+$ cation. The vibrational ellipsoids are drawn at the 50% probability level. The labeling scheme is also shown.

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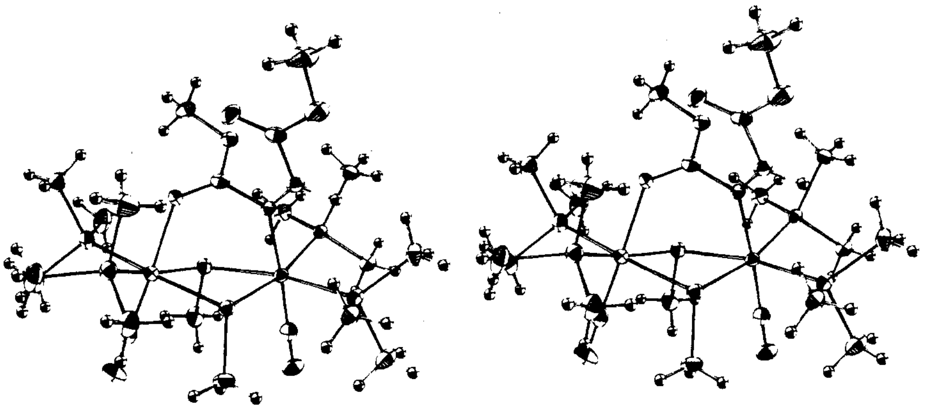

Figure 3. Stereoscopic view of the $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)]^+$ cation. The vibrational ellipsoids are drawn at the 50% probability level for the nonhydrogen atoms while those for the H atoms are drawn arbitrarily small.

Table VI. Bond Lengths (Å) for $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$

Fe(1)–Fe(2)	3.452 (1)	P(3)–C(17)	1.818 (5)
Fe(1)–C(1)	1.711 (6)	P(3)–C(18)	1.810 (5)
Fe(1)–O(4)	2.054 (3)	P(3)–C(19)	1.819 (5)
Fe(1)–P(1)	2.251 (2)	P(4)–C(20)	1.824 (5)
Fe(1)–P(2)	2.259 (1)	P(4)–C(21)	1.826 (5)
Fe(1)–S(1)	2.339 (1)	P(4)–C(22)	1.831 (5)
Fe(1)–S(2)	2.299 (1)	C(1)–O(1)	1.153 (6)
Fe(2)–C(2)	1.762 (5)	C(2)–O(2)	1.149 (5)
Fe(2)–C(3)	2.049 (4)	C(3)–C(4)	1.467 (6)
Fe(2)–P(3)	2.233 (1)	C(3)–C(6)	1.340 (6)
Fe(2)–P(4)	2.270 (1)	C(4)–O(4)	1.230 (5)
Fe(2)–S(1)	2.297 (1)	C(4)–O(5)	1.334 (5)
Fe(2)–S(2)	2.364 (1)	C(5)–O(5)	1.455 (6)
S(1)–C(9)	1.819 (5)	C(6)–C(7)	1.479 (6)
S(2)–C(10)	1.810 (5)	C(7)–O(3)	1.195 (5)
P(1)–C(11)	1.812 (5)	C(7)–O(6)	1.350 (6)
P(1)–C(12)	1.816 (5)	C(8)–O(6)	1.441 (6)
P(1)–C(13)	1.825 (5)	B–C(23)	1.680 (6)
P(2)–C(14)	1.813 (6)	B–C(29)	1.684 (6)
P(2)–C(15)	1.806 (5)	B–C(35)	1.683 (6)
P(2)–C(16)	1.821 (5)	B–C(41)	1.680 (6)

Table VII. Bond Angles (Deg) for $[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2(CH_3COOCCHCOOCH_3)][B(C_6H_5)_4]$

C(1)–Fe(1)–O(4)	171.5 (2)	C(12)–P(1)–Fe(1)	116.7 (2)
C(1)–Fe(1)–P(1)	89.4 (2)	C(13)–P(1)–Fe(1)	116.8 (2)
C(1)–Fe(1)–P(2)	94.0 (2)	C(14)–P(2)–C(15)	101.5 (3)
C(1)–Fe(1)–S(1)	92.1 (2)	C(14)–P(2)–C(16)	104.0 (3)
C(1)–Fe(1)–S(2)	96.5 (2)	C(14)–P(2)–Fe(1)	111.6 (2)
O(4)–Fe(1)–P(1)	84.3 (1)	C(15)–P(2)–C(16)	99.7 (2)
O(4)–Fe(1)–P(2)	92.2 (1)	C(15)–P(2)–Fe(1)	115.5 (2)
O(4)–Fe(1)–S(1)	93.7 (1)	C(16)–P(2)–Fe(1)	121.9 (2)
O(4)–Fe(1)–S(2)	78.2 (1)	C(17)–P(3)–C(18)	101.7 (2)
P(1)–Fe(1)–P(2)	94.8 (1)	C(17)–P(3)–C(19)	103.1 (2)
P(1)–Fe(1)–S(2)	93.4 (1)	C(17)–P(3)–Fe(2)	116.6 (2)
P(1)–Fe(1)–S(1)	175.2 (1)	C(18)–P(3)–C(19)	99.1 (2)
P(2)–Fe(1)–S(2)	166.7 (1)	C(18)–P(3)–Fe(2)	115.0 (2)
P(2)–Fe(1)–S(1)	89.6 (1)	C(19)–P(4)–C(21)	118.6 (2)
S(1)–Fe(1)–S(2)	81.9 (1)	C(20)–P(4)–C(21)	102.3 (2)
C(2)–Fe(2)–C(3)	176.6 (2)	C(20)–P(4)–C(22)	99.0 (2)
C(2)–Fe(2)–P(3)	93.1 (2)	C(20)–P(4)–Fe(2)	121.7 (2)
C(2)–Fe(2)–P(4)	87.2 (2)	C(21)–P(4)–C(22)	98.8 (2)
C(2)–Fe(2)–S(1)	97.5 (2)	C(21)–P(4)–Fe(2)	116.3 (2)
C(2)–Fe(2)–S(2)	87.5 (2)	C(22)–P(4)–Fe(2)	114.9 (2)
C(3)–Fe(2)–P(3)	89.9 (1)	Fe(1)–C(1)–O(1)	177.6 (5)
C(3)–Fe(2)–P(4)	94.0 (1)	Fe(2)–C(2)–O(2)	179.2 (8)
C(3)–Fe(2)–S(1)	79.4 (1)	C(4)–O(4)–Fe(1)	127.7 (3)
C(3)–Fe(2)–S(2)	90.8 (1)	C(4)–C(3)–C(6)	114.3 (4)
P(3)–Fe(2)–P(4)	95.2 (1)	C(4)–C(3)–Fe(2)	115.4 (3)
P(3)–Fe(2)–S(1)	167.8 (1)	C(6)–C(3)–Fe(2)	130.0 (3)
P(3)–Fe(2)–S(2)	92.9 (1)	C(3)–C(4)–O(4)	125.2 (4)
P(4)–Fe(2)–S(1)	91.4 (1)	C(3)–C(4)–O(5)	113.2 (4)
P(4)–Fe(2)–S(2)	170.5 (1)	O(4)–C(4)–O(5)	121.3 (4)
S(1)–Fe(2)–S(2)	81.4 (1)	C(4)–O(5)–C(5)	115.8 (4)
C(9)–S(1)–Fe(1)	108.1 (2)	C(3)–C(6)–C(7)	123.2 (4)
C(9)–S(1)–Fe(2)	109.4 (2)	C(6)–C(7)–O(3)	127.3 (4)
Fe(1)–S(1)–Fe(2)	96.2 (1)	O(3)–C(7)–O(6)	122.1 (4)
C(10)–S(2)–Fe(1)	110.7 (2)	C(6)–C(7)–O(6)	110.5 (4)
C(10)–S(2)–Fe(2)	111.1 (2)	C(7)–O(6)–C(8)	115.0 (4)
Fe(1)–S(2)–Fe(2)	95.5 (1)	C(23)–B–C(41)	103.2 (5)
C(11)–P(1)–C(12)	103.3 (2)	C(23)–B–C(35)	113.0 (5)
C(11)–P(1)–C(13)	100.5 (2)	C(23)–B–C(29)	112.1 (5)
C(11)–P(1)–Fe(1)	116.4 (2)	C(35)–B–C(41)	113.6 (5)
C(12)–P(1)–C(13)	100.5 (3)	C(29)–B–C(41)	112.3 (5)
		C(29)–B–C(35)	102.9 (5)

Fe(2) is occupied by the C(3) vinylic carbon atom and for Fe(1) by the O(4) oxygen atom of a carbonyl ester group. The dihedral angle between the Fe(1)–S(1)–S(2) and Fe(2)–S(1)–S(2) planes is 157.8°, and the separation between the two iron atoms is 3.452 (1) Å. This opening around the S–S axis is the largest found to date in a series[23-30] of sulfur-bridged, dinuclear complexes of iron, as shown in Table VIII. This wide opening allows the two SCH_3 groups to be in a syn configuration which, for example, is forbidden for steric reasons in $[(\mu\text{-}SCH_3)Fe(CO)_3]_2$.[23]

A principal feature of the structure is that the 1,2-bis(carbomethoxy)ethylene group is σ bonded to atom Fe(2) through the C(3) vinylic carbon atom and to atom Fe(1) through the O(4) oxygen atom of the carbonyl ester group. The two methoxy carbonyl groups are mutually cis, and the added proton on atom C(6) is cis to the Fe(2) atom with respect to the C(3)=C(6) double bond. Even though the formation of chelate complexes with the 1,2-bis(carbomethoxy)ethylene group is not uncommon when the adduct results from trans addition,[19,20] to our knowledge this is the first example where chelation involves an oxygen atom of the α-carbomethoxy group.[31]

The four phosphorus atoms of the phosphine ligands are

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Table VIII. Bond Distances (Å) and Bond Angles (Deg) in Some Dinuclear Sulfur-Bridged Iron Complexes

	distance or angle					
	Fe–Fe	Fe–S[j]	Fe–S–Fe[j]	Fe–P	Fe–C(CO)	dihedral angle[o]
$[Fe(SC_2H_5)(CO)_3]_2$[a]	2.537 (10)	2.259 (7)	68.3 (3)		1.81 (2)	95.2 (5)
$[Fe(SC_6H_5)(CO)_3]_2$[b]	2.516 (2)	2.270 (2)	67.3 (1)			
$[Fe(SCH_3)(CO)_2(P(CH_3)_3)]_2$[c]	2.518 (1)	2.273 (1)	67.3 (1)	2.221 (2)	1.745 (4)	90.9
$[Fe(SCH_3)(CO)_2(P(CH_3)_2C_6H_5)]_2H$[d]	2.594 (3)	2.274 (4)	69.5 (1)	2.242 (5)	1.75 (2)	93.3
$Fe_2(SCF_3)_3(CO)_6$[e]	3.062 (6)	2.305 (4)	83.3 (1)		1.80	
$[Fe(SCH_3)(CO)_3]_2(C_4F_6)$[f]	3.266 (1)	2.304 (1)	88.8 (1)		1.816 (4),[k] 1.840 (6)[l]	
$[Fe(SCH_3)(CO)_3]_2(C_2F_4)$[g]	3.311 (1)	2.310 (3)	91.61 (5)		1.801 (5),[k] 1.859 (6)[l]	135.0
$[(C_5H_5)Fe(CO)(SC_6H_5)]_2$[h]	3.39	2.262 (6)	98		1.71	
$[((\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)_2)_2\text{-}(CH_3COOCCHCOOCH_3)]^+$[i]	3.452 (1)	2.297 (1), 2.339 (1)	96.2 (1), 95.5 (1)	2.253 (1)	1.711 (6),[m] 1.762 (5)[n]	157.8

[a] Reference 23. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] Reference 27. [f] Reference 28. [g] Reference 29. [h] Reference 30. [i] This work. [j] Averaged values from equivalent distances or angles are given. [k] C trans to S. [l] C trans to C of C_2F_4 or C_4F_6. [m] C trans to O(4). [n] C trans to C(3). [o] Angle between Fe(1)–S(1)–S(2) and Fe(2)–S(1)–S(2).

trans to the bridging sulfur atoms, as deduced from spectroscopic data. The Fe–P bond lengths are in the range usually found in sulfur-bridged, dinuclear compounds of iron (see Table VIII). Similarly, the Fe–C (of carbonyl groups) distances are in the usual range, but the Fe(1)–C(1) bond length of 1.712 (6) Å trans to atom O(4) is significantly shorter than the Fe(2)–C(2) bond of 1.762 (5) Å trans to atom C(3) as a result of the different trans effects. The Fe(2)–C(3) bond length of 2.049 (3) Å is in the range found for other Fe–C(sp^2)[32] or Ru–C(sp^2)[33] compounds.

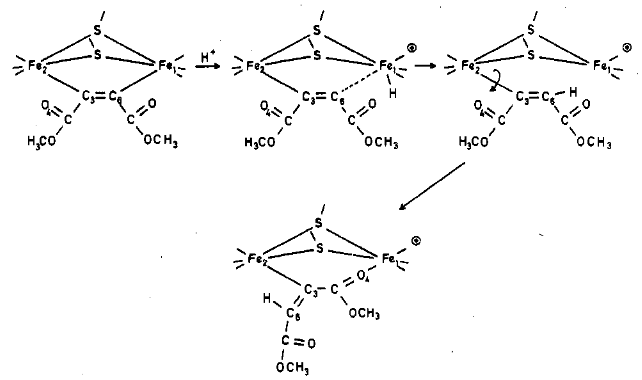
The Fe(1)–S(1)–Fe(2)–S(2) ring is surprisingly asymmetric with two equivalent Fe(1)–S(2) and Fe(2)–S(1) bond lengths, 2.299 (1) and 2.297 (1) Å, respectively, while the other two, Fe(1)–S(1) and Fe(2)–S(2), are significantly longer, 2.339 (1) and 2.364 (1) Å. Usually such rings are found with equivalent Fe–S bond lengths (Table VIII).

The C(4)–O(4) bond length of 1.230 (5) Å is longer than the C(7)–O(3) bond length of 1.195 (5) Å, as a result of the coordination of atom O(4) to Fe(1). All other distances in the 1,2-bis(carbomethoxy)ethylene group are normal.[33,34]

Model building shows clearly that the conformation of the alkene group is essentially the result of steric constraints imposed by the iron dimer complex on this cis geometry. The dihedral angle between the vinyl plane and the methoxy group, i.e., through atoms C(3), C(4), C(6), C(7) and O(4), O(5), C(4), C(5), respectively, is 68.5°.

Thus, the protonation of the dimetalated alkyne in $[(\mu\text{-}SCH_3)Fe(CO)(P(CH_3)_3)]_2(CH_3COOCCCOOCH_3)$ gives a monometalated alkene in which the added proton is cis to the carbon-bound iron atom. But does protonation occur through a direct attack of H^+ on a metalated carbon atom of the alkyne group, or is an iron hydride species formed with subsequent insertion of the Fe–H group into the coordinated alkyne bond? We favor the second alternative. The action on **1** of CH_3^+ (as the trimethyloxonium or methyltrifluorosulfonate salt) gives the same protonated product. Presumably CH_3^+ adds to an iron atom, and a hydride is generated through α-elimination, as has already been observed in molybdenum complexes.[35] Scheme I shows a possible mechanism[36] for the proton addition, i.e., protonation of atom Fe(1) to form the hydride intermediate, proton transfer to atom C(6) of the alkyne group, and then rotation about the Fe(2)–C(3) bond with subsequent formation of the Fe(1)–O(4) bond. The mechanism involving a metal hydride intermediate, followed by insertion of the metal–hydrogen bond into an alkyne bond, has been invoked in the protonation of a mononuclear platinum alkyne complex.[3]

Scheme I



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Registry No. **1**, 73574-62-6; **2**, 73574-64-8; **3**, 73610-82-9; $[(\mu\text{-}SCH_3)Fe(CO)_3]_2(CH_3COOCCCOOCH_3)$, 65585-29-7.

Supplementary Material Available: Table IV, the idealized positions of the hydrogen atoms, Table V, the root-mean-square amplitudes of vibration, and a listing of structure amplitudes (22 pages). Ordering information is given on any current masthead page.

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(36) We are indebted to the reviewer for comments on this mechanism.