Preparation, Properties, and Reactions of Metal-Containing Heterocycles. 58.[1] Cyclocotrimerization of Methylthioxophosphane with Alkynes

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Dichloromethylthioxophosphorane (1) reacts with $Mn_2(CO)_{10}$ (2) in the presence of activated magnesium to give the three-membered metallacycle $(OC)_4\overline{Mn{-}S\overset{\cdot\cdot}{-}P}(CH_3)Mn(CO)_5$ (**3**). Cyclocotrimerization of **3** with the electron-poor alkynes RC≡CR (R = CO_2CH_3 (**a**), $CO_2C_2H_5$ (**b**), $CO_2C_6H_{11}$ (**c**)) results in the formation of the bicycloheptadienes **6a–c**. This reaction proceeds via thiaphosphamanganacyclopentadienes $(OC)_4\overline{MnCRCRSP}(CH_3)Mn(CO)_5$ (**5**), which was proved in the case of **5b**. The cyclocotrimerization products **6a–c** were characterized by IR, NMR (^1H, ^{13}C, and ^{31}P), and mass spectroscopy. **6a** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. The cell dimensions are a = 11.253 (3) Å, b = 14.238 (3) Å, and c = 17.077 (4) Å.

Introduction

Recently we have been successful in the stabilization of methylthioxophosphane being protected by the coordination sphere of carbonylmanganese complexes.[2,3] An X-ray structure analysis of the compound $(OC)_4\overline{Mn{-}S\overset{\cdot\cdot}{-}P}(CH_3)Mn(CO)_5$ (3) confirmed the presence of the $H_3C{-}\bar{P}{=}S$ ligand. Due to comparable atomic radii and electronegativities of phosphorus and sulfur thioxophosphanes $RP\overset{\cdot\cdot}{-}S$ often behave like alkenes in cycloaddition reactions with dienes.[4-6] On the other hand, the $P\overset{\cdot\cdot}{-}S$ group functions also as an alkyne, which was demonstrated by the cyclocotrimerization of thiophosphinites with different electron-poor acetylenes.[7-10] Owing to the analogy of **3** with the η^2-thiophosphinito complex n-$C_3F_7(OC)_3Fe(\eta^2$-$S\overset{\cdot\cdot}{-}PEt_2)$[9] such a reaction should be possible with **3** as well. In contrast to previous results the cyclcotrimerization product of **3** with alkynes should be a suitable precursor for the direct synthesis of phosphole complexes[11] with a $(OC)_5Mn$ substituent attached to the phosphorus atom.

Experimental Section

General Procedures. All preparations were carried out under an atmosphere of purified nitrogen. n-Hexane and $CHCl_3$ were rendered water- and oxygen-free by distillation from $LiAlH_4$ and P_4O_{10}, respectively. For chromatographic purification of the products columns (diameter 2.5 cm) with silica gel 60 (Merck) were used. Instrumentation: mass spectra, Varian MAT 711 A; IR, Beckman IR 12 and Bruker FT-IR spectrometers, Model IFS 113c; ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, Bruker WP 80 and Bruker AC 80 spectrometers at 80, 20.12, 32.39, and 80.13, 20.15, 32.44 MHz, respectively. Elemental analyses were carried out with a Carlo Erba Model 1104 and a Perkin-Elmer Model 4000 atomic absorption spectrometer. Esters of acetylene dicarboxylic acid were prepared by alcoholysis of the corresponding acid.[12]

2-(Pentacarbonylmanganio)-5,5,5,5-tetracarbonyl-2-methyl-1λ^3-thia-2λ^5-phospha-5-mangana-1,3-cyclopentadiene-3,4-dicarboxylic Acid Diethyl Ester (5b). To a solution of 110 mg (0.25 mmol) of $(CH_3PS)Mn_2(CO)_9$ (3)[2,3] in 200 mL of n-hexane at 20 °C was added within 6 h the solution of 0.04 mL (0.25 mmol, d = 1.06 g/cm^3) of $H_5C_2O_2CC{\equiv}CCO_2C_2H_5$ (**4b**) in 50 mL of n-hexane. The reaction mixture was stirred for 1 h. After filtration (P3) and removal of the solvent under reduced pressure the residue was dissolved in 2 mL of $CHCl_3$. The resulting solution was purified by chromatography on a 10-cm silica gel column eluting with n-hexane/$CHCl_3$ (2:3). Fraction 1 contains **5b**, which was isolated as a pale yellow powder by recrystallization from CCl_4/n-hexane at −25 °C in 42% yield (64 mg). **5b** dissolves well in polar organic solvents: decomp >125 °C; ^1H NMR ($CDCl_3$, 30 °C) δ 1.12–1.56 (m, CH_2CH_3), 2.20 (d, $^2J_{PH}$ = 9.4 Hz, PCH_3), 4.02–4.48 (m, CH_2CH_3); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, −50 °C) δ 88.6; FDMS (8 kV), m/e 610 (M^+). Anal. Calcd for $C_{18}H_{13}Mn_2O_{13}PS$: C, 35.43; H, 2.15; Mn, 18.01; S, 5.25. Found: C, 35.57; H, 2.03; Mn, 17.67; S, 5.07.

General Preparation of the Thiaphosphamanganabicycloheptadienes (6a–c). To $(CH_3PS)Mn_2(CO)_9$ (3) dissolved in 200 mL of n-hexane was added $RO_2CC{\equiv}CCO_2R$ (**4a–c**) at 20 °C. After being stirred for 12 h the product was filtered off (P3) and washed with 10 mL of n-hexane. Recrystallization from $CHCl_3$/n-hexane yielded yellow crystalline compounds that dissolve well in polar organic solvents.

3-(Pentacarbonylmanganio)-7,7,7-tricarbonyl-3-methyl-2λ^3-thia-3λ^5-phospha-7-mangana-η^2-bicyclo[2.2.1]hepta-2,5-diene-1,4,5,6-tetracarboxylic Acid Tetramethyl Ester (6a). **3** (110 mg, 0.25 mmol) and 0.16 mL (1.25 mmol, d = 1.16 g/cm^3) of **4a** were reacted: yield 82% (143 mg); decomp >155 °C; ^1H NMR ($CDCl_3$, 30 °C) δ 2.23 (d, $^2J_{PH}$ = 8.4 Hz, PCH_3), 3.62–3.97 (m, OCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 30 °C) δ 51.93–52.87 (m, OCH_3); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, −50 °C) δ 82.7; FDMS (8 kV); m/e 696 (M^+). Anal. Calcd for $C_{21}H_{15}Mn_2O_{16}PS$: C, 36.23; H, 2.17; Mn, 15.78; S, 4.60. Found: C, 36.01; H, 2.05; Mn, 15.64; S, 4.73.

3-(Pentacarbonylmanganio)-7,7,7-tricarbonyl-3-methyl-2λ^3-thia-3λ^5-phospha-7-mangana-η^2-bicyclo[2.2.1]hepta-2,5-diene-1,4,5,6-tetracarboxylic Acid Tetraethyl Ester (6b). **3** (110 mg, 0.25 mmol) and 0.2 mL (1.25 mmol, d = 1.06 g/cm^3) of **4b** were reacted: yield 79% (149 mg); decomp >160 °C; ^1H NMR ($CDCl_3$, 30 °C) δ 1.12–1.49 (m, CH_2CH_3), 2.22 (d, $^2J_{PH}$ = 8.5 Hz, PCH_3), 3.99–4.48 (m, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 30 °C) δ 13.76–14.13 (m, CH_2CH_3), 61.36–61.91 (m, CH_2CH_3); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, −50 °C) δ 80.9; FDMS (8 kV), m/e 752 (M^+). Anal. Calcd

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[1] Part 57: Lindner, E.; Auch, K.; Hiller, W.; Fawzi, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1987**, *42B*, 454.

[2] Lindner, E.; Auch, K. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 320.

[3] Lindner, E.; Auch, K.; Weiss, G. A.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1986**, *119*, 3076.

[4] Nakayama, S.; Yoshifuji, M.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 546.

[5] Hussong, R.; Heydt, H.; Regitz, M. *Z. Naturforsch., B: Anorg. Chem., Org. chem.* **1986**, *41B*, 915.

[6] Quin, L. D.; Szewczyk, J. *J. Chem. Soc., Chem. Commun.* **1986**, 844.

[7] Lindner, E.; Rau, A.; Hoehne, S. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 787.

[8] Lindner, E.; Bouachir, F.; Hoehne, S. *Chem. Ber.* **1983**, *116*, 46.

[9] Lindner, E.; Krieg, C.-P.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1985**, *118*, 1398.

[10] Lindner, E.; Frick, K. E., unpublished results.

[11] (a) Santini, C. C.; Mathey, F. *J. Org. Chem.* **1985**, *50*, 467. (b) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding* (Berlin) **1983**, *55*, 153.

[12] Walton, W. L.; Hughes, R. B. *J. Am. Chem. Soc.* **1957**, *79*, 3985.

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of 6a

formula	$C_{21}H_{15}Mn_2O_{16}PS$
fw	696.26
space group	$P2_12_12_1$
a, Å	11.253 (3)
b, Å	14.238 (3)
c, Å	17.077 (4)
V, Å^3	2737.3
Z	4
d_{calcd}, g cm^{-3}	1.689
$F(000)$, e	1400
μ(Mo Kα), cm^{-1}	10.89
radiatn (graphite monochromator, λ = 0.71073 Å)	Mo Kα
θ limits, deg	3–30
scan type	ω/θ
max scan time	40 s
h,k,l range	0→15, 0→20, 0→24
reflectns measd	4430
no. of unique data with $I \geq 3\sigma(I)$	1897
no. of variables	371
R	0.044
R_w	0.049
weighting scheme	$w^{-1} = \sigma^2(F)$
secondary extinctn coeff	6.7 (3) × 10^{-9}

for $C_{25}H_{23}Mn_2O_{16}PS$: C, 39.91; H, 3.08; Mn, 14.60; S, 4.26. Found: C, 39.87; H, 2.89; Mn, 14.48; S, 4.07.

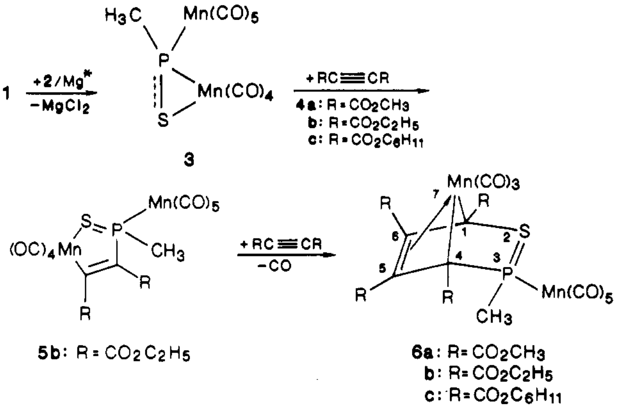
3-(Pentacarbonylmanganio)-7,7,7-tricarbonyl-3-methyl-2λ^3-thia-3λ^5-phospha-7-mangana-η^2-bicyclo[2.2.1]hepta-2,5-diene-1,4,5,6-tetracarboxylic Acid Tetracyclohexyl Ester (6c). **3** (110 mg, 0.25 mmol) and 0.35 g (1.25 mmol) of **4c** were reacted. Yield 76% (184 mg): decomp >150 °C; ^{1}H NMR (CDCl$_3$, 30 °C) δ 1.06–2.31 (m, C_6H_{11}), 2.20 (d, $^2J_{PH}$ = 8.4 Hz, PCH$_3$), 4.59–5.06 (m, C_6H_{11}); 13C{^{1}H} NMR (CDCl$_3$, 30 °C) δ 23.22–25.43, 31.27–31.95, 74.01–76.15 (m, C_6H_{11}); ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, −50 °C) δ 78.4; FDMS (8 kV), m/e 968 (M$^+$). Anal. Calcd for $C_{41}H_{47}Mn_2O_{16}PS$: C, 50.84; H, 4.89; Mn, 11.34; S, 3.31. Found: C, 50.67; H, 4.75; Mn, 11.30; S, 3.17.

X-ray Structure Determination of 6a. Yellow crystals of **6a** were obtained by crystallization from acetonitrile. A suitable crystal with approximate dimensions 0.2 × 0.2 × 0.3 mm was mounted on a glass fiber and then transferred to an Enraf-Nonius CAD-4 diffractometer. The lattice constants were determined with 25 precisely centered high-angle reflections. The final cell parameters and specific data collection parameters for **6a** are summarized in Table I. Precession photography suggested the space group to $P2_12_12_1$. The usual corrections for Lorentz and polarization effects were applied to the intensity data. No decay in the intensities of three standard reflections was observed. The structure was solved by direct methods,[13] and difference Fourier syntheses[14] were used to locate the remaining non-hydrogen atoms. The DIFABS[15] method of absorption correction was applied after isotropic refinement of all non-hydrogen atoms. The hydrogen atoms could not be located and were not calculated on the basis of the staggered geometry. A secondary extinction parameter[16] was refined in the final cycles of least squares. The atomic scattering factors used were those from Cromer and Waber.[17] The absolute structure was not determined.

Results and Discussion

The incorporation of methylthioxophosphane into the coordination sphere of carbonyl manganese complexes results in the formation of $(OC)_4\overline{Mn—S}$⌐$P(CH_3)Mn(CO)_5$ (**3**),[2,3] which is the first example of an η^2-thiophosphinito complex with manganese. The bulky (OC)$_5$Mn group at the phosphorus atom seems to be responsible for the kinetic stability of the compound preventing a dimerization. Such a dimerization takes place in the case of other thiophosphinito complexes of manganese[7] and nickel[8] to give $[L_nM(SPR_2)]_2$ systems (L_nM = (OC)$_4$Mn, η^5-C$_5$H$_5$Ni), each containing two organic substituents at the phosphorus atom. Recently, we have found that the six-membered manganese heterocycles $[(OC)_4Mn(SPR_2)]_2$ undergo a cyclocotrimerization with activated alkynes.[18] For this reaction a monomeric (OC)$_4$Mn(η^2-S⌐PR$_2$) species is assumed to be the real starting material, which is trapped in solution by the alkyne. An equilibrium exists between the monomer (OC)$_4$Mn(η^2-S⌐PR$_2$) and the dimer $[(OC)_4Mn(SPR_2)]_2$. This hypothesis was proved in the case of the monomeric iron complexes n-C$_3$F$_7$(OC)$_3$Fe(η^2-S⌐PR$_2$)[9] being active for cyclocotrimerizations with electron-poor alkynes. In the course of this cyclocotrimerization thiaphosphametallacyclopentadienes are isolated as a reactive intermediate. These are kinetically labile toward alkynes reacting with the latter to give seven-membered thiaphosphametallabicycloheptadienes. In the case of nickel, the heterocyclopentadiene is the final product because no further ligand is available at the nickel that can be substituted by an alkyne. The relative kinetic stability of the iron compounds n-C$_3$F$_7$(OC)$_3$Fe(η^2-S⌐PR$_2$) compared to the corresponding manganese and nickel systems can be traced back to the electron-withdrawing property of the strongly electronegative n-C$_3$F$_7$ substituent attached to the iron atom. Meanwhile active η^2-thiophosphinito complexes of cobalt were also prepared.[10] Their dimerization tendency depends on the spaciousness of the phosphane ligands at the cobalt. With complex **3** now the first organometallic substituted η^2-thiophosphinito complex is accessible, which was proved to be a starting compound for cyclocotrimerization with electron-poor alkynes. This reaction presents in principle a possibility for a convenient preparation of phosphole complexes by separating sulfur from the compounds **6**.[18]

Scheme I[a]



[a] **1**: CH$_3$P(S)Cl$_2$. **2**: Mn$_2$(CO)$_{10}$.

When **3** was reacted with excess of **4a**, **4b**, and **4c** (Scheme I), the corresponding thiaphosphamanganabicycloheptadienes **6a**, **6b**, and **6c**, respectively, could be isolated in high yields. The reaction proceeds via a five-membered thiaphosphamanganacyclopentadiene. This was proved with the reaction sequence **3** → **5b** → **6b**. The structure of **5b** is similar to other heterometallacyclopentadienes with vibrations of localized C=C and P=S

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(13) Sheldrick, G. M. SHELXS-86, University of Göttingen, Göttingen, West Germany.

(14) Structure Determination Package SDPVAX, B. A. Frenz & Associates, College Station, TX, and Enraf-Nonius, Delft, Netherlands.

(15) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, *39A*, 158.

(16) Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(18) Lindner, E.; Rau, A.; Hoehne, S. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 788; *J. Organomet. Chem.* 1981, *218*, 41.

Table II. $^{13}C\{^1H\}$ NMR Data (in $CDCl_3$; δ; J, Hz)[a]

	compd no.		
	6a	6b	6c
C-1	59.87 (s)	60.43 (s)	60.93 (s)
C-4	56.70 (d, $^1J_{PC}$ = 36 Hz)	56.88 (d, $^1J_{PC}$ = 36 Hz)	57.52 (d, $^1J_{PC}$ = 35 Hz)
C-5	103.97 (d, $^2J_{PC}$ = 3 Hz)	103.50 (d, $^2J_{PC}$ = 3 Hz)	103.63 (d, $^2J_{PC}$ = 3 Hz)
C-6	100.99 (s)	101.33 (s)	101.61 (s)
PCH_3	28.93 (d, $^1J_{PC}$ = 21 Hz)	29.00 (d, $^1J_{PC}$ = 22 Hz)	29.45 (d, $^1J_{PC}$ = 22 Hz)

[a] All spectra were recorded at 20.15 MHz; chemical shifts in δ units (positive values to low field) relative to internal Me_4Si; for assignment of ester C atoms see Experimental Section.

Table III. Characteristic Vibrations (cm^{-1}) in the IR Spectra of 5 and 6

5b	6a	6b	6c	assignmt
2130 m[a]	2134 m[b]	2134 m[b]	2133 m[b]	$\nu(C\equiv O)$
2080 m-s	2088 w	2087 w	2087 w	
2051 vs	2054 s	2054 vs	2052 vs	
2040 vs	2045 s	2046 s-vs	2044 s-vs	
2028 s	2036 m-s	2036 m-s	2033 m-s	
2004 s-vs	2021 vs	2019 vs	2018 vs	
1997 sh	1951 m-s	1949 m-s	1944 m-s	
1956 s	1937 sh	1934 sh		
1698 s	1749 m	1750 m	1751 m	$\nu(>C{=}O)$ and $\nu(C{=}C)$[c]
1676 s	1715 m	1720 m	1693 m	
1530 m	1691 m	1682 m	1646 m	
	1666 m	1664 m		
549 m	536 w	541 w	544 w	$\nu(P{=}S)$[c]

[a] In CCl_4. [b] In n-hexane/$CHCl_3$ (1:1). [c] In KBr.

bonds[19,20] observed in the IR spectrum. Complex **3** is much more reactive than the iron compounds n-$C_3F_7(OC)_3Fe(\eta^2\text{-}S\frown PR_2)$ and the six-membered manganese and nickel rings. Compared to these heterocycles no dissociation energy is necessary for **3**. In contrast to the iron compounds n-$C_3F_7(OC)_3Fe(\eta^2\text{-}S\frown PR_2)$ the Mn–P bond of the heterocyclic unit is cleaved much easier. While the n-C_3F_7 substituent at the iron atom stabilizes the whole complex fragment, the $(OC)_5Mn$ group at the phosphorus atom, which is more electronegative than an alkyl group, decreases the basicity of the phosphorus atom and thus weakens the Mn–P bond.

Considering other cyclocotrimerization products of manganese[7,18] the ^{31}P and ^{13}C signals of the methyl group at the phosphorus atom as well of C-1 and C-4 in the spectra of **6a–c** are shifted to lower fields (Table II). Though the $(OC)_5Mn$–P bond in **3** is rather long (2.39 Å), the $(OC)_5Mn$ group is preserved in the course of the whole cyclocotrimerization process. This is a basic requirement for the envisaged synthesis of phosphole complexes.

Due to the low symmetry of the $(OC)_5Mn$, $(OC)_4Mn$, and $(OC)_3Mn$ groups, five, four, and three CO absorptions, respectively, are observed in the IR spectra (Table III) of **3**, **5b**, and **6a**,**b**. As a result of the low volatility of **5b** and **6a–c**, their molecular peaks only appear in field desorption mass spectra. The yellow to orange compounds are little sensitive toward air and moisture and dissolve well in polar organic solvents.

Description of the Crystal Structure of 6a. The molecular structure and labeling scheme of complex **6a** are shown in Figure 1. Final atomic positional parameters for **6a** are listed in Table V. Table IV contains selected bond distances and angles.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for 6a

Bond Lengths			
Mn(1)–C(1)	2.110 (8)	P–C(15)	1.839 (11)
Mn(1)–C(4)	2.136 (9)	C(1)–C(6)	1.440 (13)
Mn(1)–C(5)	2.098 (8)	C(4)–C(5)	1.452 (12)
Mn(1)–C(6)	2.090 (8)	C(5)–C(6)	1.417 (12)
Mn(2)–P	2.354 (3)	C(1)–C(31)	1.489 (13)
S–P	2.068 (4)	C(4)–C(41)	1.483 (13)
S–C(1)	1.821 (9)	C(5)–C(51)	1.488 (13)
P–C(4)	1.815 (10)	C(6)–C(61)	1.503 (13)
Bond Angles			
C(1)–Mn(1)–C(4)	79.3 (4)	C(1)–C(6)–C(5)	116.4 (8)
Mn(1)–C(1)–S	123.7 (5)	C(6)–C(5)–C(4)	116.7 (8)
Mn(1)–C(1)–C(6)	69.2 (5)	P–C(4)–C(5)	121.1 (7)
Mn(1)–C(4)–P	118.7 (5)	C(1)–C(6)–C(61)	121.5 (8)
Mn(1)–C(4)–C(5)	68.5 (5)	C(5)–C(6)–C(61)	122.1 (8)
P–S–C(1)	99.2 (3)	C(4)–C(5)–C(51)	119.1 (8)
S–P–Mn(2)	108.2 (1)	C(6)–C(5)–C(51)	123.5 (8)
S–P–C(4)	100.6 (3)	S–C(1)–C(31)	111.3 (7)
S–P–C(15)	104.3 (4)	C(6)–C(1)–C(31)	117.5 (8)
Mn(2)–P–C(4)	119.0 (3)	P–C(4)–C(41)	108.1 (7)
Mn(2)–P–C(15)	114.7 (4)	C(5)–C(4)–C(41)	117.9 (8)
S–C(1)–C(6)	116.3 (7)		

Table V. Fractional Atomic Coordinates (Estimated Standard Deviations in Parentheses) of 6a with Equivalent Isotropic Thermal Parameters U_{eq}

atom	x	y	z	U_{eq},[a] Å^2
Mn(1)	0.0265 (1)	–0.0042 (1)	0.02880 (8)	0.0314 (6)
Mn(2)	0.4573 (1)	0.0597 (1)	0.17586 (9)	0.0369 (7)
S	0.1562 (2)	0.1414 (2)	0.1673 (2)	0.043 (1)
P	0.2876 (2)	0.0835 (2)	0.0978 (2)	0.033 (1)
O(7)	0.0186 (9)	0.1528 (6)	–0.0810 (5)	0.082 (7)
O(8)	–0.2309 (7)	–0.0313 (7)	0.0212 (6)	0.084 (7)
O(9)	0.0202 (8)	–0.1426 (6)	–0.0981 (4)	0.070 (6)
O(10)	0.6049 (7)	0.1364 (6)	0.0452 (4)	0.058 (5)
O(11)	0.4203 (9)	0.2527 (6)	0.2385 (5)	0.075 (7)
O(12)	0.2969 (8)	–0.0246 (7)	0.2972 (5)	0.076 (6)
O(13)	0.5168 (8)	–0.1298 (5)	0.1110 (5)	0.071 (6)
O(14)	0.6520 (7)	0.0300 (7)	0.2918 (5)	0.075 (8)
O(32)	–0.1735 (6)	0.0722 (5)	0.1698 (4)	0.049 (4)
O(33)	–0.0768 (6)	0.2075 (5)	0.1568 (4)	0.045 (4)
O(42)	0.3809 (6)	–0.0310 (5)	–0.0228 (4)	0.055 (5)
O(43)	0.2515 (6)	–0.1498 (5)	–0.0194 (4)	0.048 (4)
O(52)	0.2651 (6)	–0.1922 (5)	0.1530 (4)	0.046 (4)
O(53)	0.0937 (7)	–0.2377 (5)	0.1012 (5)	0.054 (5)
O(62)	–0.1030 (8)	–0.1455 (6)	0.1901 (5)	0.071 (6)
O(63)	–0.0199 (7)	–0.0479 (5)	0.2757 (3)	0.044 (4)
C(1)	0.0313 (8)	0.0694 (7)	0.1360 (5)	0.032 (5)
C(4)	0.2100 (8)	–0.0179 (6)	0.0586 (6)	0.035 (5)
C(5)	0.1356 (8)	–0.0762 (6)	0.1083 (5)	0.026 (4)
C(6)	0.0423 (9)	–0.0302 (6)	0.1488 (5)	0.031 (4)
C(7)	0.022 (1)	0.0903 (7)	–0.0373 (6)	0.048 (6)
C(8)	–0.1319 (9)	–0.0194 (7)	0.0272 (7)	0.045 (6)
C(9)	0.0270 (9)	–0.0918 (7)	–0.0478 (5)	0.040 (5)
C(10)	0.5521 (9)	0.1076 (7)	0.0963 (6)	0.042 (6)
C(11)	0.434 (1)	0.1802 (7)	0.2151 (6)	0.047 (7)
C(12)	0.3550 (9)	0.0085 (8)	0.2511 (6)	0.046 (6)
C(13)	0.4885 (9)	–0.0585 (8)	0.1332 (6)	0.046 (6)
C(14)	0.5812 (9)	0.0424 (9)	0.2458 (6)	0.051 (8)
C(15)	0.307 (1)	0.1689 (7)	0.0181 (7)	0.052 (6)
C(31)	–0.0841 (9)	0.1142 (6)	0.1564 (5)	0.034 (5)
C(34)	–0.1887 (9)	0.2564 (7)	0.1713 (7)	0.050 (7)
C(41)	0.2900 (9)	–0.0655 (7)	0.0022 (6)	0.050 (5)
C(44)	0.318 (1)	–0.202 (1)	–0.0773 (7)	0.076 (8)
C(51)	0.1715 (9)	–0.1750 (7)	0.1236 (5)	0.047 (5)
C(54)	0.125 (1)	–0.3373 (7)	0.1143 (8)	0.072 (9)
C(61)	–0.038 (1)	–0.0816 (7)	0.2044 (5)	0.040 (5)
C(64)	–0.091 (1)	–0.0877 (8)	0.3376 (6)	0.057 (8)

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

The central core of the molecule is essentially the same as the previously reported manganese complex.[18] The P–S linkage of 2.07 Å indicates a partial multiple-bond character. Compared to complex **3** the Mn–P bond is shorter.

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(19) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.
(20) Lindner, E. *Adv. Heterocycl. Chem.* **1986**, *39*, 237.

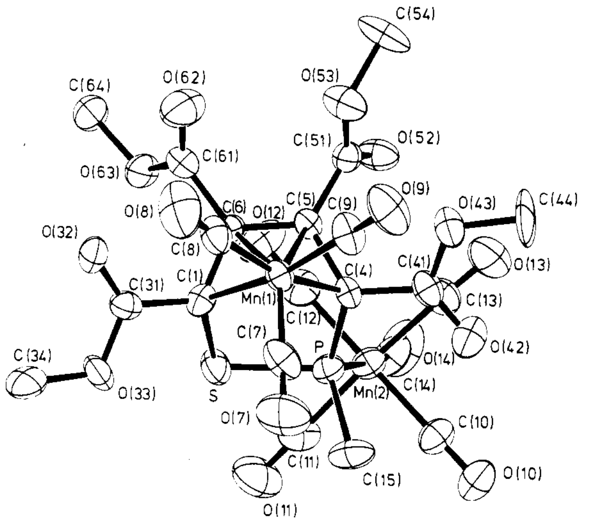

Figure 1. ORTEP plot of **6a**.

The dihedral angle between the least-squares planes C(1), C(6), C(5), C(4) and C(1), S, P, C(4) is 50.4°. The bonding of the cyclic ligand to the metal Mn(1) is identical with that observed.[18] Mn(1) is π-bonded to C(5)–C(6) and σ-bonded to C(1) und C(4), which explains the bond sequence long–short–long for C(4)–C(5), C(5)–C(6), and C(1)–C(6). The angles between the planes C(6)–C(61)–O(62) and C(1)–C(6)–C(5), and C(5)–C(51)–O(52) and C(4)–C(5)–C(6) are 59.9° and 63.4°, respectively. These values provide a satisfactory explanation for the observed single bonds C(5)–C(51) and C(6)–C(61), as there is no possibility for π-conjugation between C(5)–C(51) and C(6)–C(61).

The deviations of C(1) and C(4) from the planes S–C(6)–C(31) and P–C(5)–C(41) are 0.35 and 0.33 Å, respectively, which is consistent with sp^3-hybridized carbon atoms C(1) and C(4).

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Registry No. **3**, 89509-61-5; **4a**, 762-42-5; **4b**, 762-21-0; **4c**, 79866-97-0; **5b**, 111290-91-6; **6a**, 111290-92-7; **6b**, 111290-93-8; **6c**, 111290-94-9.

Supplementary Material Available: Tables of least-squares planes, final positional and anisotropic thermal parameters, and interatomic distances and angles for **6a** (13 pages); a listing of observed and calculated structure factors for **6a** (15 pages). Ordering information is given on any current masthead page.

An Accurate Determination of the Molecular Structure of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Et_2)$: A Seminal Type of Acetylene Complex

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A precise single-crystal X-ray structure determination of the $\perp$-diethylacetylene complex $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC{\equiv}CEt)$ has been carried out. This molecule is one of a very small number of alkyne cluster complexes in which one carbon atom of the alkyne is coordinated to all three metal atoms with the triple bond perpendicular to one M–M vector. Such molecules are thought to be important intermediates in alkyne triple-bond scission reactions leading to bis(alkylidyne) species. Crystals of the title compound are triclinic, space group $P\bar{1}$, with a = 9.446 (1) Å, b = 9.644 (1) Å, c = 10.022 (1) Å, α = 87.84 (1)°, β = 85.96 (1)°, γ = 89.58 (1)°, V = 910.2 Å^3, and Z = 2. The solution and refinement were based on 2560 observed reflections ($I \geq 3\sigma(I)$). Final R and R_w values with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic were 0.027 and 0.031. Key features of the accurate structure are as follows: (i) one carbon atom of the alkyne is bonded symmetrically to the Fe framework resembling a μ_3-alkylidyne; (ii) one Fe–Fe bond (Fe(1)–Fe(3) of 2.5666 (5) Å), that bridged perpendicularly by the alkyne is 0.1 Å longer than the two remaining, equivalent Fe–Fe bonds; (iii) the substituents on the alkyne have an anti disposition across the plane of the alkyne. Possible structural implications for the conversion of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ to $Fe_3(CO)_9(\mu_3\text{-}CR)(\mu_3\text{-}CR')$ are discussed.

Of the many transition-metal–acetylene complexes which have been characterized,[1] one of the most interesting is $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ (M = iron group metal) where the alkyne triple bond is disposed above the plane of the three metal atoms and perpendicular to one of the M–M bonds as shown in 1.[2] The unusual bonding in these molecules, in which one alkyne carbon atom interacts with all three metals, has been the subject of theoretical studies by CNDO[3] and EHMO[4] methods. Apart from the fact that

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[1] For recent reviews see: (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Einstein, F. W. B.; Tyers, K. G.; Tracey, A. S.; Sutton, D. *Inorg. Chem.* **1986**, *25*, 1631. (c) Bruce, M. I. *J. Organomet. Chem.* **1983**, *257*, 417.

[2] Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292.