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The Structure of (μ_3-Sulfido)(μ_3-*p*-Tolyphosphido)tris(tricarbonyliron)(2Fe–Fe)

JOHN P. FACKLER, Jr.*, ANTHONY M. MAZANY

Department of Chemistry, Texas A & M University, College Station, Tex. 77843, U.S.A.

DIETMAR SEYFERTH*, HOWARD P. WITHERS, Jr., TIMOTHY G. WOOD

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

and CHARLES F. CAMPANA

Nicolet Magnetics, Fremont, Calif. 94539, U.S.A.

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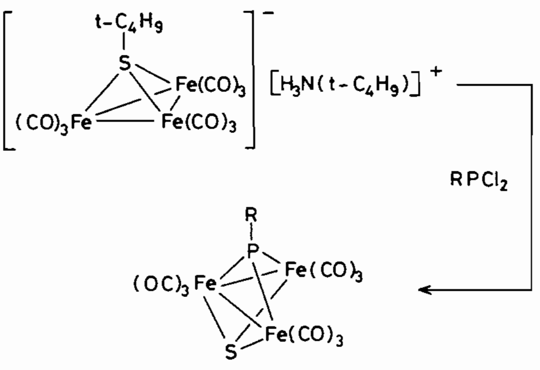
Compounds of the type $(\mu_3\text{-}S)(\mu_3\text{-}RP)Fe_3(CO)_9$ *have been prepared by the reaction of* $Fe_3(CO)_{12}$ *with* $[RP(S)S]_2$ *or* $RP(S)Cl_3$*. In this paper we report the synthesis of* $(\mu_3\text{-}S)(\mu_3\text{-}CH_3OC_6H_4P)Fe_3(CO)_9$ *using Lawesson's reagents, and the three dimensional structure of* $(\mu_3\text{-}S)(\mu_3\text{-p-}CH_3C_6H_4P)Fe_3(CO)_9$*. This material crystallizes in the space group* $P2_1/n$ *with* a = 8.558(2) Å, b = 9.022(2) Å, c = 27.506(6) Å, β = 95.40(2)°, Z = 4*. The cluster is a nido structure as found commonly for* $(\mu_3\text{-}X)(\mu_3\text{-}Y)Fe_3(CO)_9$ *complexes.*

Introduction and Results

Recently, we reported the preparation and characterization of complexes of type $(\mu_3\text{-S})(\mu_3\text{-RP})Fe_3(CO)_9$, *1*, (R = C_6H_5, *p*-$CH_3C_6H_4$, $(CH_3)_3C$) by the reactions of $Fe_3(CO)_{12}$ with the respective $RP(S)Cl_2$ compounds [1]. In an independent study, Winter, Zsolnai and Huttner [2] prepared complexes of type *1* (R = $(CH_3)_3C$, *p*-$CH_3OC_6H_4$, C_6H_5, Et_2N, CH_3, cyclo-C_6H_{11} and *p*-BrC_6H_4) by a completely different route (eqn. 1). These workers determined the structure of *1* (R = Ph) by X-ray diffraction. Subsequent to our initial communication [1] we have determined the structure of *1* (R = *p*-$CH_3C_6H_4$) by X-ray diffraction.

In related work, we have examined the potential utility of Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetan, cyclo-[*p*-$CH_3OC_6H_4P(S)S]_2$, *2*, in the synthesis of complexes of type *1*. In a reaction between *2* and $Fe_3(CO)_{12}$ in refluxing THF the expected *1* (R = *p*-$CH_3OC_6H_4$) was indeed formed, but in only very low yield.



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Experimental

Reaction of $Fe_3(CO)_{12}$ *with Cyclo-[p-*$CH_3OC_6H_4P(S)S]_2$

A 100 ml three-necked, round-bottomed flask equipped with a magnetic stir-bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and two no-air stoppers was charged with 2.10 g (4.17 mmol) of $Fe_3(CO)_{12}$ and 0.878 g (2.17

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*Authors to whom correspondence should be addressed.

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TABLE 1. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^1).

Atom	x	y	z	U
Fe(1)	–2338(1)	1485(1)	1894(1)	43(1)*
Fe(2)	–518(1)	–1031(1)	1162(1)	40(1)*
Fe(3)	–3106(1)	574(1)	992(1)	36(1)*
P	–741(1)	1319(1)	1325(1)	34(1)*
S	–2528(1)	–912(1)	1641(1)	47(1)*
C(1)	536(3)	2786(3)	1160(1)	37(1)*
C(2)	913(4)	3026(4)	688(1)	47(1)*
C(3)	2013(5)	4089(4)	596(2)	55(1)*
C(4)	2761(4)	4927(4)	968(2)	53(1)*
C(4m)	3989(5)	6078(5)	869(2)	77(2)*
C(5)	2363(4)	4700(4)	1437(2)	60(1)*
C(6)	1276(4)	3633(4)	1538(1)	50(1)*
C(11)	–2563(5)	3440(5)	1828(1)	60(1)*
O(11)	–2688(5)	4685(4)	1773(1)	95(2)*
C(12)	–882(5)	1461(5)	2396(1)	59(1)*
O(12)	100(4)	1480(5)	2706(1)	99(2)*
C(13)	–4089(5)	1264(6)	2217(2)	72(2)*
O(13)	–5154(4)	1105(6)	2426(2)	114(2)*
C(21)	673(4)	–810(4)	668(1)	50(1)*
O(21)	1435(4)	–707(4)	352(1)	77(1)*
C(22)	1016(4)	–1394(4)	1626(2)	58(1)*
O(22)	1982(4)	–1569(4)	1936(1)	93(1)*
C(23)	–1100(4)	–2908(4)	966(2)	57(1)*
O(23)	–1475(4)	–4047(3)	833(2)	87(1)*
C(31)	–3149(4)	2194(4)	619(1)	51(1)*
O(31)	–3190(4)	3223(4)	383(1)	84(1)*
C(32)	–3421(4)	–714(4)	499(1)	49(1)*
O(32)	–3719(4)	–1490(4)	176(1)	75(1)*
C(33)	–5101(4)	716(5)	1131(2)	58(1)*
O(33)	–6367(3)	768(5)	1224(2)	90(1)*

*Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ig} tensor.

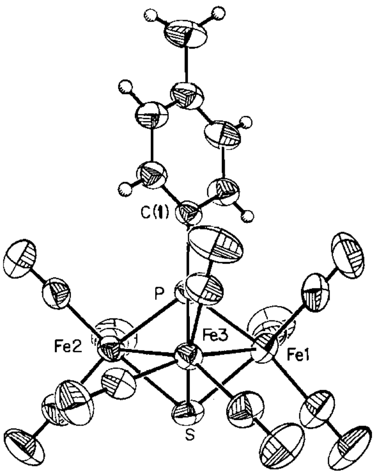

Fig. 1. The molecular structure of (μ_3-S)(μ_3-p-$CH_3C_6H_4P$)-$Fe_3(CO)_9$ (50% probability thermal elipsoids). Bond lengths: Fe(1)–Fe(3) = 2.636(1) Å, Fe(2)–Fe(3) = 2.650(1) Å, Fe(1)–Fe(2) = 3.495(1) Å, Fe(1)–S = 2.272(1) Å, Fe(2)–S = 2.266(1) Å, Fe(3)–S = 2.250(1) Å, Fe(1)–P = 2.177(1) Å, Fe(2)–P = 2.179(1) Å, Fe(3)–P = 2.244(1) Å, S···P = 2.719(2) Å. Bond Angles: Fe(1)–Fe(3)–Fe(2) = 82.8(1)°, Fe(1)–P–C(1) = 124.6(1)°, Fe(2)–P–C(1) = 126.6(1)°, Fe(3)–P–C(1) = 131.5(1)°, S–Fe(1)–P = 75.3(1)°, S–Fe(2)–P = 75.4(1)°, S–Fe(3)–P = 74.5(1)°.

mmol, 4.34 equivalents of '*p*-$CH_3OC_6H_4PS$' of [*p*-$CH_3OC_6H_4PS_2$]$_2$ (Fluka) evacuated and refilled with nitrogen. THF (40 ml) was added by syringe and the reaction mixture was heated to reflux. After 4.5 h at reflux, TLC indicated product formation and complete consumption of $Fe_3(CO)_{12}$. The solvent was removed *in vacuo* to give a black-red tarry residue, which was extracted with boiling pentane until the extracts were colorless. Filtration chromatography using pentane as eluant removed a red-purple band, which upon removal of solvent, yielded 0.010 g (0.02 mmol, 0.5%) of a black solid identified as $S_2Fe_3(CO)_9$ on the basis of its IR spectrum. Continued elution with a 10% dichloromethane/90% pentane mixture separated an orange band, which upon removal of solvent and recrystallization from pentane at –30 °C, yielded 0.029 g (0.05 mmol, 1.2%) of dark red nuggets, identified as *1* (R = *p*-$CH_3OC_6H_4$), m.p. 104–150 °C. *Anal.* Calcd. for $C_{16}H_7O_{10}SPFe_3$: C, 32.58; H, 1.20. Found: C, 32.52; H, 1.37. IR (CCl_4) ν(C≡O): 2087(w), 2060(vs), 2040(vs), 2019(s) and 1999(sh), cm^{-1}.

^1H NMR ($CDCl_3$): δ3.90 (s, 3H, $-CH_3$) and 6.95–7.40 ppm (m, 4H, Ph).

$^{31}P\{^1H\}$-NMR (C_6H_6): δ_p + 359.5 ppm (s).

Mass spec. (m/e): 562 (M^+ –1CO, 0.4%), 534 (M^+ –2CO, 0.6%), 506 (M^+ –3CO, 0.3%), 478 (M^+ –4CO, 0.5%), 450 (M^+ –5CO, 1.0%), 422 (M^+ –6CO, 1.7%), 394 (M^+ –7CO, 1.8%), 366 (M^+ –8CO, 1.7%), 338 (M^+ –9CO, 3.9%).

In a recent paper [3], Lindner and Weiss reported the preparation of this compound by the reaction of *p*-$CH_3OC_6H_4PCl_2$ with $Na_2Fe(CO)_4$ in ether. Its melting point and spectroscopic properties were identical with those of our product.

X-ray Data Collection

A crystal of (μ_3-S)(μ_3-p-$CH_3C_6H_5P$)$Fe_3(CO)_9$ was centered at ambient temperature on a Nicolet P3F diffractometer. The scan rate was varied from 4.0° to 30.00° per minute. The background time to scan time ratio was 1.0. Lorentz, polarization, decay factor and empirical absorption corrections were applied to measured intensities. The monoclinic space group $P2_1/n$ was indicated by systematic absences (*h* 0 *l*: *h* + *l* = 2n, 0*k*0: *k* = 2n). Direct methods provided the initial iron, phosphorus and sulfur atom positions. The oxygen and carbon atom positions (Table I) were determined through Fourier syntheses. All crystallographic computations were performed using SHELXTL.

Summary of crystal data for $SFe_3(CO)_9(PC_6H_4CH_3)$: a = 8.558(2) Å, b =9.022(2) Å, c = 27.506(6) Å, β = 95.40(2)°; V = 2.114 Å^3; space group $P2_1/n$ (No. 14); Z = 4; d(calc) 1.80 g/cm^3; μ(Mo) = 23.0 cm^{-1}; λ(Mo-Kα) = 0.71069 Å, F(000) = 1136. Summary of final refinement for $SFe_3(CO)_9(PC_6H_4CH_3)$: data collected, 7365 reflections, *hkl*, $hk\bar{l}$, $3° \leqslant 2\theta \leqslant 60°$; data with $I > 3\sigma(I)$, $3° \leqslant 2\theta \leqslant 60°$, 4659; least-squares parameters, 271; goodness of fit, 1.09; final R, 0.033, final R_W, 0.035.

Discussion

The structure of $(\mu_3\text{-}S)(\mu_3\text{-}p\text{-}CH_3C_6H_4P)Fe_3(CO)_9$ as determined by X-ray diffraction techniques is shown in Fig. 1. The complex consists of three iron atoms capped with a triply bridging sulfur atom and a $\mu_3\text{-}p\text{-}CH_3C_6H_4P$. The cluster is a nido structure as has been commonly observed in $(\mu_3\text{-}X)(\mu\text{-}Y)Fe_3(CO)_9$ complexes. Structural studies have been reported for $(\mu_3\text{-}S)_2Fe_3(CO)_9$ [4], $(\mu_3\text{-}Se)_2Fe_3(CO)_9$ [5], $(\mu_3\text{-}Te)_2Fe_3(CO)_9$ [6], $(\mu_3\text{-}CH_3N)_2Fe_3(CO)_9$ [7], $(\mu_3\text{-}C_6H_5P)_2Fe_3(CO)_9$ [8] and $(\mu_3\text{-}S)(\mu_3\text{-}p\text{-}CH_3C_6H_4N)Fe_3(CO)_9$ [9], and, as mentioned above, $(\mu_3\text{-}S)(\mu_3\text{-}C_6H_5P)Fe_3(CO)_9$ [2], as well as $(\mu_3\text{-}S)(\mu_3\text{-}C_6H_5As)Fe_3(CO)_9$ [2].

The iron–iron distances in $(\mu_3\text{-}S)(\mu_3\text{-}p\text{-}CH_3C_6H_4P)Fe_3(CO)_9$ are intermediate between the distances found in $(\mu_3\text{-}S)_2Fe_3(CO)_9$ (2.60(2) Å) [4] and $(\mu_3\text{-}PPh)_2Fe_3(CO)_9$, (2.717(3) Å) [8]. The S···P separation of 2.719 Å is also intermediate between the two extremes, $(\mu_3\text{-}S)_2Fe_3(CO)_9$ (2.863 (15) Å) and $(\mu_3\text{-}PPh)_2Fe_3(CO)_9$ (2.587 Å) and is essentially identical to that found in $(\mu_3\text{-}S)(\mu_3\text{-}C_6H_5P)Fe_3(CO)_9$ (2.713(5) Å [2]. However, the Fe···Fe nonbonding distance is very nearly that found for $(\mu_3\text{-}PPh)_2Fe_3(CO)_9$, almost 0.17 Å greater than that found in $(\mu_3\text{-}S)_2Fe_3(CO)_9$.

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Supplementary Materials Available

Anisotropic thermal parameters (Table SI), H atom coordinates (Table SII), and a listing of observed and calculated structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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