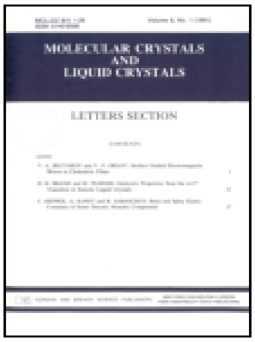

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Reaction of Triangular Cluster Complex Triiron Enneacarbonyl Disulfide with 1,2-bis(diphenylphosphino)ethane

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*Reaction of $Fe_3(\mu_3\text{-}S)_2(CO)_9$ (**A**) with 1,2-bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$, dppe) in the presence of the decarbonylating agent $Me_3NO\cdot 2H_2O$ in MeCN at room temperature afforded $[Fe_3(\mu_3\text{-}S)_2(CO)_8]_2(Ph_2PCH_2CH_2PPh_2)$ (**1**) containing bridging diphosphine ligand in 50% yield. The title complex **1** was structurally characterized by IR and NMR spectroscopic analysis. In addition, the molecular structure of **1** was further determined by X-ray crystallography. The molecule is centrosymmetric and the phosphorus atoms of DPPE reside in a basal position of the square-pyramidal geometry of the iron atoms.*

Keywords Carbonyl substitution; crystal structure; synthesis; triiron complex

1. Introduction

Derivatives of iron carbonyl complexes containing sulfur atoms are composed of two forms: binuclear, regarded as butterfly diiron dithiolate complexes of the type $Fe_2S_2(CO)_6$ related to the active site of [FeFe]-hydrogenases [1]; and trinuclear, of the type $Fe_3S_2(CO)_9$ [2]. Reactions of $Fe_3(\mu_3\text{-}S)_2(CO)_9$ with monophosphine or diphosphine ligands gave phosphine-substituted derivatives, for example, $Fe_3(\mu_3\text{-}S)_2(CO)_8[P(OC_6H_5)_3]$ [3] and $Fe_3(\mu_3\text{-}S)_2(CO)_7(\mu_2\text{-}Ph_2PC_5H_4FeC_5H_4PPh_2)$ [4]. We have recently [5] reported the reactions of $Fe_3(\mu_3\text{-}S)_2(CO)_9$ with PPh_3 or $Ph_2PCH_2PPh_2$ and three derivatives $Fe_3(\mu_3\text{-}S)_2(CO)_8PPh_3$, $Fe_3(\mu_3\text{-}S)_2(CO)_7(PPh_3)_2$, and $Fe_3(\mu_3\text{-}S)_2(CO)_7(Ph_2PCH_2PPh_2)$ were successfully prepared and characterized by spectroscopy and X-ray diffraction analysis. As a continuation of our studies on triiron enneacarbonyl disulfide clusters, one cluster complex with bridging diphosphine ligand has been successfully synthesized by carbonyl substitution reaction from **A** and DPPE. In this paper, we will describe the synthesis and structural characterization of triiron cluster containing bridging DPPE ligand.

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2. Experimental

2.1. Materials and Methods

All reactions were performed using standard Schlenk and vacuum-line techniques under N_2 atmosphere. Acetonitrile was distilled over CaH_2 under N_2. $Me_3NO{\cdot}2H_2O$, DPPE and other materials were available commercially and used as received. $Fe_3(\mu_3\text{-}S)_2(CO)_9$ [6] was prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FTIR spectrometer. ^1H (^{31}P, ^{13}C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

2.2. Synthesis of Complex 1

To a solution of **A** (0.097 g, 0.2 mmol) in MeCN (10 mL), a solution of $Me_3NO{\cdot}2H_2O$ (0.022 g, 0.2 mmol) was added in MeCN (5 mL). The mixture was stirred at room temperature for 15 min and then was added with DPPE (0.040 g, 0.1 mmol). The new mixture was stirred for 1 hr. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:3) as eluent. Collecting the main brown band afforded 0.066 g (50%) of **1** as a black solid. IR (KBr disk): $\nu_{C\equiv O}$ 2030 (vs), 2004 (vs), 1939 (vs) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 7.78–7.48 (m, 20H, PhH), 2.75, 2.46 (2s, 4H, 2CH_2) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 43.85 (s) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 210.29, (C≡O), 132.13, 132.06, 131.87, 131.79, 131.08, 131.01, 129.12, 129.04, 128.90, 128.81 (PhC), 27.39, 26.95 (CH_2) ppm.

2.3. X-Ray Structure Determination

Single crystals of **1** suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solutions of **1** at 4°C. A single crystal of **1** was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 K by using a graphite monochromator with Mo $K\alpha$ radiation (λ = 0.71073 Å) in the ω–φ scanning mode. Data collection, reduction, and absorption correction were performed by *CRYSTALCLEAR* program [7]. The structure was solved by direct methods using the SHELXS-97 program [8] and refined by full-matrix least-squares techniques SHELXL-97 [9] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

3. Results and Discussion

3.1. Synthesis and Characterization

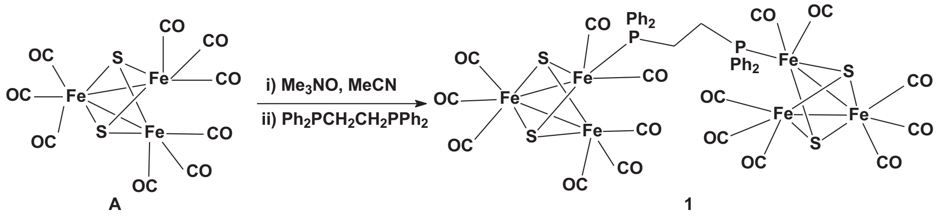
We found that treatment of complex **A** with DPPE in the presence of the decarbonylating agent $Me_3NO{\cdot}2H_2O$ in MeCN at room temperature afforded the title complex **1** in 50% yield (Scheme 1).

The new complex **1** was characterized by IR and NMR spectroscopy. For instance, the IR spectra showed three absorption bands in the range of 2030−1939 cm^{-1} for terminal carbonyls and the $\nu_{C\equiv O}$ values moved toward lower frequencies relative to complex **A** (2065, 2042, 2026, 2010, 1986 cm^{-1}) [6] due to the stronger electron-donating properties

Table 1. Crystal data and structure refinements details for **1**

Compound	**1**
Empirical formula	$C_{21}H_{12}Fe_3O_8PS_2$
Formula weight	654.95
Temperature (K)	113 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	16.894 (8)
b (Å)	12.732 (5)
c (Å)	23.304 (11)
α (°)	90
β (°)	102.933 (7)
γ (°)	90
V (Å^3)	4886 (4)
Z	8
D_{calc} (g·cm^{-3})	1.781
μ (mm^{-1})	2.039
F(000)	2616
Crystal size (mm^3)	0.20 × 0.18 × 0.10
θ_{min}, θ_{max} (°)	1.79, 27.87
Reflections collected/unique	24993/5826
R_{int}	0.0616
hkl range	$-22 \leq h \leq 22$ $-16 \leq k \leq 16$ $-30 \leq l \leq 30$
Completeness to θ_{max} (%)	99.9
Data/restraints/parameters	5826/0/316
Goodness of fit on F^2	1.106
$R1/wR2$ ($I>2\sigma(I)$)	0.0451/0.0920
$R1/wR2$ (all data)	0.0558/0.0967
Largest diff peak and hole/e Å^{-3}	0.598/−0.575

of DPPE than carbonyl [10]. The $^{31}P\{^1H\}$ NMR spectra displayed a singlet at δ 43.85 ppm for the two phosphorus atoms of DPPE, each one coordinated to one iron of the triiron subsite. The $^{13}C\{^1H\}$ NMR spectra only exhibited a singlet at δ 210.29 ppm for terminal carbonyls.



Scheme 1. Preparation of complex **1**.

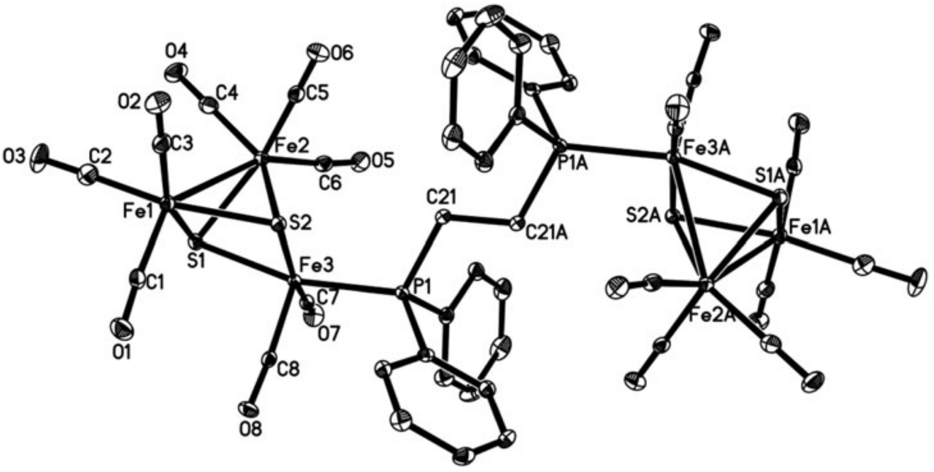


Figure 1. ORTEP view of **1** with 30% probability level ellipsoids.

3.2. *X-Ray Crystal Structures*

The molecular structure of **1** has been characterized by single crystal X-ray diffraction analysis. While the ORTEP view is shown in Fig. 1, selected bond lengths and angles are given in Table 2, respectively. Complex **1** crystallizes in monoclinic space group C2/c. As shown in Fig. 1, the crystal structure consists of two triiron disulfide clusters with 16 terminal carbonyls and 1 bridging diphosphine ligand DPPE. The molecule is centrosymmetric with the midpoint of C21–C21A as the symmetry center. The main framework is composed of a zigzag chain $Fe_3P_1C_{21}C_{21}AP_1AFe_3A$. The phosphorus atom P1 of DPPE attached to one of the nonbonding Fe_3 atom resides in a basal position of the square-pyramidal geometry of the Fe_3 atom, very similar to the structures of complexes $[Fe_3(\mu_3\text{-}S)_2(CO)_8(NHMe_2)]$ [2b] and $Fe_3(\mu_3\text{-}S)_2(CO)_8[P(SC_6H_5)_3]$ [11]. The Fe–Fe bond lengths [Fe(1)–Fe(2) = 2.5787 (10) Å and Fe(2)–Fe(3) = 2.6164 (10) Å] are similar to those corresponding bond lengths found in **A** [2.582 (9) Å and 2.609 (10) Å] [12], $Fe_3(\mu_3\text{-}S)_2(CO)_8PPh_3$ [Fe(1)–Fe(2) = 2.5524 (8) Å and Fe(2)–Fe(3) = 2.6448 (8) Å] and $Fe_3(\mu_3\text{-}S)_2(CO)_7(Ph_2PCH_2PPh_2)$ [Fe(1)–Fe(2) = 2.6141 (7) Å and Fe(2)—Fe (3) = 2.5930 (7) Å] [5]. As shown in Fig. 2, the crystal packing diagram revealed that the intermolecular hydrogen bonds stabilize the solid state of **1**.

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Fe(1)–S(2)	2.2405 (12)	Fe(2)–S(1)	2.2624 (13)
Fe(1)–S(1)	2.2416 (13)	Fe(2)–Fe(3)	2.6164 (10)
Fe(1)–Fe(2)	2.5787 (10)	Fe(3)–S(2)	2.2302 (11)
Fe(2)–S(2)	2.2528 (12)	Fe(3)–S(1)	2.2398 (12)
S(2)–Fe(1)–S(1)	80.05 (4)	S(1)–Fe(2)–Fe(1)	54.69 (3)
S(2)–Fe(1)–Fe(2)	55.20 (3)	S(2)–Fe(2)–Fe(3)	53.89 (3)
S(1)–Fe(1)–Fe(2)	55.45 (3)	S(1)–Fe(2)–Fe(3)	54.07 (3)
S(2)–Fe(2)–S(1)	79.34 (4)	Fe(1)–Fe(2)–Fe(3)	81.57 (3)
S(2)–Fe(2)–Fe(1)	54.76 (3)	P(1)–Fe(3)–Fe(2)	110.16 (4)

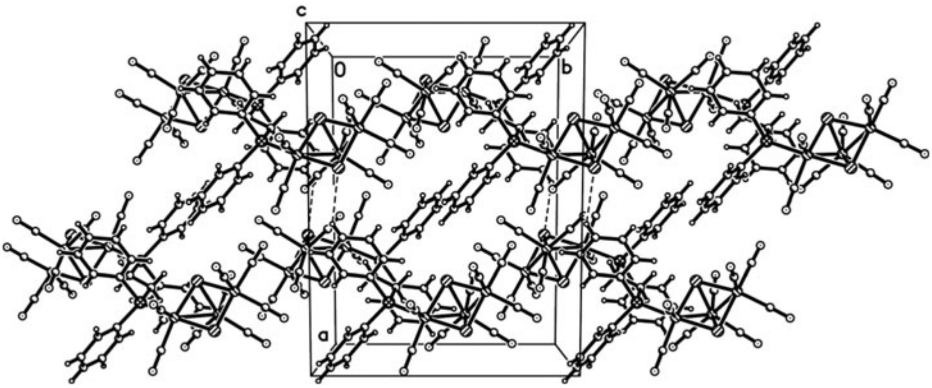


Figure 2. Crystal packing diagram of **1**.

4. Conclusions

In summary, one triiron derivative **1** was prepared by carbonyl substitution reaction. The title complex was characterized by IR, NMR spectroscopy, and its structure was confirmed by X-ray crystallography.

Appendix A. Supplementary Material

CCDC 963652 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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