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Photochemical Substitution of *fac*-Tricarbonyl[*P,P′,S*-(2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane)]manganese(I) hexafluorophosphate by Diphenylphosphine

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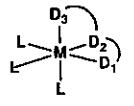
The title complex underwent ligand substitution by diphenylphosphine to form dicarbonyl[*P,P′,S*-(2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane](diphenylphosphine)manganese(I) hexafluorophosphate **2** under photochemical conditions. The crystal structure of complex **2** was determined. The reaction was kinetically independent of the concentration of diphenylphosphine, so a first-order reaction.

INTRODUCTION

In a complex wrapped by "hybrid" donor atoms, for example **I**, as the coordinating sites trans to the "hybrid" donors are in distinct environments, such a complex is expected to have a stereochemical influence on reaction mechanisms and selectivity.[1] Manganese(I) complex **1** that contains the mixed donor tripodal ligand $\mathbf{P_2S}$[2] appears to be thermally stable due to the chelating effect of the tripodal system. It reacts with halides and psudohalides stereospecifically to replace the sulfide donor (Eq. 1); here the photochemical substitution of one carbonyl ligand in **1** by diphenylphosphine is presented.



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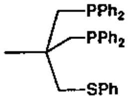
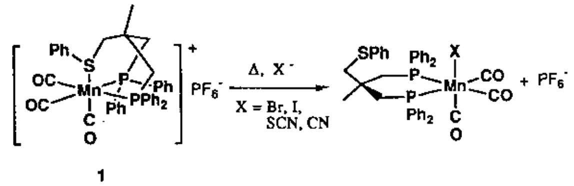


$\mathbf{P_2S}$



(1)

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RESULTS AND DISCUSSION

Under photochemical conditions, complex **1** reacted with diphenylphosphine in THF to give $[\{P,P',S\text{-}(\mathbf{P_2S})\}Mn(CO)_2(PPh_2H)]PF_6$ **2** as the exclusive product. Complex **2** was obtained as a yellow crystalline solid and characterized by both spectral and single crystal analyses. This complex exhibits two broad multiplets in ^{31}P NMR spectra, which are the consequence of the complexity of spin-spin coupling among three distinct phosphines, indicating that diphenylphosphine is at the position trans to one phosphorus donor of $\mathbf{P_2S}$. The wavenumbers associated with two carbonyl stretches 1949 and 1890 cm^{-1} in the infrared spectrum are consistent with a dicabonyl species.[3] The X-ray diffraction analysis of the crystal confirmed the formulation of the complex.

An ORTEP plot of complex **2** appears in Fig. 1 and the non-hydrogen atomic coordinates are listed in Table 1. The slightly distorted octahedral geometry around the metal center consists of three phosphines, one sulfide and two carbon-

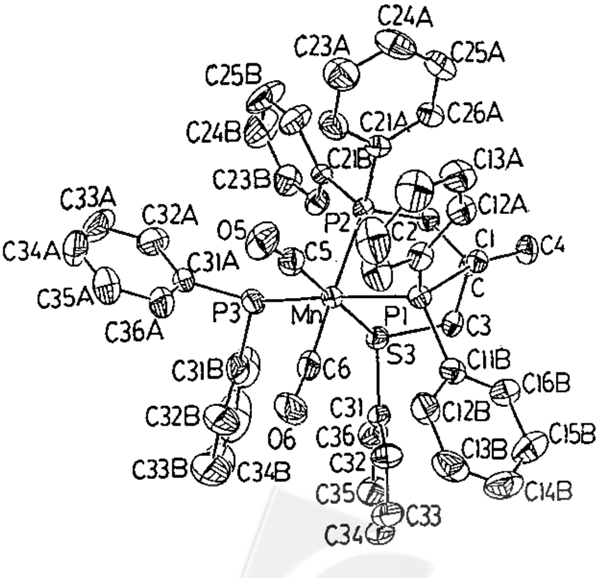

Fig. 1 ORTEP Plot of $[\{P,P',S\text{-}(P_2S)\}Mn(CO)_2\text{-}(PPh_2H)]^+$.

Dedicated to Professor Fa-Ching Chen (陳發清) on the occasion of his eightieth birthday.

Table 1. Atomic Coordinates and Isotropic Thermal Parameters of Complex **2**

	x	y	z	Beq
MN	0.56645(5)	0.22692(4)	0.22374(3)	2.195(22)
P1	0.61273(8)	0.16521(6)	0.34729(5)	2.29(4)
P2	0.52631(8)	0.36323(6)	0.31999(5)	2.18(4)
S3	0.77142(8)	0.33150(6)	0.25225(5)	2.47(4)
P3	0.54022(9)	0.29851(7)	0.10531(5)	3.09(5)
C	0.7544(3)	0.36757(21)	0.43053(18)	2.23(14)
C1	0.6811(3)	0.26594(21)	0.44475(18)	2.26(14)
C2	0.6665(3)	0.43018(21)	0.40102(18)	2.33(14)
C3	0.8448(3)	0.35761(22)	0.36630(19)	2.44(15)
C4	0.8341(3)	0.42779(23)	0.51818(19)	3.25(17)
C5	0.4068(3)	0.15976(23)	0.19879(20)	3.18(17)
O5	0.30479(21)	0.11148(18)	0.17791(16)	5.16(14)
C6	0.5915(3)	0.12113(24)	0.15498(20)	3.11(16)
O6	0.5966(3)	0.04916(17)	0.10763(15)	5.19(15)
C11A	0.4788(3)	0.08517(22)	0.37783(19)	2.77(15)
C12A	0.4479(3)	0.10185(24)	0.46007(20)	3.23(17)
C13A	0.3416(3)	0.0413(3)	0.47782(23)	4.24(20)
C14A	0.2678(3)	-0.0380(3)	0.41506(24)	4.99(21)
C15A	0.2992(4)	-0.0581(3)	0.33354(24)	5.60(23)
C16A	0.4035(3)	0.0037(3)	0.31538(21)	4.28(20)
C11B	0.7242(3)	0.08614(22)	0.34663(19)	2.62(15)
C12B	0.6900(3)	-0.00804(24)	0.29116(20)	3.64(20)
C13B	0.7694(4)	-0.0714(3)	0.29119(22)	4.79(23)
C14B	0.8827(4)	-0.0418(3)	0.34624(25)	4.97(23)
C15B	0.9180(3)	0.0511(3)	0.40066(24)	4.30(21)
C16B	0.8392(3)	0.11420(23)	0.40149(21)	3.13(18)
C21A	0.4035(3)	0.32824(22)	0.38352(19)	2.42(15)
C22A	0.2849(3)	0.2755(3)	0.33828(20)	3.70(18)
C23A	0.1878(3)	0.2473(3)	0.38219(24)	4.92(22)
C24A	0.2082(3)	0.2697(3)	0.47157(23)	4.75(21)
C25A	0.3241(3)	0.32107(24)	0.51731(20)	3.71(19)
C26A	0.4211(3)	0.35188(22)	0.47392(19)	2.86(16)
C21B	0.4892(3)	0.47042(22)	0.27968(18)	2.43(15)
C22B	0.5804(3)	0.53383(22)	0.24896(20)	2.88(16)
C23B	0.5566(3)	0.6143(3)	0.21703(22)	4.20(20)
C24B	0.4405(4)	0.6330(3)	0.2149(3)	5.8(3)
C25B	0.3496(4)	0.5711(3)	0.2460(3)	6.3(3)
C26B	0.3726(3)	0.4903(3)	0.27767(24)	4.38(21)
C31	0.8893(3)	0.28782(23)	0.20288(19)	2.68(17)
C32	0.8979(3)	0.18951(24)	0.19380(21)	3.58(19)
C33	0.9931(3)	0.1629(3)	0.15633(23)	4.18(20)
C34	1.0769(3)	0.2314(3)	0.12715(22)	4.37(22)
C35	1.0687(3)	0.3290(3)	0.13747(23)	4.63(21)
C36	0.9743(3)	0.3581(3)	0.17572(21)	3.71(18)
C31A	0.3933(3)	0.2550(3)	0.02891(19)	3.40(19)
C32A	0.3318(4)	0.3244(3)	0.00525(22)	4.62(22)
C33A	0.2196(4)	0.2901(3)	-0.05411(25)	6.4(3)
C34A	0.1714(4)	0.1900(4)	-0.08805(24)	7.0(3)
C35A	0.2318(4)	0.1224(3)	-0.06451(24)	6.8(3)
C36A	0.3432(4)	0.1547(3)	-0.00637(22)	4.96(22)
C31B	0.6567(3)	0.3060(3)	0.03552(20)	4.01(21)
C32B	0.6737(4)	0.2214(3)	-0.01583(24)	6.3(3)
C33B	0.7633(5)	0.2285(4)	-0.0684(3)	9.2(4)
C34B	0.8346(4)	0.3226(4)	-0.0685(3)	9.8(4)
C35B	0.8206(4)	0.4077(4)	-0.0187(3)	8.9(3)
C36B	0.7307(4)	0.3995(3)	0.0346(3)	6.3(3)
P	0.96931(9)	0.67536(7)	0.29520(6)	3.42(5)
F1	1.03068(22)	0.74638(16)	0.38691(13)	6.59(14)
F2	0.9047(3)	0.60390(17)	0.20414(14)	8.10(17)
F3	0.91373(21)	0.58901(15)	0.34269(14)	6.32(14)
F4	1.02240(22)	0.76303(17)	0.24907(14)	6.76(14)
F5	0.84765(21)	0.71360(17)	0.29853(16)	7.44(17)
F6	1.08839(24)	0.63685(22)	0.29242(17)	8.95(20)

yls. That the angle of P2-Mn-S3 (83.75(4)°) deviates from 90° is due to the steric requirement of the tripodal frame. The larger Mn-P2 distance is the consequence of relief of steric interaction of the phenyl groups between P2 and P3. The two Mn-C distances are essentially indistinguishable, even though one of them is trans to the phosphorus donor and the other is trans to sulfide. The average Mn-C distance 1.778(3) Å is smaller than that 1.815(8) Å in complex **1**,[2] as expected, because of the stronger ability of diphenylphosphine as σ-donor compared with a carbonyl ligand. The decreased Mn-C bond in **2** is concordant with the increased C-O distance (1.161(4) Å compared to 1.136(9) Å in **1**) and the smaller carbonyl stretching wavenumber 1890 cm^{-1} in the infrared spectrum. Examination of the dihedral angles along the chelate rings in **2** reveals two positive and four negative values (Table 3) typical of a twist-boat conformation.

The reaction pathway of carbonyl substitution in a coordinated saturated (18-electron species) manganese(I) is considered to be through dissociation.[4] The substitution of **1** by diphenylphosphine occurred through a dissociative pathway. Dissociation of a carbonyl ligand of **1** requires photochemical conditions instead of thermal ones. Kinetic measurements (experimental section) indicates that the rate law has the form: rate = k_{obs} [**1**], which is independent of the *concentration of phosphine. That this reaction is suppressed* under CO at atmospheric pressure indicates that this ligand substitution reaction involves a reversible step, dissociation of CO followed by coordination of phosphine.[5,6] Triphenylphosphine did not react with **1** under similar conditions *due to steric hindrance.*

Table 2. Selected Bond Distances/Å and Angles/deg of Complex **2**

Bond Distance/Å			
Mn-P1	2.326(1)	Mn-P2	2.394(1)
Mn-S3	2.362(1)	Mn-P3	2.300(1)
Mn-C5	1.777(3)	Mn-C6	1.780(3)
C5-O5	1.158(4)	C6-O6	1.164(4)
P1-C1	1.843(3)	P2-C2	1.838(3)
S3-C3	1.826(3)		
Bond Angle/deg			
P1-Mn-P2	86.08(4)	P1-Mn-S3	89.53(4)
P1-Mn-P3	174.32(4)	P1-Mn-C5	95.4(1)
P2-Mn-S3	83.75(4)	P2-Mn-P3	92.95(4)
P2-Mn-C5	92.5(1)	P2-Mn-C6	177.0(1)
S3-Mn-P3	84.80(4)	S3-Mn-C5	173.6(1)
S3-Mn-C6	98.4(1)	P3-Mn-C6	89.3(1)
C5-Mn-C6	85.5(2)	Mn-C5-O5	175.2(3)
Mn-C6-O6	173.9(3)		

Table 3. Dihedral Angles/deg of Chelate Rings in Complex **2**

Mn-P1-C1-C-C2-P2		Mn-P1-C1-C-C3-S3		Mn-P2-C2-C-C3-S3	
Mn-P1-C1-C	79.4(2)	Mn-P1-C1-C	82.8(2)	Mn-P2-C2-C	84.8(2)
P1-C1-C-C2	-42.0(1)	P1-C1-C-C3	-35.3(1)	P2-C2-C-C3	-42.8(1)
C1-C-C2-P2	-32.3(1)	C1-C-C3-S3	-23.2(1)	C2-C-C3-S3	-35.5(3)
C-C2-P2-Mn	59.7(1)	C-C3-S3-Mn	51.7(1)	C-C3-S3-Mn	62.9(1)
C2-P2-Mn-P1	-32.1(1)	C3-S3-Mn-P1	-27.9(1)	C3-S3-Mn-P2	-30.2(1)
P2-Mn-P1-C1	-27.9(1)	S3-Mn-P1-C1	-45.2(1)	S3-Mn-P2-C2	-32.3(1)

EXPERIMENTAL SECTION

^1H and ^{31}P NMR spectra were determined on a Bruker AC-E 200 or a Bruker AM-300WB spectrometer. Chemical shifts are given in parts per million relative to 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted. Infrared spectra were recorded on a Bio-Rad FTS-40 instrument. Elemental analyses were made on a Perkin-Elmer 240C instrument. All reactions, manipulations and purification steps involving phosphines were performed under a dry nitrogen atmosphere. The photochemical apparatus was a medium-pressure mercury vapor lamp (550-W Conrad-Hanovia Ace Glass, Inc). Complex **1** was prepared as previously reported.[2]

Dicarbonyl[*P,P′,S*-(2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane)] (diphenylphosphine)manganese(I) hexafluorophosphate (2)

Into a degassed Pyrex flask was placed complex **1** (50 mg, 0.06 mmol) and diphenylphosphine (11.5 mg, 0.062 mmol) in THF (5 mL). The mixture was irradiated with UV light for 2 h. The solvents were removed and the residue was dissolved in acetone and hexane. The desired product was crystallized as a yellow solid (35 mg, 94%): mp 198 °C (dec); IR(CH_2Cl_2) 1949, 1890 cm^{-1}; ^1H NMR δ 7.93 - 6.64 (*m*, 35 H), 5.31 (*m*, 1 H), 3.95 (*d*, J = 12Hz, 1 H), 3.11 - 2.98 (*m*, 3 H), 2.87 (*d*, J = 12 Hz, 1 H), 2.46 - 2.26 (*m*, 1 H), 1.61 (*s*, 3 H); ^{31}P NMR δ 58.4 (br), 37.3 (br); Anal. Calcd for $C_{49}H_{45}F_6MnP_4O_2S$ C, 59.41; H, 4.58, Found C, 59.6; H, 4.66.

Kinetic Study

The kinetic determinations were performed on the infrared spectrometer with measurement of the disappearance and appearance of the linesassociated with carbonyl stretching at wavenumbers 2030 cm^{-1} for **1** and 1890 cm^{-1} for **2** respectively. All reactions were performed at 25 °C. All runs showed a satisfactorily linear plot of $\ln(A-A_\infty)$; the results are:

[1], M	[Ph_2PH], M	k_{obs}, s^{-1}
0.012	0.12	1.05×10^{-3}
0.012	0.6	1.06×10^{-3}
0.012	1.2	1.03×10^{-3}

Structural Analysis of 2

Complex **2** was recrystallized from acetone and hexane. Measurement and data collection were carried out on an Enraf-Nonius CAD-4 diffractometer. Empirical formula: $C_{49}H_{45}F_6MnO_2P_4S$, $F_w = 990.85$. Crystal size $0.25 \times 0.35 \times 0.50\ mm^3$. Space group: triclinic, P-1. a = 11.219(2), b = 14.008(4), c = 15.886(4) Å, $\alpha = 100.17(2)$, $\beta = 97.45(2)$, $\gamma = 103.34(2)$°, V = 2353(1) Å^3, T = 298 K, Z = 2, F(000) = 1020, $D_{calcd} = 1.40\ Mg\ m^{-3}$, $\mu = 0.51\ mm^{-1}$, $\lambda = 0.7107$ Å. The intensity data were collected in the ω-2θ scan mode. 2θ max = 50°, $-13 \le h \le 12$, $0 \le k \le 16$, $-18 \le l \le 18$. A total of 8264 unique reflections were measured, of which 5766 were observed with $I > 2.0\ \sigma(I)$. Transmission factors were 0.92 - 1.00.

The heavy-atom method was used and least-squares refinement was undertaken with all non-hydrogen atoms anisotropic. Refinement details follow: F_o and F_c are the observed and calculated structure factor amplitudes respectively; the function minimized was $\Sigma w\ (F_o-F_c)^2$, with $w^{-1} = \sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics; $R_f = \Sigma/F_o-F_c// \Sigma(F_o)$; $R_w = [\Sigma w(F_o-F_c)^2/\Sigma w(F_o)^2]^{1/2}$; $S = [\Sigma(w(F_o-F_c)^2)/(\text{No. of reflections - No. of params})]^{1/2}$. For significant reflections, $R_f = 0.037$, $R_w = 0.027$, S = 2.07. Atomic scattering factors were taken from: the International Tables for X-ray Crystallography.[7] The computing program was the: NRCC SDP VAX package.[8]

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Key Words

Tripodal phosphines; Photochemical ligand substitution.

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