Study of the Effects on Coordination of Thioether Sites. 1. Complexation Study of Bromopentacarbonylmanganese(I) with Tripodal $P_{3-n}S_n$ (n = 0–3) Ligands

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Manganese(I) complexes *fac*-(η^2-$P_{3-n}S_n$)$Mn(CO)_3Br$ (n = 0–3) [P_3 W = Z = PPh_2; P_2S W = PPh_2, Z = SPh; PS_2 Z = SPh, W = PPh_2; S_3 W = Z = SPh in $CH_3C(CH_2W)_2(CH_2Z)$] formed from the corresponding tripodal ligand have been prepared and isolated as pairs of isomers. The reaction of P_2S with $BrMn(CO)_5$ in chloroform produced a pair of stereoisomers, *syn-fac*-(*P*,*P*'-P_2S)$Mn(CO)_3Br$ (**1a**) and *anti-fac*-(*P*,*P*'-P_2S)$Mn(CO)_3Br$ (**1b**), which were separated and fully characterized. Equilibration (K_1 = 2/3) between **1a** and **1b** was established. For PS_2, the equilibrium constant (K_2) between *syn-fac*-(*P*,*S*-PS_2)$Mn(CO)_3Br$ (**2a**) and *anti-fac*-(*P*,*S*-PS_2)$Mn(CO)_3Br$ (**2b**) was unity. Kinetic studies of isomerization of **1a** to **1b** and **2a** to **2b** were carried out by using an NMR spectrometer. The activation parameters were obtained: $\Delta H^{\ddagger}_{1a}$ = 30.5 ± 0.4 kcal/mol, $\Delta S^{\ddagger}_{1a}$ = 11 ± 1 eu for complex **1a**; $\Delta H^{\ddagger}_{2a}$ = 24.9 ± 0.7 kcal/mol, $\Delta S^{\ddagger}_{2a}$ = 7 ± 2 eu for complex **2a**. A mechanistic pathway for these isomerizations is proposed. Crystal structures were determined for three complexes: **1a**, **1b**, and **2a**. X-ray data were collected on a CAD-4 diffractometer at room temperature and were refined by a least-squares treatment. For **1a**: a = 10.669(2) Å, b = 17.864(3) Å, c = 18.841(12) Å, β = 105.30(2)°, monoclinic, Z = 4, $P2_{1/c}$, $R(F_o)$ = 0.051, $R_w(F_o)$ = 0.042 for 3043 reflections with $I_o > 2\sigma(I_o)$. For **2b**: a = 10.855(3) Å, b = 20.322(7) Å, c = 17.887(9) Å, β = 104.73(3)°, monoclinic, Z = 4, $P2_{1/n}$, $R(F_o)$ = 0.059, $R_w(F_o)$ = 0.047 for 3316 reflections with $I_o > 2\sigma(I_o)$. For **2a**: a = 8.670(5) Å, b = 9.539(3) Å, c = 18.921(9) Å, α = 93.09(3)°, β = 90.27(5)°, γ = 101.21(4)°, triclinic, Z = 2, $P\bar{1}$, $R(F_o)$ = 0.052, $R_w(F_o)$ = 0.054 for 2513 reflections with $I_o > 2\sigma(I_o)$. The conformations of the chelate rings are discussed.

Introduction

The development of various polydentate phosphine ligands for coordination chemistry and homogeneous catalysis has received much attention in recent years. Of particular interest are "hybrid" donor polydentate ligands, which allow some weak donors to form transition metal (TM) complexes through the chelate effect. The relatively poor σ-donor and π-acceptor natures of a simple thioether, compared to phosphine, make a metal–sulfur (TM–S) bond quite weak, especially with those transition metals in low oxidation states.[1-3]. By means of chelates involving "hybrid" sulfur and phosphorus ligands, the preparation of TM–S complexes has become increasingly feasible and reports of many of P–S hybrid ligands have appeared.[4] We described the synthesis of 2,2-bis((diphenylphosphino)methyl)-1-(phenylthio)propane (P_2S)[5] and 2,2-bis((phenylthio)methyl)-1-(diphenylphosphino)propane (PS_2).[6] The weak interaction of thioether sites in both ligands with various transition metals was illustrated. Thus, the thioether site in P_2S remains uncoordinated in the complexes of $(CO)_4M(\eta^2\text{-}P_2S)$ (M = Cr, Mo),[5] unlike $(CO)_3M(\eta^3\text{-}P_3)$ (M = Cr, Mo),[7] where $P_3 = CH_3C(PPh_2)_3$. We also observed the intramolecular exchange of sulfur sites in the complex $(PS_2)PdCl_2$ in CD_2Cl_2 solution.[6]

The complexes of thioether with manganese(I) have been little investigated.[1-3,7,8] Due to the imposed facial geometry of the tripod, tripodal ligands $P_{3-n}S_n$ (n = 0–3) may be suitable for systematic investigation of the interaction of Mn(I)–S. We describe here our works on the coordination chemistry of Mn(I) with tripodal ligands.

Results and Discussion

Coordination of P_nS_{3-n} toward Mn(I). An equimolar mixture of bromopentacarbonylmanganese(I) and P_nS_{3-n} (n = 1–3) in chloroform (eq 1) was heated at reflux until the infrared spectra of the carbonyl region changed no further. The desired complexes were then isolated by crystallization in almost quantitative yield. For P_2S, the thermal reaction provided a mixture of **1a** and **1b** in a ratio of 3:2. Both complexes have similar carbonyl

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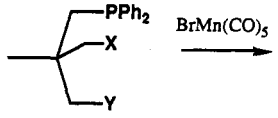
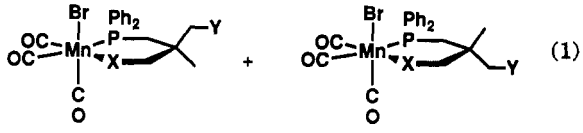


P_2S, X = PPh_2, Y = SPh

PS_2, X = Y = SPh

P_3, X = Y = PPh_2



(1)

1a (60)	1b (40)
2a (50)	2b (50)
3a (60)	3b (40)

absorptions in their infrared spectra, and those peaks are characteristic of *fac*-$L_2Mn(CO)_3Br$.[9] The separation of **1a** and **1b** was achieved by fractional recrystallization in dichloromethane and hexane; complex **1a** crystallized first as a yellow crystalline solid whereas **1b** precipitated as an orange crystalline solid. With the use of single-crystal analyses of **1a** and **1b**, we determined their isomeric structures; their ORTEP plots appear in Figures 1 and 2, respectively. In both **1a** and **1b**, the sulfur donor remained uncoordinated; the difference between these two isomers is the uncoordinated (phenylthio)methyl substituent situated either opposite (**1b**, *anti* isomer) to or on the same side (**1a**, *syn* isomer) as the bromide ligand along the six-membered chelate ring. Both complexes have almost identical spectral data (see Experimental Section), except for ^1H NMR signals. The chemical shift of the methyl group in **1a** (δ 1.13) is quite downfield from that in **1b** (δ 0.36). That the product ratio between **1a** and **1b** (3:2) was a result of thermodynamic distribution is demonstrated by the following evidence. When a pure complex of either **1a** or **1b** was heated in boiling chloroform for 14 h, a mixture of **1a** and **1b** was obtained in a ratio of 6:4 (K_1 = $^2/_3$). Hence complex **1a** is more stable than **1b** by only 0.24 kcal/mol at 298 K.

Similarly to P_2S, the thermal substitution reaction of $Mn(CO)_5Br$ with PS_2 gave two stereoisomeric products **2a** and **2b** in a ratio of 1:1. Complex **2a** was obtained in a pure form by recrystallization from a solution of chloroform and hexane and its detailed structure (Figure 3) was confirmed by X-ray analysis of a single crystal. The resonance of the methyl group of **2a** in ^1H NMR appeared at δ 0.68, which is an upfield shift by 0.5 ppm from the *anti* isomer **2b**. This trend resembles that of complexes **1a** and **1b**, but thermal equilibration (K_2 = 1) between **2a** and **2b** in chloroform occurred more rapidly at room temperature (see kinetic part).

The reaction of P_3 with $Mn(CO)_5Br$ also gave *fac*-(η^2-P_3)$Mn(CO)_3Br$ in a mixture of two stereoisomers **3a** and **3b**. The *syn* species **3a** was separated from the mixture by recrystallization. The pure *anti* species was obtained from the photochemical substitution of $[(\eta^3\text{-}P_3)Mn(CO)_3]^+$ with bromide, reported by Ellerman and co-workers.[10] The chemical shift of the methyl group in **3a** is upfield by 0.6 ppm from than that of **3b**, consistent with our observations of other complexes. The ^{31}P NMR chemical shift of **3b** appears at δ −27.76 for an uncoordinating phosphine and at δ 29.39 for coordinating ones, but for **3a** at δ −26.94 and δ 29.81, respectively.

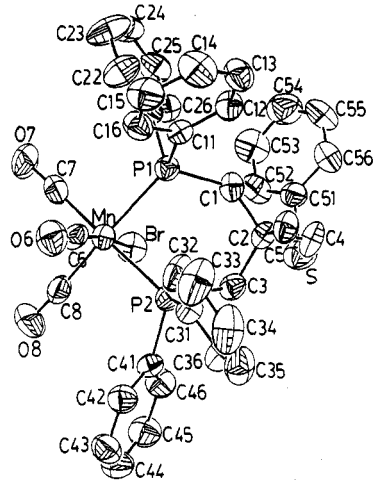


Figure 1. ORTEP plot of **1a**.

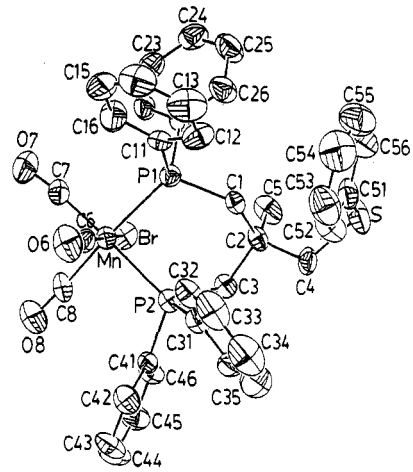


Figure 2. ORTEP plot of **1b**.

With the sulfur ligand S_3, the reaction produced (η^2-*S*,*S*'-S_3)$Mn(CO)_3Br$ indicated by the infrared absorption of carbonyls and ^1H NMR. The attempted isolation of the desired complex by chromatography or crystallization led to decomposition with the recovery of free ligand S_3. The coordination between manganese(I) and thioether appears relatively weak even with chelation.

All tripodal ligands act as bidentate with no indication of formation of (η^3-tripodal)$Mn(CO)_2Br$ or [(η^3-tripodal)-$Mn(CO)_3$]Br, even under reflux of **1a**, **1b**, **2a**, or **2b** in acetone solution. This property differs from that of (η^2-P_3)$Mn(CO)_3Br$, which gave $[(\eta^3\text{-}P_3)Mn(CO)_2]Br$ under reflux in polar solvents. Obviously, the weak coordination ability of thioether is responsible for this distinction.

All complexes (η^2-tripodal)$Mn(CO)_3Br$ were characterized by spectral methods and elemental analysis. Infrared absorptions in the carbonyl region are consistent with facial tricarbonylmanganese complexes. The chemical shifts of the methyl groups in all *cis* isomers are upfield from those of the *trans* ones by about 0.6 ppm; this difference becomes a unique way to identify these isomeric species. The protons of all methylene units in complexes **2b** are diastereotopic, as shown by the ^1H NMR splitting pattern. The structures of complexes **1a**, **1b**, and **2a** were further confirmed by X-ray analysis of single crystals.

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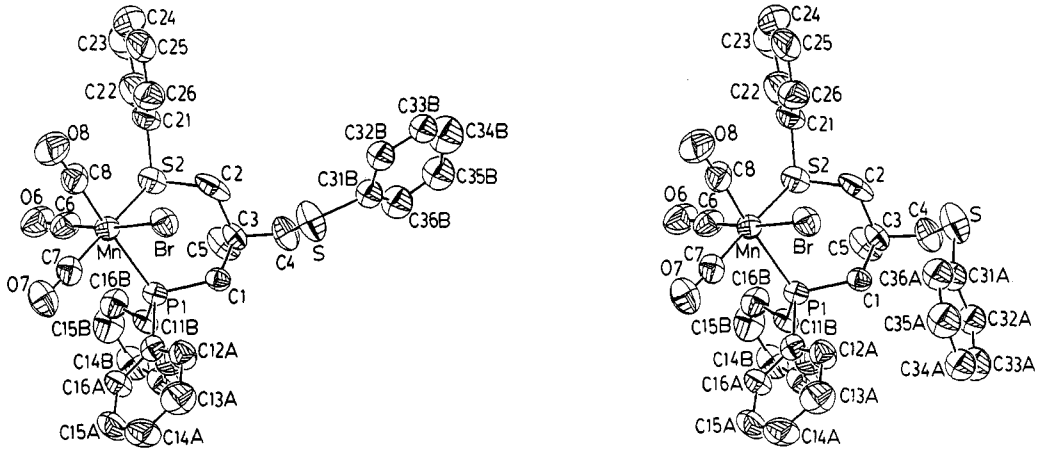


Figure 3. ORTEP drawing of **2a** with 50% disorder of –SPh in two orientations.

Table I. Rate Constants of Isomerization

complex	temp, °C	k_{obs}, s^{-1}	complex	temp, °C	k_{obs}, s^{-1}
1a	25	5.31×10^{-8}	**2a**	10	8.09×10^{-6}
	36	3.16×10^{-7}		20	4.09×10^{-5}
	46	1.66×10^{-6}		25	6.99×10^{-5}
	55	6.80×10^{-6}		39	6.78×10^{-4}
	60	1.28×10^{-5}		49	2.04×10^{-3}

Table II. Crystal Data

compd	**1a**	**1b**	**2a**
formula	$MnBrP_2SO_3C_{38}H_{34}$	$MnBrP_2SO_3C_{38}H_{34}\cdot CH_2Cl_2$	$MnBrPS_2O_3C_{32}H_{29}$
fw	767.54	852.47	662.28
a, Å	10.669(2)	10.855(3)	8.670(5)
b, Å	17.864(3)	20.322(7)	9.539(3)
c, Å	18.841(12)	17.887(9)	18.921(9)
α, deg			93.09(3)
β, deg	105.30(2)	104.73(3)	90.27(5)
γ, deg			101.21(4)
V, Å^3	3468(2)	3816(3)	1532(1)
Z	4	4	2
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
T, °C	25(2)	25(2)	25(2)
λ, Å	0.7093	0.7093	0.7093
ρ(calcd), g cm^{-3}	1.336	1.470	1.488
μ, cm^{-1}	1.69	1.54	1.91
transm coeff	0.91–1.0	0.87–1.0	0.97–1.0
$R(F_o)$	0.051	0.059	0.052
$R_w(F_o)$	0.042	0.047	0.054
S	2.73	2.52	0.97

Kinetic and Mechanistic Studies. By measuring the integration ratio of methyl groups between *syn* and *anti* isomers, we found that the isomerization of **1a** or **2a** to their corresponding *anti* species (eq 2) in $CDCl_3$ under

$$\textit{syn}\ \text{isomer} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \textit{anti}\ \text{isomer}$$

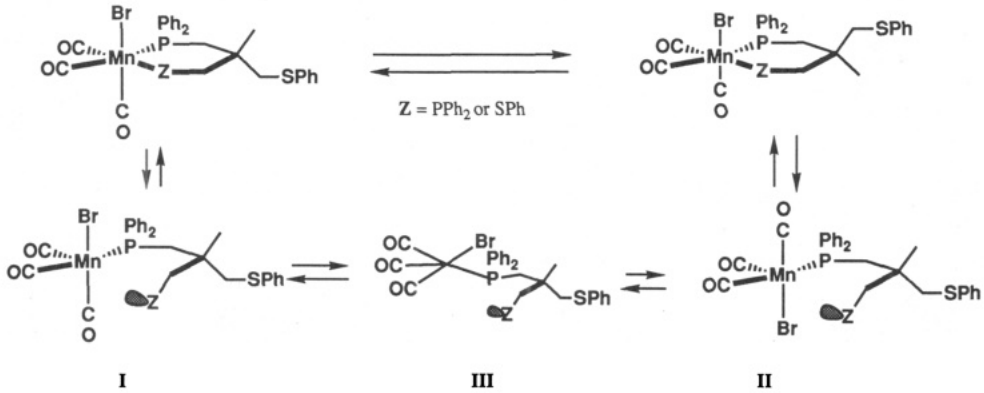
$$K_1 = {}^2/_3\ \text{(for complex 1)},\ K_2 = 1.0\ \text{(for complex 2)} \qquad (2)$$

first-order conditions obeyed the rate law $-d[\textit{syn}\ \text{isomer}]/dt = (k_1 + k_{-1})([\textit{syn}\ \text{isomer}] - [\textit{syn}\ \text{isomer}]_\infty)$. The rate constants of the isomerization at various temperatures for **1a** and **2a** are summarized in Table I. The activation parameters for isomerizations were obtained: $\Delta H^*_{1a} = 30.5 \pm 0.4$ kcal/mol, $\Delta S^*_{1a} = 11 \pm 1$ eu for complex **1a**; $\Delta H^*_{2a} = 24.9 \pm 0.7$ kcal/ mol, $\Delta S^*_{2a} = 7 \pm 2$ eu for complex **2a**. Based on the activation parameters, a proposed mechanism for this isomerization is shown in Scheme I. One donor in the tripodal ligands (phosphorus in **1a**; sulfur in **2a**) dissociates first to generate a pentavalent intermediate I, which is rapidly converted into another II, followed by recoordination of the donor atom. For **2a**, the recoordinating of sulfur atom was either sulfur donor of

Table III. Atomic Coordinates and Isotropic Thermal Parameters of 1a

	x	y	z	B_{iso}, Å^2
Mn	0.73403(14)	0.50932(8)	0.21882(7)	3.49(7)
Br	0.94140(11)	0.57304(6)	0.28962(6)	5.00(6)
P1	0.83296(24)	0.39545(13)	0.26748(12)	3.26(12)
P2	0.82639(24)	0.49438(14)	0.12058(13)	3.60(13)
S	1.2839(3)	0.45329(16)	0.25009(15)	5.89(16)
C1	0.9994(8)	0.3835(5)	0.2588(4)	3.7(5)
C2	1.0331(8)	0.3869(5)	0.1851(4)	3.7(5)
C3	0.9960(8)	0.4627(5)	0.1465(4)	3.8(5)
C4	1.1829(8)	0.3785(5)	0.2010(5)	4.9(6)
C5	0.9777(9)	0.3210(5)	0.1367(5)	4.6(5)
C6	0.5817(8)	0.4793(5)	0.1672(4)	3.8(5)
O6	0.4765(6)	0.4653(3)	0.1330(3)	5.6(4)
C7	0.6727(9)	0.5203(5)	0.2973(5)	4.6(5)
O7	0.6300(7)	0.5295(4)	0.3469(3)	7.4(5)
C8	0.6885(9)	0.6033(5)	0.1931(5)	4.3(5)
O8	0.6572(6)	0.6646(3)	0.1793(4)	6.4(4)
C11	0.7478(8)	0.3066(4)	0.2399(4)	3.1(4)
C12	0.8130(8)	0.2396(5)	0.2431(5)	4.0(5)
C13	0.7465(9)	0.1735(5)	0.2256(5)	5.0(6)
C14	0.6142(9)	0.1729(5)	0.2058(5)	5.7(6)
C15	0.5460(9)	0.2379(5)	0.2033(5)	5.3(6)
C16	0.6138(8)	0.3052(5)	0.2210(5)	4.3(5)
C21	0.8612(8)	0.3875(4)	0.3668(4)	3.6(5)
C22	0.7643(9)	0.3589(5)	0.3956(5)	5.8(6)
C23	0.7798(11)	0.3534(6)	0.4699(5)	7.0(7)
C24	0.8930(10)	0.3746(5)	0.5183(5)	5.9(7)
C25	0.9894(10)	0.4038(5)	0.4917(5)	5.2(6)
C26	0.9735(9)	0.4103(5)	0.4173(5)	4.5(5)
C31	0.7531(8)	0.4354(5)	0.0427(4)	3.5(5)
C32	0.6627(9)	0.3823(5)	0.0457(5)	5.3(6)
C33	0.6112(10)	0.3367(6)	–0.0124(6)	7.2(7)
C34	0.6500(10)	0.3427(6)	–0.0760(5)	6.6(7)
C35	0.7398(9)	0.3941(6)	–0.0786(5)	5.6(6)
C36	0.7923(9)	0.4396(5)	–0.0204(4)	4.7(6)
C41	0.8355(8)	0.5835(5)	0.0749(4)	3.5(5)
C42	0.7325(9)	0.6048(5)	0.0182(5)	4.4(5)
C43	0.7319(9)	0.6732(5)	–0.0162(5)	5.1(6)
C44	0.8337(10)	0.7210(5)	0.0066(5)	5.6(6)
C45	0.9382(9)	0.7011(5)	0.0647(5)	5.5(6)
C46	0.9383(9)	0.6325(5)	0.0992(5)	4.8(5)
C51	1.3167(8)	0.4256(5)	0.3424(5)	4.3(5)
C52	1.3057(10)	0.4781(5)	0.3938(5)	5.8(6)
C53	1.3366(11)	0.4612(6)	0.4662(5)	7.0(7)
C54	1.3796(10)	0.3923(6)	0.4903(5)	7.5(7)
C55	1.3912(11)	0.3416(6)	0.4398(6)	8.5(8)
C56	1.3618(10)	0.3568(5)	0.3651(6)	6.9(7)

Scheme I. Mechanistic Pathway for Isomerization



PS_2. Intermediates I and II might interconvert through an intermediate III.[11] That the value of $\Delta H^{\ddagger}_{2a}$ is smaller than $\Delta H^{\ddagger}_{1a}$ reflects the weak coordinating ability of the sulfur atom to the metal and is consistent with the dissociation process as the rate determining step.

Structural Analyses. The data for crystals for complexes **1a**, **1b**, and **2a** are summarized in Table II. ORTEP plots of **1a**, **1b**, and **2a** are depicted in Figures 1-3; the non-hydrogen atomic coordinates of these complexes are collected in Tables III-V, respectively. In all instances, the manganese metal displays a slightly distorted octahedral geometry with the two donor atoms of the tripodal ligand (two phosphorus atoms in P_2S; one phosphorus and one sulfur in PS_2) and bromide being in a facial arrangement. All bond distances and bond angles lie within normal ranges,[12] illustrated in Table VI. The Mn–P and Mn–S bond lengths are essentially indistinguishable, except for M–P2 in **1a**. The distances of Mn–C *trans* to bromide are slightly less than those *trans* to Mn–P or Mn–S, as expected, because of the *trans* influences.[13] For **2a**, the metal–carbon bond *trans* to the phosphorus donor [Mn–C8, 1.81(2) Å] is slightly longer than that *trans* to sulfur [Mn–C7, 1.78(2) Å], another consequence of the *trans* influence of donor atoms.

Examination of those dihedral angles along the chelate ring [Mn–P1–C1–C2–C3–Z] of *cis* complexes **1a** and **2a** (Table VII) reveals alternating +gauche/–gauche angles typical of a chairlike six-membered ring (Figure 4). That these angles deviate from the ideal 60° of the cyclohexane ring presumably arises from the variation of the bond lengths within the chelate rings (e.g. M–P vs C–C). In order to retain a chair conformation, the congestion between diphenylphosphino moieties and the metal center causes distortion of P1–Mn–C6 from 90° [102.1(3)° in **1a**, 101.1(5)° in **2a**]. The bulky (phenylthio)methyl group is situated at an equatorial position in the six-membered chelate ring. The phenyl group of the coordinating thioether in **2a** is positioned equatorially to avoid the unfavored diaxial interactions; such an arrangement also causes steric repulsion between this phenyl group and carbonyl C8O8, as indicated by the larger angle of S2–Mn–C8 [97.7(6)°]. The angles of bromide to the plane defined by P1–Mn–Z are 86.78(6)° [Z = P2] and 91.0(1)° [Z = S2] for **1a** and **2a**, respectively, indicating that the bromide ligands points over the chelating ring in both complexes, with no other conformational isomer present. This behavior is consistent with other observations of *fac*-

Table IV. Atomic Coordinates and Isotropic Theraml Parameters of 1b

	x	*y*	*z*	B_{iso}, Å^2
Mn	0.95523(15)	0.09860(7)	0.20135(8)	2.80(7)
Br	0.89823(11)	0.00633(5)	0.10232(7)	4.23(6)
P1	0.8251(3)	0.17505(12)	0.11673(14)	2.67(12)
P2	1.1208(3)	0.13033(12)	0.14673(14)	2.63(12)
S	0.9533(3)	0.29209(15)	–0.09912(16)	5.39(18)
C1	0.9053(8)	0.2174(4)	0.0515(5)	2.5(4)
C2	0.9718(9)	0.1788(4)	–0.0010(5)	2.8(5)
C3	1.0738(9)	0.1285(4)	0.0411(5)	2.8(5)
C4	1.0446(10)	0.2286(5)	–0.0379(5)	3.8(5)
C5	0.8748(10)	0.1430(5)	–0.0644(5)	4.5(6)
C6	0.9950(9)	0.1546(5)	0.2793(5)	3.3(5)
O6	1.0229(7)	0.1880(3)	0.3333(4)	5.1(4)
C7	0.8301(9)	0.0666(5)	0.2385(5)	3.2(5)
O7	0.7581(7)	0.0421(4)	0.2677(4)	5.9(5)
C8	1.0599(10)	0.0400(5)	0.2593(5)	4.2(6)
O8	1.1246(7)	0.0027(4)	0.2986(4)	6.2(5)
C11	0.7807(8)	0.2445(4)	0.1706(5)	2.8(5)
C12	0.8018(10)	0.3094(5)	0.1569(6)	4.2(6)
C13	0.7605(11)	0.3583(5)	0.1995(6)	5.6(7)
C14	0.7023(11)	0.3433(6)	0.2562(6)	5.6(7)
C15	0.6818(11)	0.2798(6)	0.2704(6)	5.9(7)
C16	0.7202(11)	0.2300(5)	0.2269(6)	4.9(6)
C21	0.6673(9)	0.1527(4)	0.0551(5)	3.0(5)
C22	0.6049(9)	0.0969(5)	0.0674(5)	3.7(5)
C23	0.4838(10)	0.0834(5)	0.0245(6)	4.3(6)
C24	0.4237(9)	0.1256(5)	–0.0328(6)	4.7(6)
C25	0.4822(10)	0.1809(5)	–0.0463(6)	5.4(6)
C26	0.6029(10)	0.1955(5)	–0.0014(6)	4.5(6)
C31	1.2023(9)	0.2095(4)	0.1680(5)	3.0(5)
C32	1.1601(10)	0.2598(5)	0.2082(5)	3.8(5)
C33	1.2242(11)	0.3193(5)	0.2226(6)	5.2(7)
C34	1.3303(12)	0.3295(5)	0.1969(6)	6.4(7)
C35	1.3723(11)	0.2808(5)	0.1555(7)	6.0(7)
C36	1.3092(9)	0.2210(5)	0.1416(6)	4.2(6)
C41	1.2542(8)	0.0733(4)	0.1699(5)	2.7(4)
C42	1.3543(10)	0.0860(5)	0.2337(5)	4.1(6)
C43	1.4553(10)	0.0438(5)	0.2546(6)	5.4(6)
C44	1.4575(10)	–0.0132(5)	0.2112(6)	5.3(6)
C45	1.3583(10)	–0.0254(5)	0.1481(6)	4.4(6)
C46	1.2568(9)	0.0166(4)	0.1278(5)	3.2(5)
C51	0.9380(10)	0.3561(5)	–0.0350(5)	4.0(6)
C52	1.0310(11)	0.3744(5)	0.0283(6)	5.1(6)
C53	1.0103(12)	0.4272(5)	0.0728(6)	6.0(7)
C54	0.8982(12)	0.4597(6)	0.0541(7)	6.8(8)
C55	0.8067(12)	0.4428(6)	–0.0099(7)	6.9(8)
C56	0.8272(11)	0.3905(5)	–0.0526(6)	5.6(7)
Cl1	0.2966(6)	0.3585(3)	–0.0616(3)	17.07(22)
Cl2	0.4800(7)	0.4244(3)	0.0557(4)	21.2(3)
C	0.4446(24)	0.3963(12)	–0.0323(13)	23.2(10)

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Table V. Atomic Coordinates and Isotropic Thermal Parameters of 2a

	x	y	z	B_{iso}, Å^2
Mn	0.5977(3)	0.14993(24)	0.34244(12)	3.65(10)
Br	0.45542(20)	-0.01367(17)	0.24239(9)	4.67(7)
P1	0.7414(4)	0.2812(4)	0.25332(21)	3.35(17)
S2	0.8112(5)	0.0325(5)	0.34793(25)	5.08(21)
S	0.8336(7)	-0.1282(6)	0.0988(3)	7.3(3)
C1	0.8228(16)	0.1687(15)	0.1877(8)	3.6(7)
C2	0.9377(17)	0.0758(15)	0.2115(8)	4.2(7)
C3	0.8515(22)	-0.0385(16)	0.2640(10)	6.1(9)
C4	0.9864(19)	-0.0039(19)	0.1473(10)	5.7(9)
C5	1.0851(19)	0.1653(19)	0.2447(11)	6.3(10)
C6	0.6840(20)	0.2478(17)	0.4203(9)	5.3(8)
O6	0.7294(16)	0.3053(13)	0.4722(6)	7.0(7)
C7	0.4551(18)	0.2612(16)	0.3410(8)	4.4(7)
O7	0.3667(13)	0.3352(13)	0.3426(7)	6.3(6)
C8	0.4654(20)	0.0345(17)	0.3978(9)	5.2(8)
O8	0.3772(15)	-0.0322(14)	0.4331(7)	7.6(7)
C11A	0.6160(16)	0.3670(15)	0.1995(7)	3.6(7)
C12A	0.5333(18)	0.2972(17)	0.1404(9)	4.8(8)
C13A	0.4342(22)	0.3651(21)	0.1032(10)	6.5(10)
C14A	0.4125(22)	0.4975(20)	0.1242(10)	6.3(10)
C15A	0.4939(21)	0.5691(18)	0.1825(10)	5.8(9)
C16A	0.5935(19)	0.5027(16)	0.2200(9)	4.8(8)
C11B	0.9045(16)	0.4317(15)	0.2741(8)	3.8(7)
C12B	0.9735(20)	0.5149(17)	0.2209(9)	5.3(8)
C13B	1.0944(20)	0.6274(18)	0.2355(11)	6.0(10)
C14B	1.1501(20)	0.6601(18)	0.3027(11)	6.5(10)
C15B	1.0846(21)	0.5791(21)	0.3563(10)	6.9(10)
C16B	0.9599(19)	0.4645(18)	0.3417(9)	5.2(8)
C21	0.7675(20)	-0.1286(16)	0.3927(9)	5.0(8)
C22	0.872(3)	-0.1460(23)	0.4442(12)	8.5(13)
C23	0.838(3)	-0.263(3)	0.4880(13)	10.8(17)
C24	0.703(3)	-0.355(3)	0.4727(11)	9.9(16)
C25	0.603(3)	-0.3461(20)	0.4198(12)	8.6(13)
C26	0.6346(25)	-0.2297(18)	0.3798(10)	6.7(11)
C31A*	0.725(4)	-0.036(3)	0.0486(17)	4.7(7)
C32A*	0.811(4)	0.064(4)	0.0050(18)	5.1(7)
C33A*	0.728(4)	0.132(4)	-0.0404(20)	6.4(9)
C34A*	0.565(4)	0.098(4)	-0.0428(18)	5.4(8)
C35A	1/2	0	0	6.7(6)
C36A*	0.562(4)	-0.073(4)	0.0475(18)	5.6(8)
C31B*	0.929(4)	-0.257(3)	0.0531(17)	4.8(7)
C32B*	0.836(4)	-0.395(4)	0.0513(18)	5.1(7)
C33B*	0.890(4)	-0.511(3)	0.0200(17)	4.8(7)
C34B	1	-1/2	0	8.5(8)
C35B*	1.133(5)	-0.358(4)	-0.0013(22)	7.0(9)
C36B*	1.082(5)	-0.235(4)	0.0286(21)	6.6(9)

[a] Atoms with asterisks have occupance = 0.5.

$(\eta^2$-L-L)MnX(CO)$_3$ (L-L = $Me_2AsCH_2CH_2CH_2AsMe_2$);[14] the particular configuration is possibly stabilized by an attractive interaction between the halide ligand and the axial hydrogens.[14c]

In contrast, a boat conformation of the six-membered chelate ring appears in **1b** (Figure 4), although the dihedral angles of C1–C2–C3–P2 [-9.7(3)°] and P2–Mn–P1–C1 [1.9(3)°] are not 0° as for a typical boat form of the cyclohexane ring. The bulky group CH_2SPh is situated at a pseudoequatorial position, whereas the methyl group has a pseudoaxial orientation. The bromide ligand is clearly pointed over the ring. As the stability difference between **1a** and **1b** is 0.24 kcal/mol measured in solution, the adoption by **1b** of a boat conformation is probably due to the crystal packing (see below).

Although X-ray analysis clearly gives the conformation of the chelate ring in the solid state, a remaining question is whether such a form is retained in solution. For *fac*-$(CO)_3BrMnPPh_2CH_2C(Me)_2CH_2PPh_2$ (4), Kraihanzel and co-workers[15] showed that the conformation of the chelate ring retained a stable chair form and the ^{1}H NMR shifts of axial and equatorial methyl groups appeared δ 0.30 and 1.13, respectively. Both the greater shielding (δ 0.36) of the methyl group of **1a** and the similarity of the chemical shifts and the splitting pattern of methylenes attached to phosphorus atoms (compared to the axial one in **4**) indicate that the conformation of the chelate ring of **1a** in $CDCl_3$ remains in a chair form with the methyl group positioned at an axial position. The same argument applied to **2a**, which retains the chair form as in the solid state.

Table VI. Some Important Bond Distances (Å) and Bond Angles (deg)

	1a, Z = P2	1b, Z = P2	2a, Z = S2
Mn–Br	2.538(2)	2.545(2)	2.540(3)
Mn–P1	2.364(3)	2.369(3)	2.368(5)
Mn–Z	2.327(3)	2.344(3)	2.347(5)
Mn–C6	1.748(8)	1.767(9)	1.78(2)
Mn–C7	1.776(9)	1.780(9)	1.78(2)
Mn–C8	1.779(9)	1.78(1)	1.81(2)
C6–O6	1.17(1)	1.16(1)	1.13(2)
C7–O7	1.15(1)	1.16(1)	1.14(2)
C8–O8	1.16(1)	1.14(1)	1.14(2)
Br–Mn–P1	86.64(8)	92.21(9)	86.5(1)
Br–Mn–Z	88.76(9)	89.38(8)	95.1(2)
P1–Mn–Z	88.4(1)	87.1(1)	85.3(2)
Br–Mn–C6	171.2(3)	172.5(3)	172.4(5)
P1–Mn–C7	89.8(3)	95.2(3)	90.5(5)
P1–Mn–C6	102.1(3)	93.9(3)	101.1(5)
Z–Mn–C6	92.7(3)	95.3(3)	84.7(6)
Z–Mn–C8	91.9(3)	89.0(3)	97.7(6)
C7–Mn–C8	89.4(4)	88.4(4)	87.6(7)
Mn–C6–O6	174.3(7)	175.8(8)	175(2)
Mn–C7–O7	177.5(8)	173.1(8)	177(1)
Mn–C8–O8	176.9(8)	177.4(9)	176(2)

Table VII. Torsional Angles (deg) Along the Chelate Ring Mn–P1–C1–C2–C3–Z

	1a (Z = P2)	1b (Z = P2)	2a (Z = S2)
Mn–P1–C1–C2	-56.7(4)	54.3(4)	-59.4(7)
P1–C1–C2–C3	59.5(5)	-54.9(5)	62.5(9)
C1–C2–C3–Z	-61.1(5)	-9.7(3)	-70.8(10)
C2–C3–Z–Mn	61.1(4)	66.8(4)	75.3(8)
C3–Z–Mn–P1	-42.9(2)	-50.1(3)	-53.9(5)
Z–Mn–P1–C1	40.7(3)	1.9(3)	46.2(4)

If the ring in **1b** retains a boat form according to the configuration shown in Figure 5, then all protons of the methylene units would give a complicated ^{1}H NMR spectrum because all protons have different environments. Both the downfield shift of the methyl group (δ 1.13) and the splitting pattern in the ^{1}H spectrum, which are essentially similar to those in **4** (δ 1.13),[15] of the methylene groups attached to phosphorus atoms indicate that a chair conformation obtains for **1b** in $CDCl_3$ solution. If **1b** were forced into a chair conformation, analogous to that of **1a**, then the 1,3-diaxial interactions between $-CH_2SPh$ and the phenyl groups would be the only unfavorable factor for retention of such a conformation (Figure 5). Examination of a molecular model of **1a** reveals the methyl group is rotation hindered because of steric interaction with the axial phenyl groups. Thus **1b** ideally adapts a chair conformation with the phenylthio substituent pointing outward from the chelate ring, in order to minimize the unfavorable 1,3-diaxial interaction. The rotation about the carbon–carbon bond is also restricted for C–CH_2SPh. According to these assumptions, the energy difference

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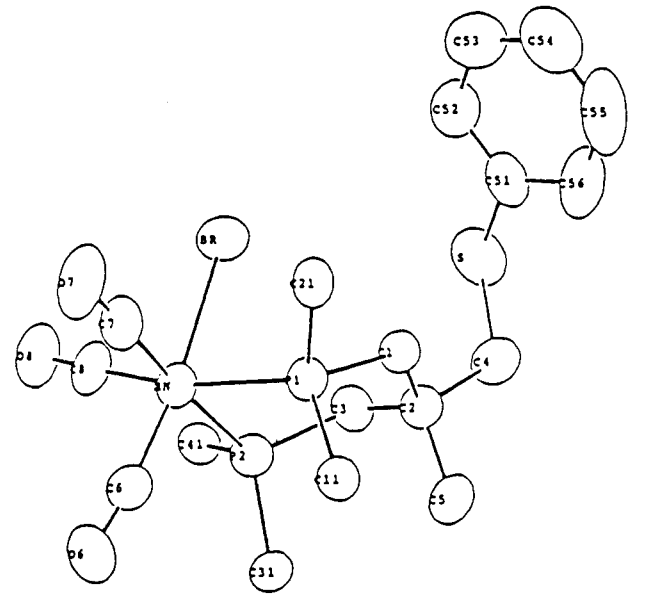
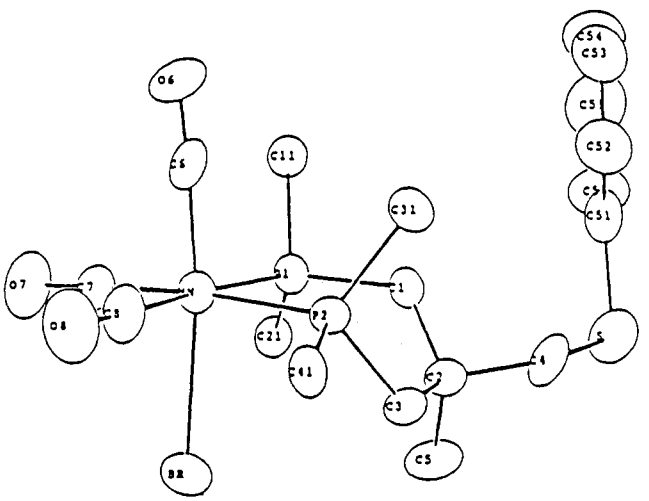


1a



1b

Figure 4. Another view of the crystal structure of **1a** and **1b** showing the chelate ring in the chair conformation for **1a** and boat conformation for **1b** (phenyl groups omitted for clear view).

between **1a** and **1b** in chair forms is expected to be relatively small, consistent with the measured value (ΔG_0 = 0.2 kcal/mol) from the equilibration measurement.

Summary

We investigated the coordination behavior of P–S hybrid tripodal ligands toward manganese(I), in which all tripodal ligands act as bidentate to form *fac*-(η^2-tripodal)$Mn(CO)_3Br$. The weak metal–sulfur interaction, relative to metal–phosphorus, is illustrated quantitatively in the kinetics of isomerization. The stable chair conformations are preferred for the chelate rings in both solution and crystal structures, except that **1b** has a boat form in the solid state. Further study of the formation of η^3-tripodal metal complexes and their properties is currently in progress.

Experimental Section

General Information. Proton magnetic resonance spectra were recorded on either a Bruker AC-E 200 or a Bruker AM-300WB spectrometer at room temperature. Proton-decoupled phosphorus-31 NMR spectra were determined on a Bruker AC-E 200 or a Bruker AM-300WB spectrometer at 81.01 or 121.49 MHz, respectively. 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 and UV/vis spectra were obtained on Perkin-Elmer 983G and Perkin-Elmer Lambda 3B instruments, respectively. 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. Air sensitive liquids were transferred by flexneedles using nitrogen pressure or by syringe. $(CO)_5MnBr$ was prepared according to the literature method.[16] The tripodal ligands P_2S and PS_2 were synthesized as described previously.[5,6] P_3 was obtained from Strem Chemicals; S_3 was prepared according to the literature procedure.[17]

***syn*- and *anti-fac*-Bromo[η^2-*P,P'*-2,2-Bis((diphenylphosphino)methyl)-1-(phenylthio)propane]tricarbonylmanganese(I), 1a and 1b.** Into a flask were placed P_2S (44.4 mg, 0.081 mmol) and $Mn(CO)_5Br$ in $CHCl_3$. The resulting mixture was heated at reflux for 2 h. Filtration and concentration of the reaction mixture gave the crude products (59.8 mg, 96%, the ratio of isomer **1a**:**1b** = 6:4). Fractional recrystallization from dichloromethane and hexane gave isomer **1a** as a yellow crystalline solid and isomer **1b** as an orange-yellow solid.

Isomer **1a**: mp 186–188 °C dec; UV/vis ($CHCl_3$) 389 nm (ϵ = 1078 cm^{-1} M^{-1}), 246 ($\epsilon = 1.25 \times 10^4$); IR ($CHCl_3$) 2029, 1961, 1899 cm^{-1}; ^1H NMR δ 7.80–7.30 (m, 25 H), 3.47 (dd, J = 14.4 Hz, J_{P-C-H} = 6.6 Hz, 2 H), 2.99 (s, 2 H), 2.31 (dd, J = 14 Hz, J_{P-C-H} = 13 Hz, 2 H), 0.36 (s, 3 H); ^{31}P NMR δ 30.52. Anal. Calcd for $C_{38}H_{34}BrO_3P_2SMn$: C, 59.46; H, 4.28. Found: C, 59.32; H, 4.28.

Isomer **1b**: mp 174–177 °C dec; UV/vis ($CHCl_3$) 389 nm (ϵ = 1078 cm^{-1} M^{-1}), 246 ($\epsilon = 1.25 \times 10^4$); IR ($CHCl_3$) 2027, 1960, 1902 cm^{-1}; ^1H NMR δ 7.63–7.61 (m, 8 H), 7.35–7.20 (m, 12 H), 7.10–7.08 (m, 3 H), 6.62–6.59 (m, 2 H), 3.33 (dd, J = 14 Hz, J_{P-C-H} = 7 Hz, 2 H), 2.55 (dd, J = 14 Hz, J_{P-C-H} = 7 Hz, 2 H), 2.33 (s, 2 H), 1.13 (s, 3 H); ^{31}P NMR δ 30.52. Anal. Calcd for $C_{38}H_{34}BrO_3P_2SMn$: C, 59.46; H, 4.28. Found: C, 58.92; H, 4.33.

***fac*-Bromo[η^2-*P,S*-2,2-bis((phenylthio)methyl)-1-(diphenylphosphino)propane]tricarbonylmanganese(I), 2a and 2b.** These complexes were prepared similarly to **1a** and **1b**. Complex *syn*-**2a** was obtained as an orange solid by recrystallization from chloroform and hexane: mp 140–142 °C dec; IR ($CHCl_3$) 2036, 1967, 1914 cm^{-1}; ^1H NMR δ 6.9–8.1 (m, 20 H), 4.39 (d, J = 11 Hz, 1 H), 3.50 (dd, J_{H-C-H} = 13 Hz, J_{P-C-H} = 6 Hz, 1 H), 3.01 (s, 2 H), 2.58 (d, J = 11 Hz, 1 H), 2.21 (dd, J_{H-C-H} = 13 Hz, J_{P-C-H} = 16 Hz, 1 H), 0.68 (s, 3 H); ^{31}P NMR δ 27.0.

Complex *anti*-**2b** was never obtained as a pure form but was identified by its spectral data: IR ($CHCl_3$) 2036, 1967, 1914 cm^{-1}; ^1H NMR δ 6.9–8.1 (m, 20 H), 4.33 (d, J = 12 Hz, 1 H), 3.50 (dd, J_{H-C-H} = 14 Hz, J_{P-C-H} = 6.5 Hz, 1 H), 2.99 (d, J = 12.8 Hz, 1 H), 2.79 (d, J = 12 Hz, 1 H), 2.40 (dd, J_{H-C-H} = 15 Hz, J_{P-C-H} = 15 Hz, 1 H), 2.31 (d, J = 12.8 Hz, 1 H), 1.22 (s, 3 H); ^{31}P NMR δ 25.8. Anal. Calcd for $C_{32}H_{29}BrO_3PS_2Mn$: C, 59.46; H, 4.28. Found: C, 58.92; H, 4.33.

***fac*-Bromo[*P,P'*-2,2-bis((diphenylphosphino)methyl)-1-(diphenylphosphino)propane]tricarbonylmanganese(I), 3a and 3b.** These complexes were prepared by a method similar to that described for **1a** and **1b**. The separation of these two stereoisomers was not achieved. Both complexes have the same infrared absorptions in the carbonyl region, 2029, 1961, and 1902 cm^{-1}. These two species were identified according to the ^1H NMR and ^{31}P NMR spectra.

3a: ^1H NMR 6.9–7.8 (m, 30 H), 3.43 (dm, J = 15 Hz, 2 H), 2.34–2.30 (m, 2 H), 2.31 (s, 2 H), 0.38 (s, 3 H); ^{31}P NMR δ –26.94 (s), 29.81 (s).

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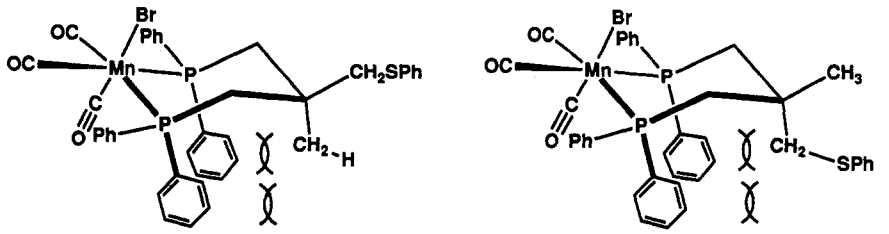

(A) (B)

Figure 5. Comparison of the chelate rings of both **1a** and **1b** in chair forms.

3b:[10] ^{1}H NMR 6.9–7.8 (m, 30 H), 3.31 (dm, J = 15 Hz, 2 H), 2.48–2.61 (m, 2 H), 1.82 (s, 2 H), 0.99 (s, 3 H); ^{31}P NMR δ –27.76, 29.39.

Kinetic Experiments. On the basis of ^{1}H NMR spectra, because the chemical shifts of the methyl groups in *syn*- and *anti*- isomers differ significantly, the measurement of the concentrations of the two species was achieved by means of the integration of these peaks. Either **1a** or **2a** was frozen in a 5-mm tube at –30 °C; deuterated solvent was added. The NMR tube was transferred to the ^{1}H NMR spectrometer. The reaction temperature (i.e. the temperature of the probe) was controlled by the instrument itself and was calibrated according to a method described by Van Geet.[18] The appearance of either **1b** or **2b** and the disappearance of either **1a** or **2a** with time were followed by monitoring the peaks of the methyl groups. All reactions reached equilibrium; the concentration of the *syn* isomer was used as the [*syn* isomer]$_\infty$ value. The first-order rate constants were determined from a plot of $\ln(X_0\text{-}X_\infty)/(X\text{-}X_\infty)$ vs time using a standard linear-squares treatment, X = molar fraction of *syn* isomer.

Crystallography. Cell parameters were determined on a CAD-4 diffractometer at 298 K by a least-squares treatment. Atomic scattering factors were taken from ref 19. Calculations were performed by using the NRCC SDP VAX package.[20] The crystal data of **1a**, **1b**, and **2a** are listed in Table II, and their non-hydrogen atomic coordinates are listed in Tables III–V, respectively. Other crystallographic data are collected as supplementary materials.

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Supplementary Material Available: Tables listing complete bond distances, bond angles, and anisotropic thermal parameters for **1a**, **1b**, and **2a** (12 pages). Ordering information is given on any current masthead page.

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