Study of Effects on the Coordination of Thioether Ligands, 2[1a]

Stereospecific Ligand Substitutions in Manganese(I) Complexes

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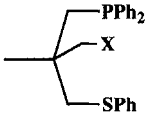
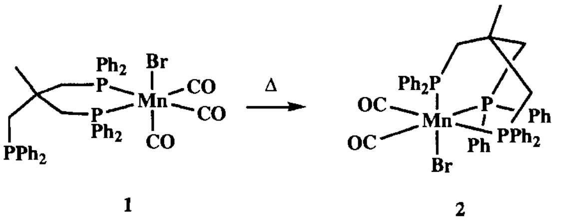
Treatment of *fac*-[($\mathbf{P_2SPh}$-*P,P'*)Mn(CO)$_3$Br] and *fac*-[($\mathbf{PS_2Ph}$-*P,S*)Mn(CO)$_3$Br] [$\mathbf{P_2SPh}$: Z = PPh$_2$; $\mathbf{PS_2Ph}$: Z = SPh in $CH_3C(CH_2PPh_2)(CH_2SPh)(CH_2Z)$] with silver hexafluorophosphate yields the η^3-tripodal manganese complexes [($\mathbf{P_2SPh}$-*P,P',S*)Mn(CO)$_3$]PF$_6$ (**7**) and [($\mathbf{PS_2Ph}$-*P,S,S'*)Mn(CO)$_3$]PF$_6$ (**9**), respectively, whereas the reaction of $CH_3C(CH_2PPh_2)_2(CH_2SH)$ with $Mn(CO)_5Br$ gives directly [$CH_3C(Ph_2PCH_2)_2(CH_2S)$-*P,P',S*]Mn(CO)$_3$ (**11**). Both ionic complexes **7** and **9** undergo stereospecifically ligand substitution upon treatment with Br^-, I^-, N_3^-, SCN^- and CN^- to give *syn-fac*-[($\mathbf{P_2SPh}$-*P,P'*)Mn(CO)$_3$X] and *syn-fac*-[($\mathbf{PS_2Ph}$-*P,S*)Mn(CO)$_3$X] (X = Br, I, SCN, N$_3$, CN) respectively, but the neutral complex **11** fails to undergo such a substitution reaction with these ions. However, reaction of I^- with the complex [($\mathbf{PSMe}$)-*P,P',S*]Mn(CO)$_3$]BF$_4$ (**20**) {$\mathbf{P_2SMe}$ = $CH_3C(CH_2PPh_2)_2(CH_2SCH_3)$}, which is obtained from the *S*-alkylation of **11** with $(CH_3)_3OBF_4$, affords *syn-fac*-[($\mathbf{P_2SMe}$)-*P,P'*]Mn(CO)$_3$I (**22s**) exclusively. The possible reaction mechanism of this ligand substitution is discussed.

As ligands bound to metal ions, thioethers exhibit the same useful properties as phosphanes. They may function both as moderate σ-donors and π-acceptors; the coordination chemistry of the "hybrid" donors has received much attention[1–3]. In a previous study, we reported that the coordinating strength of the Mn–S bond is weaker than that of Mn–P by about 6 kcal/mol in the system of *fac*-[η^2-($\mathbf{P_{3-n}S_nPh}$)]Mn(CO)$_3$Br (*n* = 2,1)[1a]. This intrinsic property seems to prevent the free sulfide donor of *fac-(P,P'*-$\mathbf{P_2SPh}$)Mn(CO)$_3$Br and *fac-(P,S*-$\mathbf{PS_2Ph}$)Mn(CO)$_3$Br from forming a η^3-type complex, in contrast to (*P,P'*-$\mathbf{P_3}$)Mn(CO)$_3$Br (**1**), where $\mathbf{P_3}$ = $CH_3C(CH_2PPh_2)_3$, which undergoes ligand substitution intramolecularly to provide (*P,P',P''*-$\mathbf{P_3}$)Mn(CO)$_2$Br (**2**) under thermal reaction conditions (Eq. 1)[4].

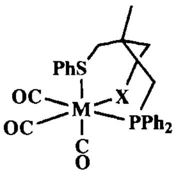


$\mathbf{P_2SPh}$, X = PPh$_2$
$\mathbf{PS_2Ph}$, X = SPh



1 **2** (1)

Due to the chelate effect and the imposed *facial* stereochemistry of tripodal ligands, it would be interesting to investigate the properties of complexes wrapped by "hybrid" donors, such as complex **3**. Since the coordinating sites *trans* to these donors are in different environments, such complexes are anticipated to have stereochemical importance on tuning reaction mechanisms and selectivities[5–7]. For example, the analysis of the stereoisomeric products obtained from the ligand substitution reaction of *fac-(4-P,P',O*)Mo(CO)$_3$ with CO discloses that the reaction takes place at both sites of the departing ligand and *trans* with respect to that position[5a]. This paper describes the preparation of the tripodal phosphine-thioether manganese(I) complexes in the form of **3** and the stereospecific ligand substitution reaction of these complexes with halides or pseudohalides.



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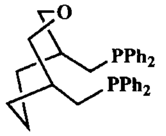

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Synthesis of Ligands

Preparations of tripodal $\mathbf{P_2SPh}$[8] and $\mathbf{PS_2Ph}$[3] have previously been reported, while $\mathbf{P_2SH}$ is obtained according to the procedures delineated in Scheme 1. The thiacyclobutane derivative **5** is obtained by the reaction of 1,1,1-tris(hydroxymethyl)ethane with diethyl carbonate followed by treatment of potassium thiocyanate[9]. Reaction of **5** with

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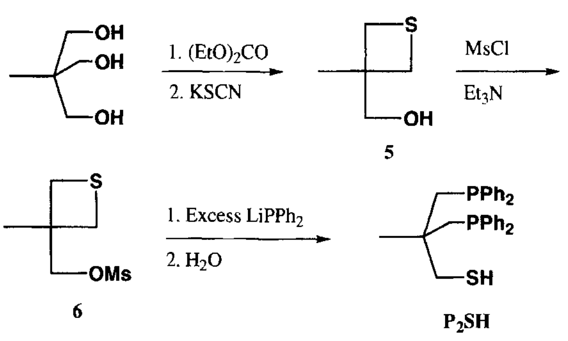
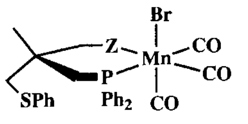
methanesulfonyl chloride in the presence of triethylamine yields the mesylate **6**, which subsequently reacts with an excess of lithium diphenylphosphide to afford the desired ligand $\mathbf{P_2SH}$. This new tripodal ligand is obtained as an air-sensitive viscous oil after chromatography on silica gel.

Scheme 1

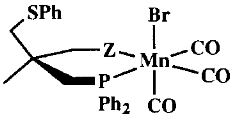


Preparation of *fac*-(η^3-tripodal)$Mn(CO)_3$ Complexes

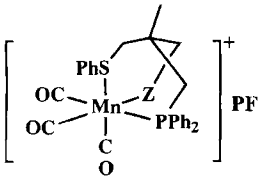
Under nitrogen, [*fac*-($\mathbf{P_2SPh}$-*P,P',S*)$Mn(CO)_3]PF_6$ (**7**) is prepared in high yield by the reaction of a mixture of complexes *syn-fac*-[($\mathbf{P_2SPh}$-*P,P'*)$Mn(CO)_3Br$] (**8s**) and *anti-fac*-[($\mathbf{P_2SPh}$-*P,P'*)$Mn(CO)_3Br$] (**8t**)[1a] with an equimolar amount of silver hexafluorophosphate in acetone. The η^3-complex **7** is isolated as a yellow crystalline solid by crystallization from acetone and hexane. A singlet shift at 30.3 ppm of ^{31}P-NMR spectrum of **7** indicates that both phosphorus atoms coordinate to the metal center. The carbonyl stretching vibrations at 2041, 1975, 1945 cm^{-1} in the infrared spectrum are consistent with the *facial* tricarbonyl species[10]. Besides the signals due to the aromatic and the methylene protons, the ^{1}H-NMR spectrum shows a triplet at $\delta = 1.60$ for the methyl group, the chemical shift of which suggests the formation of a η^3-tripodal complex[11]. The triplet splitting pattern of the methyl group ($J_{P\text{-}H} = 3$ Hz) is due to the coupling of two phosphorus atoms.



8t Z = PPh_2
10t Z = SPh

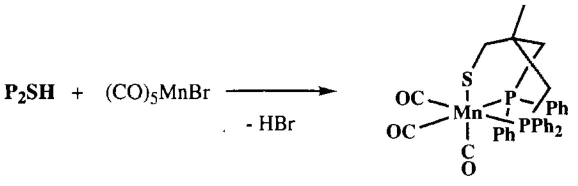


8s Z = PPh_2
10s Z = SPh



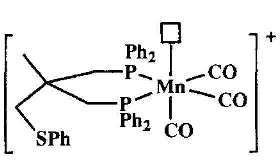
7 Z = PPh_2
9 Z = SPh

The orange-yellow complex [*fac*-(η^3-$\mathbf{PS_2Ph}$)$Mn(CO)_3]PF_6$ (**9**) is prepared from **10d** and/or **10t** by a similar method. On the other hand, reaction of the tripodal ligand $\mathbf{P_2SH}$ with $Mn(CO)_5Br$ in refluxing $CHCl_3$ provides directly the desired η^3-type complex **11** (Eq. 2). The latter complex is obtained as a yellow solid by recrystallization from hexane and chloroform. The structures of both complexes **9** and **11** can be readily identified by spectroscopic and elemental analyses.

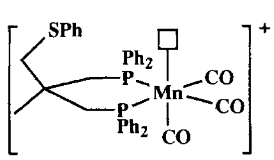


11 (2)

The formation of the complexes **7** or **9** requires the assistance of silver ion to remove the bromide ligand from the corresponding precursor to generate a coordination site for the free sulfide. These properties are quite different from those of complex **1**, which undergoes exchange of a carbonyl by a phosphane ligand to form [η^3-(tripodal)$Mn(CO)_2Br$] **2**. Either **8s** or **8t** yields the desired complex [η^3-(tripodal)-$Mn(CO)_3]^+$, indicating that the five-coordinate intermediate **8t'** is rapidly converted into **8s'** in order to permit the formation of the product. Such an interconversion of five-coordinate intermediates was also reported in both theoretical and experimental consideration in many metal complexes[5].



8t'



8s'

Stereospecific Ligand Substitution

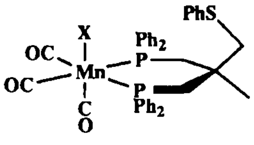
Due to strong chelation, the η^3-tripodal manganese(I) complexes are fairly stable. Complexes **7**, **9** and **11** are thermally stable in refluxing THF or acetonitrile even in the presence of thiophenol, diethylamine or methanol. It must be emphasized that the chelate effect is in correspondence with ligands, thus $\mathbf{PS_2Ph}$ is less effective than $\mathbf{P_2SPh}$ systems (P_2S or P_2S^-), as evidenced by the following observation. 1,2-Bis(diphenylphosphino)ethane (dppe) readily displaces the tripodal ligand $\mathbf{PS_2Ph}$ of **9** in solution at room temperature, whereas the displacement of $\mathbf{P_2SPh}$ of **7** requires higher temperatures. Complex **11** resists all attempts at achieving such a reaction, even under much more vigorous conditions.

Compound **7** reacts with tetrabutylammonium bromide immediately to give *syn-fac*-($\mathbf{P_2SPh}$-*P,P'*)$Mn(CO)_3Br$ (**8s**) as the exclusive product. Table 1 lists the values of k_{obs} for the reaction of **7** with bromide under pseudo-first-order conditions, and such kinetic studies indicate that the rate law has the form rate = $k_{obs}[\mathbf{7}][Br^-]$, consistent with a second-order reaction. The activation parameters for the reaction thus obtained by the Eyring plot are $\Delta H^{\neq} = 14 \pm 2$ kcal/mol and $\Delta S^{\neq} = -20 \pm 6$ eu. Moreover, complex **7** reacts with other halides or pseudohalides, such as I^-, CN^-, SCN^-, N_3^-, at room temperature, and all of these reactions have been found

Tab. 1. Rate constant for reactions of **7** with bromide in CD_2Cl_2

[**7**], (M)	[Br^-], (M)	Temp, (K)	k_{obs} ($M^{-1}sec^{-1}$)
7.62×10^{-3}	0.414	280	1.64×10^{-4}
7.62×10^{-3}	0.828	280	2.88×10^{-4}
7.62×10^{-3}	1.657	280	5.87×10^{-4}
7.62×10^{-2}	1.799	240	3.30×10^{-4}
7.62×10^{-2}	1.799	253	2.12×10^{-4}
7.62×10^{-2}	1.799	268	4.67×10^{-4}
7.62×10^{-2}	1.799	276	2.98×10^{-3}

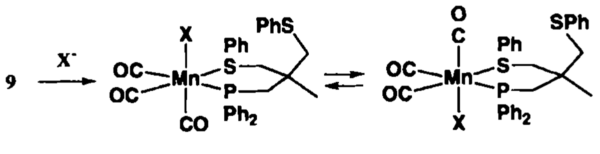
to be stereospecific. Thus, the sulfur donor in complex **7** is replaced by anionic ligands to give the corresponding *syn*-isomeric product exclusively. Apparently, ligand substitution takes place at the position where the sulfur donor originally coordinates to the metal center.



12s X = I
13s X = CN
14s X = N_3
15s X = SCN
19s X = NCS

Monitoring of the reaction of **9** with bromide by ^1H-NMR spectroscopy reveals that the substitution also occurs in the same fashion as **7** with the formation of **10s** as the exclusive product (Scheme 2). As expected, complex **9** reacts with other anionic ligands (I^-, SCN^-, N_3^-) stereospecifically to give the corresponding substitued product **14s**–**16s**. However, these *syn-fac*-[*P,S*-(PS_2Ph)]$Mn(CO)_3X$ complexes would then undergo isomerization to the *anti* isomers (Scheme 2). The isomerization of *syn-fac*-[*P,S*-(PS_2Ph)]$Mn(CO)_3Br$ **10s** into the *anti* isomer **10t** ($t_{1/2}$ = 2.7 h at 25°C) was demonstrated in our early work[1a]. Due to the slow isomerization, the stereospecific substitution of **9** with anionic ligands can be confirmed by monitoring the reaction in ^1H-NMR spectroscopy.

Scheme 2



10s X = Br
16s X = I
17s X = N_3
18s X = NCS

10t X = Br
16t X = I
17t X = N_3
18t X = NCS

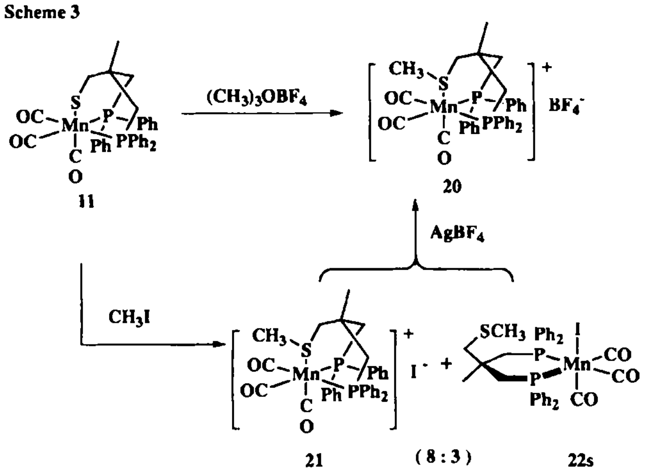
Both **8s** and **10s** have been characterized previously by X-ray crystal structural analysis, and the ^1H-NMR chemical shifts of methyl groups (e.g. δ_{8s} is located upfield by 0.5 ppm compared to δ_{8t}) may be used for the differentiation of the stereoisomer[1a]. Other products are characterized by both spectral and elemental analyses.

The initially formed complex **15s**, in which the sulfur atom is bound to the metal center, is slowly converted into the nitrogen-bound complex **19s** as evidenced by IR spectroscopy. A characteristically weak absorption at 2100 cm^{-1} due to –SCN in **15s** is found to shift to a strong absorption at 2050 cm^{-1} due to –NCS in complex **19s**[12]. However, this stereospecific ligand substitution reaction does not occur in the neutral complex **11**, even at higher reaction temperatures.

Alkylation of Complex 11 and Properties of the Resulted Complex

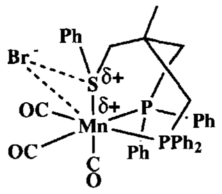
Alkyaltion of **11** with $(CH_3)_3OBF_4$ provides exclusively the corresponding cationic complex **20** (Scheme 3). In a similar experiment using an excess of methyl iodide as the alkylalting agent, a mixture of complexes **21** and **22s** in a ratio of 8:3 is obtained as revealed by ^{31}P-NMR analysis. Complex **22s** appears to be the ligand substitution product formed by reaction of **21** with the iodide (see below). Treatment of a mixture of **21** and **22s** with silver tetrafluoroborate yields exclusively **20**. The tridentate cationic complex **20** reacts stereospecifically with iodide to give the expected product **22s**, but the rate of this reaction is much slower than that of the reaction of **7**. The stronger coordinating ability of the methylthio group than the phenylthio group of **7** accounts for these results. The conversion of the neutral complex **11** into a cationic species **20** restores the reactivity toward halides.

Scheme 3



Conclusion

The ligand substitution reaction of *fac*-[(tripodal)$Mn(CO)_3$]$^+$ cation with halides or pseudohalides proceeds stereospecifically, whereas the neutral complex *fac*-[(tripodal)$Mn(CO)_3$] does not undergo such a reaction. The weakly coordinating ability of the sulfide donor as compared to that of Mn–P (difference of ca 6 kcal/mol) and the electrostatic interaction between metal ion and bromide are assumed to be responsible for this unique selectivity. Such stereoselectivity might result in a partially positive charge at sulfur center in the complexes, arising from the coordination of sulfide to the Mn(I). It may direct the anionic ligand to come to the vicinal position by electrostatic interaction to form a transition state **23**, which eventually leads to the *syn* isomers. The charge interaction assisting the substitution reaction is similar to the S_N2 reaction at α-halocarbonyl compounds[13].



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Experimental

General: ^1H- and ^{31}P-NMR spectra were recorded with 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 and tetramethylsilane (TMS) for ^{31}P-NMR and ^1H-NMR spectra respectively in $CDCl_3$, unless stated otherwise. – Infrared spectra were measured with Perkin-Elmer 983G and Biorad FT-IR instruments. Elemental analyses were performed with a Perkin-Elmer 240C instrument. – All reactions, manipulations and purification steps involving phosphanes were performed in a dry nitrogen atmosphere.

Complexes of *syn*- and *anti*-[*P,P'*-(**P₂SPh**)Mn(CO)₃Br] (**8s** and **8t**), as well as *syn*- and *anti*-[*P,S*-(**PS₂Ph**)]Mn(CO)₃Br (**10s** and **10t**)[1a] were synthesized as described previously.

3-(Hydroxymethyl)-3-methylthietane (**5**): A mixture of 1,1,1-tris-(hydroxymethyl)ethane (60 g, 0.5 mol), diethyl carbonate (58.4 g, 0.5 mol) and KOH (1.78 g, 0.03 mmol) in anhydrous alcohol (50 ml) was heated at reflux for 30 min and then the ethanol was distilled from the mixture. Potassium thiocyanate (72 g) was added to the residue and the mixture was heated again in oil bath at 160 °C under reduced pressure (130–140 Torr) for 2.5 h. Distillation of the reaction mixture gave the desired product as a yellow liquid. Yield 23.6 g (40%), b.p. 120–130 °C/2.5–3 Torr. – ^1H NMR: $\delta = 3.66$ (s, 2H), 3.03 (d, $J = 9.1$ Hz, 2H), 2.85 (d, $J = 9.1$ Hz, 2H), 2.16 (br., 1H), 1.26 (s, 3H). – $C_5H_{10}OS$: calcd. 118.0452, found 118.0447 (MS).

3-(Methylsulfonyloxymethyl)-3-methylthietane (**6**): Methanesulfonyl chloride (31.8 g, 278 mmol) was added dropwise to a solution of **5** (30 g, 254 mmol) and triethylamine (38.5 g, 380 mmol) in dichloromethane (200 ml) at ice-bath temperature. The resulting mixture was stirred for another 2 h. It was washed with 1 N NaOH, 10% HCl, saturated $NaHCO_3$ and NaCl solution. The organic portion was dried with anhydrous $MgSO_4$ and concentrated. The residue was distilled to give compound **6** as a light yellow viscous liquid. Yield 46.2 g (93%), b.p. 110 °C/0.15–0.2 Torr. – ^1H NMR: $\delta = 4.19$ (s, 2H), 3.03 (d, $J = 9.4$ Hz, 2H), 3.0 (s, 3H), 2.91 (d, $J = 9.4$ Hz, 2H), 1.33 (s, 3H). – $C_6H_{12}O_3S_2$ (196.3): calcd. C 36.72, H 6.16; found C 37.09, H 6.00.

2,2-Bis[(diphenylphosphanyl)methyl]-1-propanethiol (**P₂SH**): A solution of the diphenylphosphide anion, which was prepared by addition of a 1.60 M hexane solution of *n*-butyllithium to a solution of diphenylphosphane (6.17 g, 33 mmol) in THF (250 ml), was added to a solution of **6** (2.6 g, 13 mmol) in THF (50 ml) with stirring. The mixture was heated to reflux for 6 h and the reaction quenched with a 100 ml of water. The organic portion was separated, dried with anhydrous $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (130 g) with ethyl acetate/hexane (1:40) as the eluent. After concentration of the eluate, the tripodal ligand **P₂SH** was isolated as a viscous liquid. Yield 1.87 g (30%). – IR ($CHCl_3$): $\tilde{\nu} = 2560$ cm^{-1} (S-H). – ^1H NMR: $\delta = 7.56-7.36$ (m, 20H), 2.78 (d, $J = 12$ Hz, 2H), 2.45 (m, 5H), 1.08 (s, 3H). – ^{31}P NMR: $\delta = -25.1$. – $C_{29}H_{30}SP_2$ (472.6): calcd. C 73.71, H 6.40; found C 73.50, H 6.27.

General Procedure for Preparation [(η³-tripodal)Mn(CO)₃]⁺ Complexes: To a solution of [η²-(**P*ₙ*S₃₋ₙPh**)Mn(CO)₃Br] was added an equimolar amount of silver hexafluorophosphate in dichloromethane with stirring under nitrogen in a dark place. After stirring for 0.5 h, the reaction mixture was filtered and the filtrate was concentrated. The residue was recrystallized from acetone/hexane.

Tricarbonyl{fac-[(2,2-bis(diphenylphosphanylmethyl)-1-(phenylthio)propane]-P,P',S}manganese(I) Hexafluorophosphate (**7**): Complex **7** is a yellow crystalline solid. Yield 93%, m.p. 200–203 °C (dec). – IR (KBr): $\tilde{\nu} = 2041$ cm^{-1}, 1975, 1945 (CO). – ^1H NMR: $\delta = 7.54-7.20$ (m, 25H), 3.10 (s, 2H), 2.73 (dd, $J = 16$, 8 Hz, 2H), 2.59 (dd, $J = 16$, 10 Hz, 2H), 1.60 (t, $J_{P-H} = 3$ Hz, 3H). – ^{31}P NMR: $\delta = 30.3$. – Conductivity (acetone) 124 Ω^{-1} cm^2 mol^{-1}. – $C_{38}H_{34}F_6MnO_3P_3S$ (832.6): calcd. C 54.80, H 4.12; found C 54.96, H 4.00.

Tricarbonyl{fac-[(2,2-bis(phenylthio)-1-(diphenylphosphanylmethyl)propane)-P,S,S'}]manganese(I) Hexafluorophosphate (**9**): Complex **9** was obtained as a yellow crystalline solid. Yield 90%. – IR (KBr): $\tilde{\nu} = 2043$ cm^{-1}, 1977, 1958 (CO). – ^1H NMR: $\delta = 8.00-7.10$ (m, 20H), 3.70 (d, $J = 12$ Hz, 2H), 3.53 (d, $J = 12.6$ Hz, 2H), 3.03 (d, $J = 9$ Hz, 2H), 1.58 (s, 3H). – ^{31}P NMR: $\delta = 32.3$. – $C_{32}H_{29}F_6MnO_3P_2S_2$ (756.6): calcd. C 50.80, H 3.86; found C 51.15, H 3.77.

Tricarbonyl{fac-[(2,2-bis(diphenylphosphanylmethyl)-1-propanethiolate]-P,P',S}manganese(I) (**11**): A solution of **P₂SH** (0.5 g, 1.06 mmol) and $Mn(CO)_5Br$ (291 mg, 1.06 mmol) in THF (60 ml) was heated to reflux for 3 h. The solution was filtered through silica gel and the filtrate was concentrated. The residue was crystallized from a solution of chloroform and hexane to give the desired complex as a yellow crystalline solid. Yield 622 mg, (96%), m.p. 252–260 °C (dec.). – IR ($CHCl_3$): $\tilde{\nu} = 2016$ cm^{-1}, 1947, 1907 (CO). – ^1H NMR: $\delta = 7.86-7.67$ (m, 20H), 2.15 (dd, $J = 12$, 6 Hz, 2H), 2.1 (s, 2H), 1.95 (dd, $J = 12$, 6 Hz, 2H), 1.1 (s, 3H). – ^{31}P NMR: $\delta = 40.0$. – $C_{32}H_{29}MnO_3P_2S$ (610.5): calcd. C 62.95, H 4.79; found C 62.59, H 4.45.

General Procedures for the Ligand Substitution Reaction of [(η³-tripodal)Mn(CO)₃]⁺ Complexes with Various Anions: To a solution of [(η³-tripodal)Mn(CO)₃]PF₆ in chloroform or THF was added an excess of Bu_4NY or KY (Y = Br, I, N_3, CN, SCN) at room temperature with stirring for 0.5 h. The mixture was concentrated and the residue chromatographed or crystallized to give the corresponding complex *fac*-(η²-tripodal)Mn(CO)₃Y. The physical, spectral and elemental analyses are as follows:

syn-fac-Iodo{η²-[2,2-bis((diphenylphosphanyl)methyl)-1-(phenylthio)propane]-P,P'}tricarbonylmagnganese(I) (**12s**): Orange-yellow solid, m.p. 214–215 °C (dec). – IR ($CHCl_3$): $\tilde{\nu} = 2029$ cm^{-1}, 1961, 1903 (CO). – ^1H NMR: $\delta = 7.80-7.05$ (m, 25H), 3.47 (d, $J = 12$ Hz, 2H), 2.80–2.60 (m, 2H), 0.19 (s, 3H). – ^{31}P NMR: $\delta = 27.3$. – $C_{38}H_{34}IMnO_3P_2S$ (814.5): calcd. C 56.03, H 4.21; found C 56.13, H 4.58.

syn-fac-Cyano{η²-[2,2-bis((diphenylphosphanyl)methyl)-1-(phenylthio)propane]-P,P'}tricarbonylmanganese(I) (**13s**): Yellow solid, m.p. 216–217 °C (dec). – IR ($CHCl_3$): $\tilde{\nu} = 2017$ cm^{-1}, 2022, 1954, 1933 (CO). – ^1H NMR: $\delta = 8.00-7.10$ (m, 25H), 3.40–3.25 (m, 2H), 2.94 (s, 2H), 2.39 (s, 2H), 0.30 (s, 3H). – ^{31}P NMR: $\delta =$

38.4. – $C_{39}H_{34}MnNO_3P_2S$ (713.6): calcd. C 65.64, H 4.80, N 1.96; found C 66.00, H 4.76, N 2.04.

syn-fac-Azido{η^2-[2,2-bis((diphenylphosphanyl)methyl)-1-(phenylthio)propane]-P,P'}tricarbonylmanganese(I) (**14s**): Orange-red solid, m.p. 153°C (dec). – IR ($CHCl_3$): ṽ = 2054 cm^{-1}, 2013, 1958, 1909. – ^1H NMR: δ = 7.67–7.22 (m, 25H), 2.86 (d, *J* = 8 Hz, 2H), 2.76 (s, 2H), 2.31–2.27 (m, 2H), 0.51 (s, 3H). – ^{31}P NMR: δ = 33.2. – $C_{38}H_{34}MnN_3O_3P_2S$ (729.6): calcd. C 62.55, H 4.70, N 5.76; found C 62.69, H 4.93, N 5.80.

syn-fac-(N-Thiocyanate){η^2-[2,2-bis((diphenylphosphanyl)-methyl)-1-(phenylthio)propane]-P,P'}tricarbonylmanganese(I) (**19s**): White solid, m.p. 102–104°C (dec). – IR ($CHCl_3$): ṽ = 2029 cm^{-1}, 1961, 1899. – ^1H NMR: δ = 7.71–7.14 (m, 25H), 3.04 (s, 2H), 2.79 (d, *J* = 14 Hz, 2H), 2.53–2.39 (m, 2H), 0.42 (s, 3H). – ^{31}P NMR: δ = 34.1. – $C_{39}H_{34}MnNO_3P_2S_2$ (745.7): calcd. C 62.82, H 4.60, N 1.88; found C 62.76, H 5.00, N 1.50.

syn- and anti-fac-Iodo{η^2-[2,2-bis(phenylthio)methyl)-1-(diphenylphosphanyl)propane]-P,S}tricarbonylmanganese(I) (**16s** + **16t**): Due to isomerization, no complex was obtained in pure form, but was identified by its NMR data. – IR ($CHCl_3$): ṽ = 2030 cm^{-1}, 1965, 1915. – ^1H NMR, complex **16s**: δ = 8.00–7.05 (m, 20H), 4.30 (d, *J* = 12 Hz, 1H), 3.60 (dd, *J* = 13, 6 Hz, 1H), 3.03 (s, 2H), 2.76 (d, *J* = 12 Hz, 1H), 2.36 (dd, *J* = 13, 16 Hz, 1H), 0.64 (s, 3H) and complex **16t**: δ = 8.00–6.85 (m, 20H), 4.23 (d, *J* = 12 Hz, 1H), 3.58 (dd, *J* = 13, 6 Hz, 1H), 3.19 (d, *J* = 12 Hz, 1H), 2.75 (d, *J* = 12 Hz, 1H), 2.60 (dd, *J* = 13, 16 Hz, 1H), 2.28 (d, *J* = 12 Hz, 1H), 1.24 (s, 3H). – ^{31}P NMR; complex **16s**: δ = 24.5 and complex **16t**: δ = 23.4. – $C_{32}H_{29}IMnO_3PS_2$ (738.5): calcd. C 52.03, H 3.96; found C 51.53, H 3.88.

syn- and anti-fac-Azido{η^2-[2,2-bis((phenylthio)methyl)-1-(diphenylphosphanyl)propane]-P,S}tricarbonylmanganese(I) (**17s** + **17t**): Due to isomerization, no complex was obtained in pure form, but was identified by its NMR data. – IR ($CHCl_3$): ṽ = 2058 cm^{-1}, 2019, 1959, 1971. – ^1H NMR, complex **17s**: δ = 8.00–7.05 (m, 20H), 3.94 (d, *J* = 12 Hz, 1H), 2.94 (s, 2H), 2.54 (d, *J* = 12 Hz, 1H), 2.26 (d, *J* = 13 Hz, 1H), 2.22 (d, *J* = 13 Hz, 1H), 0.84 (s, 3H) and complex **17t**: δ = 8.00–6.90 (m, 20H), 3.80 (d, *J* = 12 Hz, 1H), 2.90 (d, *J* = 12 Hz, 1H), 2.80 (d, *J* = 12 Hz, 1H), 2.50 (d, *J* = 12 Hz, 1H), 2.45 (d, *J* = 13 Hz, 1H), 2.39 (d, *J* = 13 Hz, 1H), 1.19 (s, 3H). – ^{31}P NMR, complex **17s**: δ = 29.6 and complex **17t**: δ = 28.4. – $C_{32}H_{29}MnN_3O_3PS_2$ (653.6): calcd. C 58.80, H 4.47, N 6.43; found C 59.10, H 4.29, N 6.39.

syn- and anti-fac-(N-thiocyanate){η^2-[2,2-bis(phenylthio)methyl)-1-(diphenylphosphanyl)propane]-P,S}tricarbonylmanganese(I) (**18s** + **18t**): Due to isomerization, no complex was obtained in pure form, but was identified by its NMR data. – IR ($CHCl_3$): ṽ = 2100 cm^{-1}, 2041, 1971, 1931. – ^1H NMR, complex **18s**: δ = 7.88–7.05 (m, 20H), 3.69 (d, *J* = 12 Hz, 1H), 3.09 (s, 2H), 2.89 (dd, *J* = 13, 6 Hz, 1H), 2.74 (d, *J* = 12 Hz, 1H), 2.41 (dd, *J* = 13, 16 Hz, 1H), 0.78 (s, 3H) and complex **18t**: δ = 7.88–6.95 (m, 20H), 3.65 (d, *J* = 12 Hz, 1H), 3.13 (dd, *J* = 13, 6 Hz, 1H), 3.05 (d, *J* = 12 Hz, 1H), 2.80 (d, *J* = 12 Hz, 1H), 2.47 (dd, *J* = 13, 16 Hz, 1H), 2.44 (d, *J* = 12 Hz, 1H), 1.26 (s, 3H). – ^{31}P NMR, complex **18s**: δ = 30.6 and complex **18t**: δ = 29.7. – $C_{33}H_{29}MnNO_3PS_3$ (669.7): calcd. C 59.19, H 4.36, N 2.09; found C 59.50, H 4.50, N 2.10.

Tricarbonyl{fac-[2,2-bis(diphenylphosphanylmethyl)-1-(methylthio)propane]-P,P',S}manganese(I) Tetrafluoroborate (**20**): A solution of **11** (50 mg, 0.078 mmol) in THF (6 ml) was placed into to flask containing trimethyloxonium tetrafluoroborate (12 mg, 0.082 mmol). After stirring at room temperature for 15 min, the reaction mixture was filtered through silica gel and the gel was washed with acetone. The filtrate was concentrated and the residue crystallized from a THF/hexane solution to give **20** as a yellow crystalline solid. Yield 55 mg (99%), m.p. 172–177°C (dec). – IR (CH_2Cl_2): ṽ = 2036 cm^{-1}, 1971, 1951. – ^1H NMR: δ = 7.85–7.65 (m, 20H), 2.68 (s, 2H), 2.58 (dd, *J* = 12, 5 Hz, 2H), 2.38 (dd, *J* = 14, 5 Hz, 2H), 2.33 (s, 3H), 1.53 (s, 3H). – ^{31}P NMR: δ = 31.7. – $C_{33}H_{32}BF_4MnO_3P_2S$ (712.4): calcd. C 55.64, H 4.53; found C 55.99, H 4.33.

syn-fac-Iodo{η^2-[2,2-bis((diphenylphosphanyl)methyl)-1-(methylthio)propane]-P,P'}tricarbonylmanganese(I) (**22s**): A mixture of **20** (50 mg, 0.07 mmol) and sodium iodide (116.5 mg, 0.7 mmol) in acetone (5 ml) was stirred for 1 h. The reaction mixture was concentrated and the residue dissolved in $CHCl_3$. The excess sodium iodide was then removed by filtration. The filtrate was concentrated to give the crude product of **22s**. Recrystallization from chloroform/hexane gave **22s** as orange crystalline needles. Yield 48 mg (69%), m.p. 195–198°C (dec). – IR (CH_2Cl_2): ṽ = 2026 cm^{-1}, 1967, 1906. – ^1H NMR: δ = 7.85–7.64 (m, 20H), 3.56 (d, *J* = 13 Hz, 2H), 2.65 (m, 2H), 2.56 (s, 2H), 2.07 (s, 3H), 0.23 (s, 3H). – ^{31}P NMR: δ = 27.2. – $C_{33}H_{32}IMnO_3P_2S$ (752.5): calcd. C 52.68, H 4.29; found C 52.96, H 4.69.

Kinetic Study: The kinetic runs were monitored by following the decrease in concentration of **7** by means of the methyl shift at δ = 1.60 and the increase in concentration of **8s** by means of the methyl shift at δ = 0.36 with Bruker AC-E 200 spectrometer. The reaction temperature was controlled by the instrument itself and calibrated according to a method described by van Geet[14]. The complex **7** was the limiting reagent and the pseudo-first-order rate constant was obtained from the plot of ln ($[7]_0$-[7]) vs time. The linear regression program was used for the analysis of kinetic data. All runs showed satisfactory linearity for at least 4 half-lives. The observed rate constants are summarized in Table 1.

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