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REACTIONS OF METAL CARBONYL COMPLEXES

VI*. REACTIONS OF $C_5H_5Mn(CO)_3$ AND $C_5H_5Mn(CO)_2(CS)$ WITH SOME POLYDENTATE ORGANOPHOSPHINE LIGANDS

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Summary

The photochemical reactions of the potentially tridentate ligand Triphos, $(Ph_2PCH_2CH_2)_2PPh$, with $C_5H_5Mn(CO)_3$ and $C_5H_5Mn(CO)_2(CS)$ in benzene solution at 0° are described. The products of these reactions are $C_5H_5Mn(CO)$-(Triphos) (two isomers) and $C_5H_5Mn(CS)$(Triphos) (two isomers), respectively. A similar reaction of the bidentate ligand Diphos, $Ph_2PCH_2CH_2PPh_2$, with $C_5H_5Mn(CO)_2(CS)$ in tetrahydrofuran solution at room temperature yields $C_5H_5Mn(CS)$(Diphos). The isomeric Triphos complexes are believed to be diastereomers resulting from the bidentate coordination of two of the adjacent phosphorus atoms on the Triphos ligand. The presence of one uncoordinated phosphorus atom in the complexes was demonstrated by their reactions with $Cr(CO)_5$(THF) (THF = tetrahydrofuran) and $C_5H_5Mn(CO)_3$ to form the bimetallic species, $C_5H_5(CO)Mn(Triphos)Cr(CO)_5$, $C_5H_5(CS)Mn(Triphos)\ Cr(CO)_5$, $C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$ and $C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$ by displacement of THF or CO. In addition, $C_5H_5Mn(CS)$(Triphos) reacts with ozone to give the phosphine oxide complex, $C_5H_5Mn(CS)$(Triphos=O). The absence of CS substitution in $C_5H_5Mn(CO)_2(CS)$ by Diphos and Triphos is yet another indication of the stronger metal—carbon bonding in metal thiocarbonyls as compared to metal carbonyls. The IR spectra of the new complexes in the ν(CO) and ν(CS) regions are reported. From a comparison of the low-frequency IR spectra of $C_5H_5Mn(CS)$(Diphos) and $C_5H_5Mn(CS)$(Triphos) with those of their carbonyl analogues, the δ(Mn—C—S) modes have been assigned to the 555—530 cm^{-1} region.

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Introduction

Recently, a great deal of interest has been generated in the use of complexes of chiral phosphines as catalysts for asymmetric synthesis. For example, certain rhodium complexes have proved to be remarkably effective as catalysts for asymmetric homogeneous hydrogenation [2], while asymmetric hydrosilations have been achieved using palladium complexes as catalysts [3]. Our own interest in chiral phosphines came about following the discovery that bidentate coordination of the linear polyphosphines bis[2-(phenylphosphino)ethyl] phenylphosphine, $(Ph_2PCH_2CH_2)_2PPh$ (Triphos), and hexaphenyl-1,4,7,10-tetraphosphadecane, $[Ph_2PCH_2CH_2P(Ph)CH_2]_2$ (Tetraphos), in *fac*-$Mn(CO)_3$(Triphos)X and *fac*-$Mn(CO)_3$(Tetraphos)X (X = halogen) results in the formation of diastereomers owing to the presence of chiral phosphorus atoms [1, 4, 5]. A three-dimensional X-ray study on the two diastereomers of $Br(CO)_3Mn$(Triphos)$Cr(CO)_5$ formed by reaction of *fac*-$Mn(CO)_3$(Triphos)Br with $Cr(CO)_5$(THF) (THF = tetrahydrofuran) showed that the diastereomers differ solely in the orientation of the phenyl group on the centrally coordinated phosphorus atom with respect to the bromine atom [5].

We have now embarked upon the synthesis of a variety of complexes containing chiral phosphines and ultimately plan to test the catalytic potential of these complexes for asymmetric synthesis. We report here the results of a study on the reactions of $C_5H_5Mn(CO)_3$ and $C_5H_5Mn(CO)_2(CS)$ with Triphos. In addition to hoping that some of the complexes produced would exhibit diastereoisomerism, we were interested in comparing the behaviour of these two complexes with respect to substitution by polydentate phosphines. A previous study on the reactions of $C_5H_5Mn(CO)_2(CS)$ with a series of Group VA monodentate ligands, L, has shown that while one or two CO groups can be replaced by L, the CS does not appear to undergo substitution [6]. These results are in accord with the stronger metal—carbon bonding now expected for metal thiocarbonyls as compared to metal carbonyls on the basis of molecular orbital calculations [7] and many recent experimental observations [8, 9]. As yet, there are no reports of a CS group in a metal thiocarbonyl complex undergoing substitution and so we felt that by using the tridentate Triphos ligand, it might be possible to replace the CS as well as the two CO groups in $C_5H_5Mn(CO)_2(CS)$. In the case of $C_5H_5Mn(CO)_3$, despite extensive studies on the reactions of this complex with polydentate phosphine ligands [10—18], the reaction with Triphos had not been investigated prior to this work. Finally, to aid with the structural assignments of the Triphos complexes produced, we found it necessary to synthesize $C_5H_5Mn(CO)$(Diphos) and $C_5H_5Mn(CS)$(Diphos), and these results are also reported here.

Experimental

The tricarbonyl complex $C_5H_5Mn(CO)_3$ was a generous gift from Ethyl Corporation, New York. Diphos and Triphos were obtained from Strem Chemicals Inc., Danvers, Mass. The other starting materials, $C_5H_5Mn(CO)_2(CS)$ [19], $C_5H_5Mn(CO)$(Diphos) [10] and $Cr(CO)_5$(THF) [20] were prepared by the published methods indicated.

All reactions were performed routinely under a nitrogen atmosphere and products were purified by preparative thin layer chromatography (TLC) using silica gel plates. The UV irradiations were carried out at ice-water temperature using a 100 W Hanovia high pressure mercury lamp. The low-frequency IR spectra were recorded on a Perkin—Elmer 521 spectrometer. All other IR spectra were obtained with a Perkin—Elmer 337 spectrometer coupled to a Texas Instruments Servo/Riter II expanded scale recorder. The spectra were calibrated against the 2143.2 cm^{-1} band of CO and the 1601.4 and 1583.1 cm^{-1} bands of polystyrene; the precision of the frequencies is ± 1—2 cm^{-1}.

Except where otherwise mentioned, the yields of the new complexes were quite low (5—10%) owing to decomposition on the preparative TLC plates. Analytical and IR data for the complexes are given in Tables 1—3.

*Preparation of $C_5H_5Mn(CS)(Diphos)$**

$C_5H_5Mn(CO)_2(CS)$ (1 mmol) and Diphos (1.1 mmol) were dissolved in freshly distilled THF (100 ml) and the solution was irradiated until no further reaction occurred (≈ 12 h). The solvent was removed under reduced pressure and then the product was purified by elution of the crude material on TLC plates with a 3/2 benzene/n-hexane solution. The required product was crystallized from a CH_2Cl_2/n-hexane mixture and was dried in vacuo (25°/0.01 mm) for 24 h (yield 60%).

Reaction of $C_5H_5Mn(CO)_3$ with Triphos

A freshly distilled benzene solution (150 ml) containing $C_5H_5Mn(CO)_3$ (1.5 mmol) and Triphos (1.5 mmol) was irradiated for ≈ 6 h. The solvent volume was then reduced to ≈ 5 ml on a water aspirator and the crude product was precipitated by addition of n-hexane (25 ml). This material was eluted on TLC plates with a 1/1 acetone/n-hexane mixture. Two products were isolated. The product with the larger R_f value consisted of two compounds, γ-$C_5H_5Mn(CO)$(Triphos) and ϕ-$C_5H_5Mn(CO)$(Triphos), which could be separated on TLC plates following elution with a 1/5 benzene/n-hexane mixture. From its IR spectrum the other product was most probably $C_5H_5Mn(CO)$(Triphos=O). The three complexes were crystallized from CH_2Cl_2/n-hexane mixtures and were dried in vacuo (25°/0.01 mm) for 24 h.

Reaction of $C_5H_5Mn(CO)_2(CS)$ with Triphos

A mixture of $C_5H_5Mn(CO)_2(CS)$ (1.5 mmol) and Triphos (1.5 mmol) in freshly distilled benzene (150 ml) was irradiated for ≈ 5 h. The solvent volume was then reduced to ≈ 5 ml on a water aspirator and the crude product was precipitated by addition of n-hexane (25 ml). Elution of this material on TLC plates with a 2/1 benzene/n-hexane solution afforded three complexes. In order of decreasing R_f value these were γ-$C_5H_5Mn(CS)$(Triphos), ϕ-$C_5H_5Mn(CS)$(Triphos) and $C_5H_5Mn(CS)$(Triphos=O). The complexes were crystallized from CH_2Cl_2/n-hexane mixtures and were dried in vacuo (25°/0.01 mm) for 24 h.

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* This product has been prepared previously from the reaction of $C_5H_5Mn(CO)(CS)(C_8H_{14})$ and Diphos but only in 5% yield [21].

Reaction of $C_5H_5Mn(CO)(Triphos)$ with $C_5H_5Mn(CO)_3$

$C_5H_5Mn(CO)_3$ (1 mmol) and Triphos (1 mmol) were dissolved in freshly distilled benzene (150 ml) and the solution was irradiated for 8 h. After a further addition of $C_5H_5Mn(CO)_3$ (1.5 mmol), the irradiation was continued for an additional 12 h. The solvent was then removed under reduced pressure and the crude material was eluted on TLC plates with 1/1 acetone/n-hexane mixtures. Tw isomers of $C_5H_5(CO)Mn(Triphos)Mn(CO)_2(C_5H_5)$ were isolated. These two complexes were crystallized from CH_2Cl_2/n-hexane and were dried in vacuo (25°/0.01 mm) for 24 h.

Reaction of $C_5H_5Mn(CS)(Triphos)$ with $C_5H_5Mn(CO)_3$

$C_5H_5Mn(CO)_2(CS)$ (0.5 mmol) and Triphos (0.5 mmol) were dissolved in freshly distilled benzene (150 ml) and the solution was irradiated for 3 h. $C_5H_5Mn(CO)_3$ (1.0 mmol) was then added and the solution was irradiated for a further 10 h. Following solvent removal under reduced pressure, the crude material was eluted on TLC plates with a 5/7 acetone/n-hexane mixture. One major fraction was separated. Subsequent elution of this fraction with a 2/1 benzene/n-hexane mixture afforded two products analyzing as $C_5H_5(CS)Mn(Triphos)Mn(CO)_2(C_5H_5)$. The two new products were crystallized from CH_2Cl_2/n-hexane mixtures and were then dried in vacuo (25°/0.01 mm) for 24 h.

Reaction of $C_5H_5Mn(CO)(Triphos)$ with $Cr(CO)_5(THF)$

$C_5H_5Mn(CO)(Triphos)$ (0.2 mmol) was added to a THF solution (100 ml) of freshly prepared $Cr(CO)_5(THF)$ [from $Cr(CO)_6$ (1 mmol)] and the solution was stirred at room temperature for 20 h. The solvent was evaporated off under reduced pressure and the excess $Cr(CO)_6$ was removed by vacuum sublimation (60°/0.01 mm). The crude product was then eluted on TLC plates with a 3/5 acetone/n-hexane mixture, one major fraction being isolated. Elution of this product on TLC plates with a 1/1 benzene/n-hexane mixture afforded two isomers of $C_5H_5(CO)Mn(Triphos)Cr(CO)_5$. These two isomers were crystallized from CH_2Cl_2/n-hexane solution and were dried in vacuo (25°/0.01 mm) for 24 h.

Reaction of $C_5H_5Mn(CS)(Triphos)$ with $Cr(CO)_5(THF)$

$C_5H_5Mn(CS)(Triphos)$ (0.2 mmol) was added to a THF solution (100 ml) of $Cr(CO)_5(THF)$ [freshly prepared from $Cr(CO)_6$ (1 mmol)] and the solution was stirred at room temperature for 12 h. Following solvent removal under reduced pressure, the excess $Cr(CO)_6$ was sublimed off (60°/0.01 mm). The crude product remaining was eluted on TLC plates with a 3/5 benzene/n-hexane solution. Two products analyzing as $C_5H_5(CS)Mn(Triphos)Cr(CO)_5$ were isolated from the plates. These were crystallized from CH_2Cl_2/n-hexane and were dried in vacuo (25°/0.01 mm) for 24 h.

Preparation of $C_5H_5Mn(CS)(Triphos{=}O)$

The isomeric mixture of $C_5H_5Mn(CS)(Triphos)$ (0.1 mmol) was dissolved in CH_2Cl_2 (20 ml) and ozone (0.12 mmol) was bubbled through the solution*.

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* The ozone was produced in a Welsbach ozone generator at a rate of 7 mmol/h and so this reaction was continued for about 10 min in order to achieve complete oxidation of the uncoordinated phosphorus atom. The ozone was introduced into the reaction mixture in a stream of O_2 gas.

Solvent was then removed under reduced pressure and the crude material was eluted on TLC plates with a 1/1 acetone/n-hexane solution. One major component, $C_5H_5Mn(CS)(Triphos{=}O)$, was obtained which was crystallized from a CH_2Cl_2/n-hexane mixture and dried in vacuo (25°/0.01 mm) for 24 h.

Results and discussion

Ultraviolet irradiation of a benzene solution of $C_5H_5Mn(CO)_3$ and Triphos afforded three products which could be separated by preparative thin layer chromatography but with extensive decomposition. All three products exhibited one strong $\nu(CO)$ absorption in the IR at $\approx$ 1850 cm^{-1}, similar to that for $C_5H_5Mn(CO)(Diphos)$ and related bidentately coordinated polyphosphine complexes of the type, $C_5H_5Mn(CO)(Polyphosphine)$ [10—18]. Elemental analyses of the two products with the larger R_f values are consistent with their being isomers of $C_5H_5Mn(CO)(Triphos)$. These results imply that the Triphos ligand is bonded to the manganese atom in these complexes through only two of its three phosphorus atoms. By analogy with our previous study on the reaction of $Mn(CO)_5Br$ with Triphos [4, 5], such a situation is thought to occur through adjacent phosphorus atoms. Two diastereomers of $C_5H_5Mn(CO)(Triphos)$ would then result because of the chirality of the central phosphorus atom of the Triphos ligand. These diastereomers differ in the orientation of the R and Ph groups on the central phosphorus atom with respect to the π-cyclopentadienyl ring (Fig. 1)[*].

The third product isolated from the reaction mixture (the one with the smallest R_f value) is thought to be phosphine oxide complex, $C_5H_5Mn(CO)(Triphos{=}O)$, formed by air-oxidation of the uncoordinated phosphorus atom. However, because of the small quantity isolated, only IR data were recorded for this complex.

The reaction of $C_5H_5Mn(CO)_2(CS)$ with Triphos also yielded three products. Elemental analyses and IR data [one strong band in the $\nu(CS)$ stretching region] for the two complexes with the larger R_f values suggested that these were the two diastereomers γ- and ϕ-$C_5H_5Mn(CS)(Triphos)$. The third product isolated from the reaction mixture (smallest R_f value) was not obtained pure. However, comparison of IR [$\nu(CS)$ = 1203 cm^{-1}] and thin layer chromatography data with those for an authentic sample (vide infra) suggested that this complex should be formulated as $C_5H_5Mn(CS)(Triphos{=}O)$.

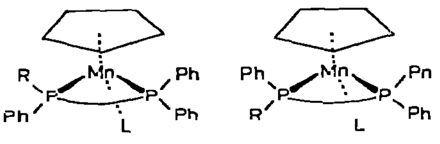

Fig. 1. Two diastereomers of $C_5H_5Mn(L)(Triphos)$ (L = CO, CS; R = $CH_2CH_2PPh_2$).

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[*] The diastereomer with the larger R_f value is designated as the γ-isomer, while the other is referred to as the ϕ-isomer.

TABLE 1

ANALYTICAL DATA FOR THE NEW CYCLOPENTADIENYLMANGANESE(I) COMPLEXES

Complex [a]	Decomp. (°C)	Analysis found (calcd.) (%)		
		C	H	P
$C_5H_5Mn(CS)(Diphos)$ [b]	≈140	67.9 (68.3)	5.6 (5.2)	14.6 (15.0)
γ-$C_5H_5Mn(CO)(Triphos)$	≈ 55	69.9 (70.4)	6.1 (5.6)	
ρ-$C_5H_5Mn(CO)(Triphos)$ [b]	≈ 55	70.0 (70.4)	6.0 (5.6)	
γ-$C_5H_5Mn(CS)(Triphos)$ [b]	≈ 75	68.3 (68.8)	6.0 (5.5)	13.6 (13.3)
ρ-$C_5H_5Mn(CS)(Triphos)$	73– 77	68.6 (68.8)	6.0 (5.5)	13.1 (13.3)
γ-$C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$	81– 84	65.4 (65.7)	5.2 (5.0)	
ρ-$C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$	93– 96	66.1 (65.7)	5.4 (5.0)	
γ-$C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$	97–100	65.0 (64.5)	5.3 (5.0)	
ρ-$C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$	97–100	64.9 (64.5)	5.5 (5.0)	
γ-$C_5H_5(CO)Mn(Triphos)Cr(CO)_5$	54– 56	61.5 (61.8)	4.6 (4.4)	10.3 (10.6)
ρ-$C_5H_5(CO)Mn(Triphos)Cr(CO)_5$	54– 56	61.4 (61.8)	4.7 (4.4)	
γ-$C_5H_5(CS)Mn(Triphos)Cr(CO)_5$	83– 86	60.2 (60.7)	4.5 (4.3)	10.4 (10.4)
ρ-$C_5H_5(CS)Mn(Triphos)Cr(CO)_5$	83– 86	60.9 (60.7)	4.8 (4.3)	10.2 (10.4)
$C_5H_5Mn(CS)(Triphos{=}O)$	108–113	66.9 (67.2)	5.8 (5.4)	13.4 (13.0)

[a] The complexes are yellow unless otherwise stated. [b] Orange complex.

The $C_5H_5Mn(CO)(Triphos)$ and $C_5H_5Mn(CS)(Triphos)$ complexes should contain "dangling" phosphorus atoms. Reactions with $Cr(CO)_5(THF)$ and $C_5H_5Mn(CO)_3$ were undertaken to show the presence of the uncoordinated phosphorus atoms. Bimetallic complexes were obtained in every case (see Table 1). Thus, reaction of $C_5H_5Mn(CS)(Triphos)$ with $Cr(CO)_5(THF)$ yielded two isomers of $C_5H_5(CS)Mn(Triphos)Cr(CO)_5$. These isomers most probably correspond to the γ- and ρ-$C_5H_5Mn(CS)(Triphos)$ isomers in which the "dangling" phosphorus atoms are now coordinated to the $Cr(CO)_5$ moiety.

Reaction of $C_5H_5Mn(CS)(Triphos)$ with ozone afforded $C_5H_5Mn(CS)(Triphos{=}O)$. A similar reaction with the carbonyl analogue resulted in decomposition. Since the P=O and CS stretching regions overlap, the characteristic band at 1131 cm^{-1} provided the necessary IR spectral evidence indicative of the P=O group [22] in $C_5H_5Mn(CS)(Triphos{=}O)$.

Previous studies [10–18] on the reactions of $C_5H_5Mn(CO)_3$ with various polyphosphine ligands have shown that compounds of the type C_5H_5-$Mn(CO)(Polyphosphine)$ and $[C_5H_5Mn(CO)_2]_2(Polyphosphine)$, in which the polyphosphines are bidentately coordinated, are produced. However, under the reaction conditions of the present work, no polyphosphine-bridged species were isolated. From the changes in the IR spectra (CO stretching region) recorded during the reactions, it was apparent that other intermediate complexes

TABLE 2

IR SPECTRA (cm^{-1}) IN THE CO AND/OR CS STRETCHING REGION FOR THE CYCLOPENTADIENYLMANGANESE(I) COMPLEXES (CS_2 SOLUTION)

Complex	ν(CO) [a]			ν(CS) [a]
$C_5H_5Mn(CO)(Diphos)$ [b]		1845		
$C_5H_5Mn(CS)(Diphos)$ [c]				1206
γ-$C_5H_5Mn(CO)(Triphos)$ [d]		1839		
ϕ-$C_5H_5Mn(CO)(Triphos)$ [d]		1841		
γ-$C_5H_5Mn(CS)(Triphos)$ [e]				1203
ϕ-$C_5H_5Mn(CS)(Triphos)$ [e]				1206
γ-$C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$	1929	1865	1834 m	
ϕ-$C_5H_5(CO)Mn(Triphos)Mn(CO)_2C_5H_5$	1929	1864	1845 sh	
γ-$C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$	1930	1865		1204 m
ϕ-$C_5H_5(CS)Mn(Triphos)Mn(CO)_2C_5H_5$	1931	1867		1208 (sh)
γ-$C_5H_5(CO)Mn(Triphos)Cr(CO)_5$	2061 m	1980 w 1933	1942 (sh) 1838	
ϕ-$C_5H_5(CO)Mn(Triphos)Cr(CO)_5$	2061 m	1979 w 1933	1942 (sh) 1845	
γ-$C_5H_5(CS)Mn(Triphos)Cr(CO)_5$	2061 m	1979 w 1932	1943 (sh)	1205 m
ϕ-$C_5H_5(CS)Mn(Triphos)Cr(CO)_5$	2061 m	1981 w 1933	1943 (sh)	1209 m
$C_5H_5Mn(CO)(Triphos{=}O)$		1839		
$C_5H_5Mn(CS)(Triphos{=}O)$ [f]				1203

[a] All the bands are strong unless otherwise stated. [b] ν(CO) 1837 cm^{-1} (CS_2 solution) [10]. ^{1}H NMR (Varian T-60 spectrometer, relative to TMS τ 10.00, CS_2 solution): τ 6.00 (triplet, separation of outer peaks 1.5 Hz), C_5H_5. [c] ν(CS) 1208 cm^{-1} (CS_2 solution) [19]. ^{1}H NMR (CS_2 solution): τ 5.85 (triplet, separation of outer peaks 1.5 Hz), C_5H_5. [d] ^{1}H NMR (CS_2 solution): τ 5.90 (complex), C_5H_5. [e] ^{1}H NMR (CS_2 solution): τ 5.86 (complex), C_5H_5. [f] Characteristic band of P=O group (q "X-sensitive" mode [22]) at 1131 cm^{-1} in Nujol mull spectrum.

such as $C_5H_5Mn(CO)_2(Triphos)$ were being produced but the reactions were always continued to completion and no attempt was made to isolate these intermediate complexes.

There was no evidence for CS replacement in $C_5H_5Mn(CO)_2(CS)$ by Triphos under the photochemical conditions employed, whereas the two CO groups were readily displaced. This is yet another indication of the stronger metal—carbon bonding in metal thiocarbonyls compared to that in metal carbonyls. The original theoretical predictions of Richards [7] that CS should be a better σ-donor and π-acceptor than is CO have now been borne out by a number of different studies [8, 9]. The fact that there are no known examples of C_5H_5Mn(Polyphosphine) suggests that steric factors preclude the coordination of three phosphorus atoms to manganese in such complexes.

Considerable effort has been directed in the past towards the assignment of the δ(M—C—O) and ν(M—C) modes in the low-frequency IR spectra of metal carbonyls [23, 24]. Since there are now over fifty metal thiocarbonyls known, it is expected that similar efforts will be directed toward the assignment of the δ(M—C—S) and ν(M—CS) modes in these complexes. Consequently, we felt that it would be of interest to study the low-frequency IR spectra of the two $C_5H_5Mn(CS)(Triphos)$ diastereomers and $C_5H_5Mn(CS)(Diphos)$ to see if we could make any such assignments. The low-frequency IR spectra (750—400 cm^{-1}) of these three thiocarbonyl complexes are compared with those of the analogous carbonyl complexes in Table 3. From our previous work on $C_5H_5Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)(CS)_2$ [25], it was anticipated that the δ(Mn—C—S) modes

TABLE 3

COMPARISON OF IR-ACTIVE δ(Mn—C—O) AND δ(Mn—C—S) MODES FOR THE RELATED DIPHOS AND TRIPHOS COMPLEXES [a]

Complex			
	δ(Mn—C—O)		
$C_5H_5Mn(CO)(Diphos)$ [b]	616 m	594 s	586 m
γ-$C_5H_5Mn(CO)(Triphos)$	620 m	592 s	
ϕ-$C_5H_5Mn(CO)(Triphos)$	622 m	595 s	
	δ(Mn—C—S)		
$C_5H_5Mn(CS)(Diphos)$	555 m	543 s	
γ-$C_5H_5Mn(CS)(Triphos)$	552 m	532 s	
ϕ-$C_5H_5Mn(CS)(Triphos)$	550 m	530 s	

[a] Nujol mulls. [b] δ(Mn—C—O) 616 ms, 594 vs, 586 vs [24].

would occur in a similar region to the δ(Mn—C—O) modes in the corresponding metal carbonyls, while the ν(Mn—CS) modes would lie below 400 cm^{-1}, i.e., out of the range of the present investigation. Therefore, unlike in the case of C_5H_5-$Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)(CS)_2$ where the assignment of the δ(Mn—C—S) modes is difficult because of confusion with the δ(Mn—C—O) modes, it is possible to make unambiguous assignments for the δ(Mn—C—S) modes in the three polyphosphine thiocarbonyls because there are no δ(Mn—C—O) modes possible for these complexes and also there are no interfering ligand vibrations.

As would be expected on the basis of the mass difference between S and O, the δ(Mn—C—S) modes in the polyphosphine thiocarbonyls appear ≈ 60 cm^{-1} lower than the δ(Mn—C—O) modes in the analogous carbonyl complexes (see Table 3). The observed range for the δ(Mn—C—S) modes (555—530 cm^{-1}) supports the tentative assignments made previously [25] for the δ(Mn—C—S) modes in $C_5H_5Mn(CO)_2(CS)$ and $C_5H_5Mn(CO)(CS)_2$.

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