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REACTIONS OF METAL CARBONYL COMPLEXES

V*. REACTIONS OF $Mn(CO)_5X$ (X = Br, I) WITH HEXAPHENYL-1,4,7,10-TETRAPHOSPHADECANE

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Summary

The reactions of the potentially tetradentate ligand Tetraphos, $[Ph_2PCH_2CH_2P(Ph)CH_2]_2$, with $Mn(CO)_5X$ (X = Br, I) are described. The main products of these reactions are *fac*-$Mn(CO)_3$(Tetraphos)Br (two isomers), *cis*-$Mn(CO)_2$(Tetraphos)X and $[Mn(CO)_3Br]_2$(Tetraphos). These products were characterized by elemental analyses, molecular weight determinations, IR spectra and chemical reactions. The possibility that the two isomers of *fac*-$Mn(CO)_3$(Tetraphos)Br contain the *meso* form of the Tetraphos ligand is discussed.

Introduction

In previous papers [2,3], we have reported on the reactions of $Mn(CO)_5X$ (X = Cl, Br, I) with the linear triphosphine ligand bis(2-diphenylphosphinoethyl)-phenylphosphine (Triphos), to form *fac*-$Mn(CO)_3$(Triphos)X (two isomers) and *cis*-$Mn(CO)_2$(Triphos)X. Recently, we have become interested in the coordination properties of tetraphosphine ligands. Only four such ligands are currently known: $P(C_6H_4\text{-}o\text{-}PPh_2)_3$ [4], $P(CH_2CH_2PPh_2)_3$ [5], $(Ph_2PCH_2)_4C$ [6] and $[Ph_2PCH_2CH_2P(Ph)CH_2]_2$ (Tetraphos) [5] and little work has been reported on the reactions of these ligands with metal carbonyls [4,7 - 12].

In the present paper, we describe the reactions of $Mn(CO)_5X$ (X = Br, I) with Tetraphos to form complexes in which the polyphosphine acts as a monometallic-bidentate, monometallic-tridentate, bimetallic-tridentate and bimetallic-

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TABLE 1

ANALYTICAL DATA FOR THE NEW TETRAPHOS COMPLEXES

Complex	Empirical formula	Colour	Yield(%)	Decomp. (°C)	Analysis found (calcd.) (%)			
					C	H	P	Br
αα-*fac*-Mn(CO)$_3$(Tetraphos)Br	$C_{45}H_{42}O_3BrMnP_4$	yellow	10	~ 63	59.4 (60.8)	4.4 (4.8)	11.9 (13.9)	
ββ-*fac*-Mn(CO)$_3$(Tetraphos)Br	$C_{45}H_{42}O_3BrMnP_4$	yellow	20	~ 66	60.5 (60.8)	5.0 (4.8)	13.4 (13.9)	
[Mn(CO)$_3$Br]$_2$(Tetraphos) [a]	$C_{48}H_{42}O_6Br_2Mn_2P_4$	yellow	45	~165	52.5 (52.0)	4.0 (3.8)	11.2 (11.2)	14.5 (14.4)
[Br(CO)$_3$Mn(Tetraphos)]$_2$Mo(CO)$_4$ · CHCl$_3$ [b]	$C_{95}H_{85}O_{10}Br_2Cl_3Mn_2MoP_8$	yellow	70	~135	53.9 (54.2)	4.2 (4.0)	11.4 (11.8)	
cis-Mn(CO)$_2$(Tetraphos)Br	$C_{44}H_{42}O_2BrMnP_4$	bright-yellow	40	~115	61.4 (61.3)	5.0 (4.9)	13.6 (14.4)	8.2 (9.7)
cis-Mn(CO)$_2$(Tetraphos)I [c]	$C_{44}H_{42}O_2IMnP_4$	bright-yellow	40	98-102	59.4 (58.2)	5.1 (4.7)		
cis-Mn(CO)$_2$(Tetraphos=O)Br	$C_{44}H_{42}O_3BrMnP_4$	yellow	60	~130	60.6 (60.2)	5.3 (4.8)	14.5 (14.1)	8.2 (9.1)
cis-Mn(CO)$_2$(Tetraphos=O)I [c]	$C_{44}H_{42}O_3IMnP_4$	yellow	60	~115	57.8 (57.2)	4.9 (4.6)		
Br(CO)$_2$Mn(Tetraphos)Mn(C$_5$H$_5$)(CO)$_2$	$C_{51}H_{47}O_4BrMnP_4$	orange	50	~ 93	60.3 (59.0)	5.2 (4.6)	11.6 (11.9)	

[a] Mol. wt.: Found (calcd.) 1307 (1108) in CHCl$_3$. [b] Mol. wt.: Found (calcd.) 1620 (1987) in CHCl$_3$. [c] The C and H analyses for these complexes were performed in this laboratory on a Hewlett—Packard Model 185 CHN analyser.

tetradentate ligand. Prior to this study, Tetraphos had not been observed to act in the latter fashion.

In addition, our previous success in separating the two diastereomers of *fac*-$Mn(CO)_3$(Triphos)X (X = Cl, Br, I) [2,3] and the recent resolution of the diastereomers of an analogous tetraarsine ligand, $Me_2As(CH_2)_3As(Ph)CH_2CH_2As(Ph)(CH_2)_3AsMe_2$ [13], by reaction with a cobalt salt, led us to hope that the diastereomers of Tetraphos could be similarly separated. However, we have since learned that this would be impossible because commercially available Tetraphos is in fact either the pure *dl* or *meso* diastereomer but it is not known which [14]. We believe that our study enables us to identify the commercial Tetraphos as the *meso* form and this aspect of the work is also described here.

Experimental

The tetraphosphine ligand, hexaphenyl-1,4,7,10-tetraphosphadecane (Tetraphos), was used as purchased without further purification (Strem Chemicals). (*nor*-C_7H_8)$Mo(CO)_4$ [15], $Mn(CO)_5X$ (X = Br, I) [16] and $C_5H_5Mn(CO)_2C_8H_{14}$ [17] were prepared by the literature methods indicated.

All reactions were carried out under an atmosphere of nitrogen. The IR spectra were recorded as described previously [18].

Analytical and IR data for the new complexes are given in Tables 1 and 2, respectively.

Reaction of $Mn(CO)_5Br$ and Tetraphos

A chloroform solution (20 ml) containing $Mn(CO)_5Br$ (0.3 mmol) and Tetraphos (0.33 mmol) was refluxed with stirring, until the IR spectrum (CO stretching region) showed no further changes (~ 30 min). The solvent was removed under reduced pressure and the crude product was eluted with benzene on silica gel preparative TLC plates. Three major products were isolated. The first two of these were the α,α isomer (largest R_f value) and β,β isomer of *fac*-$Mn(CO)_3$(Tetraphos)Br. The third product, with the smallest R_f value, was the bimetallic complex $[Mn(CO)_3Br]_2$(Tetraphos). [This bimetallic complex could be prepared in higher yield (68%) with little monometallic product formation, if the above reaction was repeated using a 2/1 $Mn(CO)_5Br$/Tetraphos ratio.] The products were crystallized from chloroform/n-hexane mixtures.

cis-$Mn(CO)_2$(Tetraphos)X (X = Br, I)

A xylene solution (40 ml) containing $Mn(CO)_5X$ (1 mmol) and Tetraphos (1 mmol) was stirred at 60° for 1 h and then at 130° until the IR spectrum [ν(CO)] remained constant (~ 10 h). Solvent was removed under reduced pressure and the crude product was eluted on a silica gel preparative TLC plate with a 1/1 acetone/n-hexane mixture. The product was crystallized from a chloroform/n-hexane mixture.

cis-$Mn(CO)_2$(Tetraphos=O)X (X = Br, I)

cis-$Mn(CO)_2$(Tetraphos)X (0.1 mmol) was dissolved in dichloromethane (20

TABLE 2

IR SPECTRA IN THE C—O STRETCHING REGION OF THE NEW TETRAPHOS COMPLEXES (CH_2Cl_2 SOLUTION)

Complex	$\nu(CO)$ [a] (cm^{-1})		
αα-*fac*-$Mn(CO)_3$(Tetraphos)Br	2021	1953	1915
ββ-*fac*-$Mn(CO)_3$(Tetraphos)Br	2021	1954	1913
$[Mn(CO)_3Br]_2$(Tetraphos)	2024	1954	1913
$[Br(CO)_3Mn(Tetraphos)]_2Mo(CO)_4$	2023	1953 m	1908 (br) 1881 (sh)
cis-$Mn(CO)_2$(Tetraphos)Br [b]		1932	1864
cis-$Mn(CO)_2$(Tetraphos)I		1935	1868
cis-$Mn(CO)_2$(Tetraphos=O)Br [c]		1932	1864
cis-$Mn(CO)_2$(Tetraphos=O)I [d]		1935	1869
$Br(CO)_2Mn(Tetraphos)Mn(C_5H_5)(CO)_2$ [e]		1930	1860
αα-$Br(CO)_3Mn(Tetraphos)Mn(CO)_4Br$ [f]	2092 m 1958	2024 1917	2009 (sh)
ββ-$Br(CO)_3Mn(Tetraphos)Mn(CO)_4Br$ [f]	2091 m 1958	2024 1918	2009 (sh)

[a] All bands strong unless otherwise stated: m = medium, (br) = broad, vs = very strong, (sh) = shoulder. [b] Ref. 7: $\nu(CO)$ = 1933, 1862 in CH_2Cl_2. [c] $\nu(P{=}O)$ 1168 s(br). Characteristic "X-sensitive modes" [22] at 1120(q), 720(x) and 530(y) cm^{-1}. [d] $\nu(P{=}O)$ 1175 s(br). Characteristic "X-sensitive modes" [22] at 1120(q), 728(x) and 538(y) cm^{-1}. [e] IR recorded in CS_2 showed no band splitting, $\nu(CO)$ 1931, 1863. The IR $\nu(CO)$ of $C_5H_5Mn(CO)_2(PPh_3)$: 1931, 1860 cm^{-1} in CH_2Cl_2. [f] IR recorded in $CHCl_3$.

ml) and ozone (0.13 mmol) was bubbled through the resultant solution. The solvent was then removed under reduced pressure and the crude product was eluted on silica gel preparative TLC plates with a 2/1 acetone/n-hexane mixture. Crystallization from dichloromethane/n-hexane gave the required product.

$[Br(CO)_3Mn(Tetraphos)]_2Mo(CO)_4 \cdot CHCl_3$

A xylene solution (15 ml) containing (*nor*-C_7H_8)$Mo(CO)_4$ (0.12 mmol) and *fac*-$Mn(CO)_3$(Tetraphos)Br (0.1 mmol) (mixture of α,α and β,β isomers) was stirred for 6 h at 60°. After the solvent had been removed under reduced pressure, the product was crystallized from a chloroform/n-hexane mixture to give the required complex in high yield. Only one isomer was detected on a silica gel TLC plate.

$Br(CO)_2Mn(Tetraphos)Mn(C_5H_5)(CO)_2$

A chloroform solution (20 ml) containing $C_5H_5Mn(CO)_2C_8H_{14}$ (0.13 mmol) and *cis*-$Mn(CO)_2$(Tetraphos)Br (0.1 mmol) was refluxed for 24 h. Solvent was then removed under reduced pressure and the resulting mixture was eluted on a silica gel TLC plate using a 1/1 acetone/n-hexane mixture. The desired product was obtained in high yield and was crystallized from a chloroform/n-hexane mixture.

Results and discussion

Changes in the IR spectrum [$\nu(CO)$ region] were readily detected when $Mn(CO)_5Br$ and Tetraphos were refluxed together in chloroform. After 0.5 h, the spectrum remained constant. Thin layer chromatography revealed that the reaction mixture contained at least three new products.

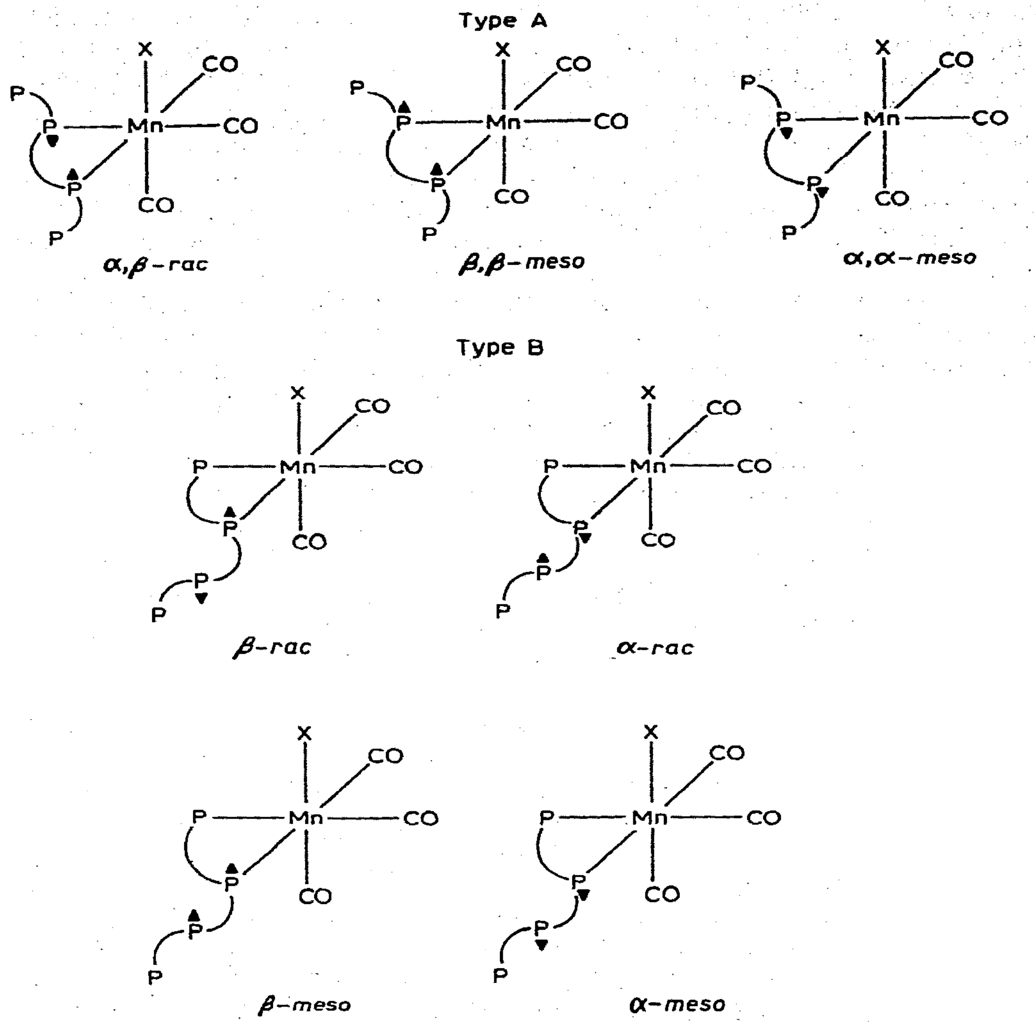

Fig. 1. Diastereomers of *fac*-Mn(CO)$_3$(Tetraphos)X (X = Br). All methylene and phenyl groups have been omitted for the sake of clarity. ▲ represents the orientation of a phenyl ring pointing in the same direction as the halogen (β-isomer); ▼ in the opposite direction. Note that *αβ-rac* and *βα-rac* are enantiomers.

The three major products were separated by preparative thin layer chromatography. Elemental analyses, the presence of three strong CO absorptions in the IR and chemical reactions (see later) showed that the two complexes with the larger R_f values are of the type *fac*-Mn(CO)$_3$(Tetraphos)Br[*]. The third product with the smallest R_f value was the bimetallic complex [Mn(CO)$_3$Br]$_2$-(Tetraphos).

Seven diastereomers, in which adjacent P atoms bond to the metal, are possible for *fac*-Mn(CO)$_3$(Tetraphos)Br. The likelihood of isomer formation in

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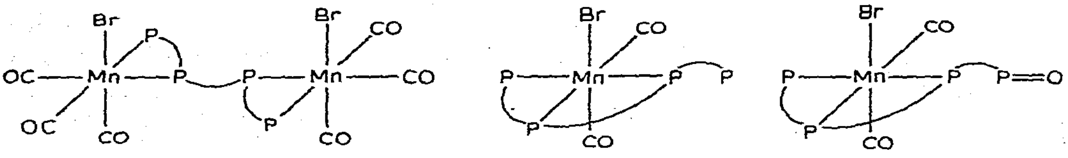
[*] The complex with the largest R_f value will be called the α,α-isomer to distinguish it from the other isomer, to be called the β,β-isomer. The reason for this nomenclature will become clear as the text proceeds.



(I) (II) (III)

Fig. 2. Possible structures for some of the Tetraphos complexes isolated in this study. All methylene and phenyl groups have been omitted for the sake of clarity.

which the polyphosphine bonds to the manganese through non-adjacent P atoms seems doubtful, particularly in light of the crystal structures reported previously [3] for the two Triphos diastereomers α- and β-$Br(CO)_3Mn(Triphos)Cr(CO)_5$. The seven Tetraphos diastereomers are shown schematically in Fig. 1. In this figure, the diastereomers are designated according to both the orientation of the phenyl rings on the coordinated P atoms and the optically active form of the ligand*. In all seven of these isomers there are two uncoordinated P atoms which should be able to undergo typical "tertiary phosphine type" reactions.

Reaction of the isomeric mixture of α,α- and β,β-*fac*-$Mn(CO)_3$(Tetraphos)Br with (*nor*-C_7H_8)$Mo(CO)_4$ gave a single product, which from IR data appears to be $[Br(CO)_3Mn(Tetraphos)]_n[Mo(CO)_4]$ ($n = 1,2$). Analytical data, together with a molecular weight determination, are most consistent with the product for which $n = 2$.

Small scale reactions of the separate isomers α,α-*fac*-$Mn(CO)_3$(Tetraphos)Br (~ 5 mg) and β,β-*fac*-$Mn(CO)_3$(Tetraphos)Br (~ 5 mg) with $Mn(CO)_5Br$ (~ 2 mg) in chloroform (~ 3 ml) at 60° were also attempted. The IR [ν(CO)] spectra were monitored during the course of the reactions and in both cases the final spectrum was consistent with a product of the type $Br(CO)_3Mn$(Tetraphos)-$Mn(CO)_4Br$ and not with the bridging complex $[Mn(CO)_3Br]_2$(Tetraphos). Since Type B tricarbonyl complexes would be expected to undergo reactions in which two CO groups are readily displaced from $Mn(CO)_5Br$ under these reaction conditions [21], the α,α- and β,β-isomers are thought to be of Type A.

The third complex obtained from the reaction of $Mn(CO)_5Br$ and Tetraphos (smallest R_f value) could be obtained in much higher yield by using a 2/1 ratio of the reactants $Mn(CO)_5Br$/Tetraphos. The IR spectrum [three strong absorptions in the ν(CO) region] of this complex, its lack of reactivity towards (*nor*-C_7H_8)$Mo(CO)_4$ and $Mn(CO)_5Br$, elemental analyses and a molecular weight determination all suggest the formulation (I) shown in Fig. 2. This bimetallic complex is almost certainly of Type B (Fig. 1) in which the "dangling" P atoms are now coordinated to the second manganese atom. Moreover, molecular models indicate that reactions of the Type A isomers to give this bimetallic complex are highly unlikely.

If the reaction of $Mn(CO)_5Br$ and Tetraphos is allowed to continue for longer periods of time or, preferably, if the reaction is carried out in xylene at 130°, the dicarbonyl complex *cis*-$Mn(CO)_2$(Tetraphos)Br is obtained. This complex has

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* In the Type A and B isomers, Tetraphos is acting as the bidentate ligands $RR'PCH_2CH_2PRR'$ (R = Ph; $R' = CH_2CH_2PPh_2$) and $R_2PCH_2CH_2PRR''$ [R = Ph; $R'' = CH_2CH_2P(Ph)CH_2CH_2PPh_2$], respectively, i.e., as unsymmetrical diphosphines. Little work has been reported on the separation of such unsymmetrical diphosphine [2,19] (or diarsine [20]) ligands by metal atoms.

been reported previously [7]. A similar reaction to that above, with $Mn(CO)_5I$, gave the analogous monometallic complex *cis*-$Mn(CO)_2$(Tetraphos)I. These complexes are thought to be similar to the corresponding Triphos complexes in which one CO group is *trans* to the Br atom (Fig. 2, structure II).

The dicarbonyl Tetraphos complexes should still contain one "dangling" P atom. This was confirmed by reaction of the dicarbonyls with ozone to give *cis*-$Mn(CO)_2$(Tetraphos=O)X (X = Br, I) (Fig. 2, structure III). These new phosphine oxide complexes exhibit two strong bands in the ν(CO) stretching region suggesting that the original stereochemistry is unaffected by the ozone reactions. The presence of the phosphine oxide was indicated by a strong absorption in the IR at ~ 1180 cm^{-1} [ν(P=O)] and other characteristic absorptions in the 1600—400 cm^{-1} region [22] (see footnotes *c* and *d* to Table 2). These phosphine oxide complexes were also obtained as side-products in the reactions of $Mn(CO)_5X$ with Tetraphos, presumably as a result of air oxidation.

The presence of one uncoordinated P atom in *cis*-$Mn(CO)_2$(Tetraphos)Br was also confirmed by its reaction with $C_5H_5Mn(CO)_2C_8H_{14}$. Only one isomer of the product $Br(CO)_2Mn$(Tetraphos)$Mn(C_5H_5)(CO)_2$ was obtained. Its IR spectrum showed only two strong CO bands, presumably due to the superposition of the two sets of bands for both metal carbonyl moieties.

A variety of other complexes were also obtained from the reaction of $Mn(CO)_5Br$ and Tetraphos but in very low yield. From their position on thin layer plates and their IR spectra, the products are most likely *fac*-$Mn(CO)_3$(Tetraphos=O)$_n$Br (n = 1,2) i.e., products of the type shown in Fig. 1. with either one or two of the P atoms oxidized to a phosphine oxide.

Tetraphos contains two chiral P atoms. So, it was hoped that separation of the *meso* and *racemic* isomers might be possible when the ligand underwent reaction with $Mn(CO)_5Br$. However, as mentioned in the Introduction, this should not have really been expected because commercially available Tetraphos is apparently either the pure *racemic* or the pure *meso* ligand but it is not known which [14]. Nevertheless, two isomers of *fac*-$Mn(CO)_3$(Tetraphos)Br could be separated and these isomers are considered to be Type A isomers (Fig. 1). Such a situation could only occur if the original Tetraphos ligand was the *meso* form. From our previous study [2] on the reaction of $Mn(CO)_5Br$ with Triphos, the product with the largest R_f value, the α isomer, had the phenyl group on the central P atom *trans* to the Br atom. Thus, it is tentatively suggested that both α,α- and β,β-*fac*-$Mn(CO)_3$(Tetraphos)Br contain the *meso*-Tetraphos ligand with the former having the two phenyl groups on the coordinated P atoms *trans* to the Br atom, while in the latter they are both *cis* to the Br atom. Confirmation of this suggestion must await single crystal X-ray diffraction studies on these two complexes.

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