Journal of Organometallic Chemistry, 57 (1973) 355–362
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF METAL CARBONYL COMPLEXES

III*. SYNTHESIS AND REACTIONS OF $Mn(CO)_3(Triphos)X (X=Cl, Br, I)$

N. J. COVILLE and I. S. BUTLER**
Department of Chemistry, McGill University, P.O. Box 6070, Montreal 101, Quebec (Canada)

(Received January 3rd, 1973)

SUMMARY

The halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X (X=Cl, Br, I)$, react with $PPh(CH_2CH_2PPh_2)_2$(Triphos) to give two isomers of *fac*-$Mn(CO)_3$(Triphos)X in which the Triphos ligand is only coordinated to the manganese atom through two of its three phosphorus atoms. The *fac*-$Mn(CO)_3$(Triphos)X complexes may be considered as "monodentate ligands" in that the free phosphorus atoms readily displace CO and other groups in a variety of metal carbonyls to give a series of novel bimetallic complexes, *e.g.*, $Br(CO)_3Mn(Triphos)Cr(CO)_5$ and $I(CO)_3Mn(Triphos)Mn(CO)_4I$. The reactions of $Mn(CO)_2[P(OMe)_3](Triphos)Br$ with $Cr(CO)_5THF$ and $Mn(CO)_3$(Triphos)X (X = Br, I) with O_2 (and O_3) to produce $Br(CO)_2[P(OMe)_3]Mn(Triphos)Cr(CO)_5$ and *fac*-$Mn(CO)_3$(Triphos=O)X, respectively, are also described. The IR-active CO stretching absorptions exhibited by the new complexes are discussed.

INTRODUCTION

In a previous publication[1], we reported that the tri-tertiary phosphine $PPh(CH_2CH_2PPh_2)_2$(Triphos) reacts with the halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X$ (X=Cl, Br, I), to form the halodicarbonyl complexes, $Mn(CO)_2$(Triphos)X. It was pointed out that these reactions were slow enough for the intermediate complexes, $Mn(CO)_3$(Triphos)X, to be isolated and characterized. The Triphos ligand in these complexes is coordinated to the manganese atom through only two of its three phosphorus atoms. We now wish to report the experimental details of these reactions and to describe the reactions of these "monodentate phosphine ligands" with various metal carbonyls to produce a new class of Triphos complexes in which the Triphos ligand acts as a bimetallic triligate ligand***, *e.g.*, $Br(CO)_3Mn(Triphos)Cr(CO)_5$.

---

[*] For Part II of this series see ref. 13.

[**] To whom correspondence should be addressed.

[***] For an explanation of this nomenclature system see ref. 2.

EXPERIMENTAL

Chemicals were obtained from the sources indicated: dimanganese decacarbonyl (Alfa Inorganics, Inc.); bis[2-(diphenylphosphino)ethyl]phenylphosphine (Triphos) (Strem Chemical Co.); 1,2-bis(diphenylphosphino)ethane (Diphos) (Aldrich Chemical Co.). The ligands were used without further purification.

The literature methods were used to prepare and purify $Mn(CO)_5X$ (X=Cl, Br[3], I[4]), π-$C_5H_5Mn(CO)_2(C_8H_{14})$[5], and $Mn(CO)_2[P(OMe)_3](Triphos)X$[1].

All preparative reactions were carried out under an atmosphere of nitrogen using dry, degassed, reagent-grade solvents. The air-stable reaction products were dried *in vacuo* (0.01 mmHg/25°) for 24 h.

IR spectra were recorded as described previously[1]. The decomposition points were determined in capillaries on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, New York, U.S.A., unless otherwise stated.

Analytical data and CO stretching frequencies for all the new complexes are given in Tables 1 and 2, respectively.

Preparation of Triphos complexes

fac-$Mn(CO)_3(Triphos)X$ *(X=Cl, Br, I)*. A mixture of the appropriate $Mn(CO)_5X$ complex (1 mmol) and Triphos (1 mmol) was dissolved in chloroform (25 ml) and the solution was maintained at reflux until the IR spectrum indicated that all of the starting material had reacted (1–6 h). The reaction mixture was then filtered and the solvent volume was reduced to about 5 ml on a rotary evaporator. Addition of n-hexane (40 ml) afforded a yellow product which was filtered off and then recrystallized from a chloroform/n-hexane mixture.

Thin-layer chromatography of the products revealed that they were in fact mixtures of two compounds. However, complete separation on a preparative scale was only successful in the case of the iodo complex (chromatography on a silica gel column using a 1/1 acetone/n-hexane mixture as eluent). Partial separation was achieved for the bromo complex on a silica gel preparative thin layer chromatography plate eluted with benzene.

α-$I(CO)_3Mn(Triphos)Mn(CO)_4I$. A dichloromethane solution (15 ml) containing $Mn(CO)_5I$ (1 mmol) and Triphos (0.5 mmol) was refluxed for 12 h. At this stage, the relative intensities of the CO stretching absorptions in the IR spectrum of the reaction mixture remained constant. The solution was filtered and then reduced in volume on a rotary evaporator to about 5 ml. Separation of the desired product from the starting materials was accomplished by preparative thin layer chromatography (silica gel plates/benzene eluent). Three components were isolated; the required product being the second eluted. Purification of the product was achieved by recrystallization from a chloroform/n-hexane mixture.

α- and β-$Br(CO)_3Mn(Triphos)Mn(CO)_4Br$. An equimolar mixture of $Mn(CO)_5Br$ and *fac-*$Mn(CO)_3(Triphos)Br$ in dichloromethane (15 ml) was maintained at reflux until no further changes took place in the IR spectrum (CO stretching region) of the reaction mixture (≈10 h). The solvent was then removed under reduced pressure and the two products were isolated by preparative thin layer chromatography (silica gel plates eluted with benzene). These products were recrystallized from dichlo-

TABLE 1

ANALYTICAL DATA FOR THE NEW MANGANESE(I) COMPLEXES

Complex	*Colour*	*Yield* (%)	*Decompn.* (°C)	*Analysis found* (*calcd.*) (%)			
				C	*H*	*P*	*X*
fac-Mn(CO)$_3$(Triphos)Cl^a	Yellow	45	97–100	62.7 (62.7)	4.8 (4.7)	13.6 (13.1)	
fac-Mn(CO)$_3$(Triphos)Br^{a,b}	Yellow	68	127–130	57.9 (59.0)	5.5 (4.4)	12.1 (12.3)	11.0 (10.6)
α-*fac*-Mn(CO)$_3$(Triphos)I	Yellow	60	≈ 85	55.3 (55.5)	4.1 (4.2)	11.5 (11.6)	
β-*fac*-Mn(CO)$_3$(Triphos)I	Yellow	10	≈ 145	55.7 (55.5)	4.1 (4.2)	11.4 (11.6)	
fac-Mn(CO)$_3$(Triphos=O)Br^c	Yellow	75	≈ 110	57.4 (57.8)	4.6 (4.3)	11.9 (12.1)	11.5 (10.4)
fac-Mn(CO)$_3$(Triphos=O)I	Yellow	75	102–106	54.6 (54.4)	4.3 (4.1)	11.4 (11.4)	15.1 (15.6)
α-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$	Yellow	30	96–100	54.0 (53.4)	3.4 (3.5)	9.8 (9.8)	
β-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$	Orange	30	≈ 85	53.6 (53.4)	3.5 (3.5)	10.0 (9.8)	
α-Br(CO)$_3$Mn(Triphos)Mo(CO)$_5$	Yellow	20	96–100	50.2 (51.0)	4.0 (3.4)	8.8 (9.4)	8.1 (8.1)
β-Br(CO)$_3$Mn(Triphos)Mo(CO)$_5$	Yellow	20	94–98	51.0 (51.0)	3.3 (3.4)	8.4 (9.4)	8.6 (8.1)
α-I(CO)$_3$Mn(Triphos)Mo(CO)$_5$	Yellow	75	99–105	48.1 (48.7)	3.2 (3.2)	8.7 (9.0)	12.5 (12.3)
α-Br(CO)$_3$(Triphos)Mn(CO)$_4$Br	Yellow	25	≈ 158	49.6 (49.2)	3.7 (3.3)	9.8 (9.3)	15.2 (16.0)
β-Br(CO)$_3$(Triphos)Mn(CO)$_4$Br	Yellow	25	≈ 160	49.4 (49.2)	3.8 (3.3)	9.4 (9.3)	
α-I(CO)$_3$(Triphos)Mn(CO)$_4$I	Yellow	35	≈ 168	45.8 (45.0)	3.5 (3.0)		21.7 (23.2)
α-Br(CO)$_3$(Triphos)Mn(π-C$_5$H$_5$)-(CO)$_2$	Yellow	30	105–110	57.4 (56.9)	4.9 (4.1)	9.5 (10.0)	
β-Br(CO)$_3$(Triphos)Mn(π-C$_5$H$_5$)-(CO)$_2$	Yellow	30	≈ 108	57.6 (56.9)	4.7 (4.1)	9.6 (10.0)	
α-Br(CO)$_2$[P(OMe)$_3$]Mn(Triphos)-Cr(CO)$_5$^{d}	Yellow	25	≈ 95	51.3 (50.8)	4.1 (4.1)		
β-Br(CO)$_2$[P(OMe)$_3$]Mn(Triphos)-Cr(CO)$_5$^{d}	Yellow	25	≈ 98	50.8 (50.8)	4.2 (4.1)		
fac-Mn(CO)$_3$(Diphos)Cl	Yellow	45	168–172	59.7 (60.8)	4.5 (4.2)		
[Mn(CO)$_4$Br]$_2$(Diphos)	Orange	35	178–184	45.2 (45.8)	2.5 (2.7)		

[a] Mixture of α- and β-isomers. [b] Found (calcd.) Mn: 7.53 (7.29)%. [c] Conductivity in CH$_3$NO$_2$ at 21° (1×10^{-3} *M*): $\Lambda_m = 2.52\ \mathrm{cm}^{-1} \cdot \Omega^{-1} \cdot M^{-1}$ [d] The C and H analyses for these complxes were performed in our laboratory on a Hewlett–Packard Model 185 CHN analyser.

TABLE 2

IR SPECTRA IN THE CO STRETCHING REGION OF THE NEW TRIPHOS COMPLEXES (CH_2Cl_2 SOLUTION)

Complex	*ν(CO) (cm^{-1})*[a]				
fac-$Mn(CO)_3$(Triphos)Cl[b]	2024	1955	1911		
α-*fac*-$Mn(CO)_3$(Triphos)Br[b,c]	2022	1953	1917		
β-*fac*-$Mn(CO)_3$(Triphos)Br[b,c]	2022	1955	1910		
α-*fac*-$Mn(CO)_3$(Triphos)I	2015	1949	1918		
β-*fac*-$Mn(CO)_3$(Triphos)I	2015	1949	1913		
fac-$Mn(CO)_3$(Triphos=O)Br[d]	2022	1953	1917		
fac-$Mn(CO)_3$(Triphos=O)I[e]	2018	1952	1915		
α-$Br(CO)_3$Mn(Triphos)$Cr(CO)_5$	2063 w	2022 m	1981 sh	1940 vs	
β-$Br(CO)_3$Mn(Triphos)$Cr(CO)_5$	2064 w	2024 m	1982 sh	1935 vs	1914 (sh)
α-$I(CO)_3$Mn(Triphos)$Cr(CO)_5$	2062 w	2018 m	1980 w	1938 vs	1923 (sh)
β-$I(CO)_3$Mn(Triphos)$Cr(CO)_5$	2064 w	2019 m	1978 w	1937 vs	1917 (sh)
α-$Br(CO)_3$Mn(Triphos)$Mo(CO)_5$	2073 w	2022	1943 vs	1924 (sh)	
β-$Br(CO)_3$Mn(Triphos)$Mo(CO)_5$	2074 w	2024	1945 vs	1916 (sh)	
α-$I(CO)_3$Mn(Triphos)$Mo(CO)_5$	2083 vw	2073	2019	1945 (br)	1935 (sh)
β-$I(CO)_3$Mn(Triphos)$Mo(CO)_5$	2083 vw	2073	2017	1948 (br)	1919
α-$Br(CO)_3$Mn(Triphos)$Mn(CO)_4$Br	2091 m	2022	2011	1956	1918
β-$Br(CO)_3$Mn(Triphos)$Mn(CO)_4$Br	2091 m	2022	2012	1957	1913
α-$I(CO)_3$Mn(Triphos)$Mn(CO)_4$I	2084 m	2019	2004 (sh)	1955	1919 m
α-$Br(CO)_3$Mn(Triphos)Fe(CO)$(NO)_2$[f,g]	2022	2002 (sh)	1954	1918	
β-$Br(CO)_3$Mn(Triphos)Fe(CO)$(NO)_2$[f,g]	2023	2002 (sh)	1956	1914	
α-$Br(CO)_3$Mn(Triphos)Mn(π-C_5H_5)$(CO)_2$	2022	1952	1923	1859	
β-$Br(CO)_3$Mn(Triphos)Mn(π-C_5H_5)$(CO)_2$	2022	1954	1929	1915	1862
α-$Br(CO)_2$[$P(OMe)_3$]Mn(Triphos)$Cr(CO)_5$	2061 w	1979 (sh)	1944 (sh)	1936 vs	1873
β-$Br(CO)_2$[$P(OMe)_3$]Mn(Triphos)$Cr(CO)_5$	2062 w	1980 (sh)	1944 (sh)	1935 vs	1872
[$Mn(CO)_4I$]$_n$(Triphos)[h]	2080	2014	1997	1952	

[a] The bands are strong in every case except where otherwise stated; s strong, w weak, v very, (sh) shoulder, (br) broad. Precision: ± 1–2 cm^{-1}. The assignments for the CO stretching vibrations (in order of decreasing frequency) of the monometallic *fac*-$Mn(CO)_3$(Triphos)X complexes are A'^2, A'^1, and A'' (see ref. 8). [b] Compare with the spectra of the related *fac*-$Mn(CO)_3$(Diphos)X complexes; X = Cl, 2025 s, 1957 s, 1915 s; X = Br, 2022 s, 1956 s, 1915 s cm^{-1} (CH_2Cl_2 solution). [c] ^1H NMR CH_2Cl_2 solution; TMS as internal standard (τ 10 ppm); Varian Associates A-60 spectrometer for the isomeric mixture: τ 2.75 (complex multiplet), Ph; $\tau \approx 7.5$ (broad), CH_2. [d] In Nujol mull: ν(P=O), 1168 cm^{-1}. For further details on the vibrational assignments of tertiary phosphine oxides see ref. 12. ^1H NMR: τ 2.58 (complex multiplet), Ph; $\tau \approx 7.5$ (broad), CH_2. [e] In Nujol mull: ν(P=O) 1175 cm^{-1}. [f] ν(NO) 1762 s, 1716 s cm^{-1} (α); 1760 s, 1714 s cm^{-1} (β). [g] No analytical data for this complex owing to insufficient yield. [h] Compare with the spectrum of [$Mn(CO)_4Br$]$_2$(Diphos): 2091 s, 2018 s, 2005 s, 1960 s cm^{-1} (CH_2Cl_2 solution).

romethane/n-hexane mixtures.

Reaction of $Mn(CO)_5Br$ (1 mmol) with Triphos (0.5 mmol) in refluxing dichloromethane (20 ml) for 12 h also afforded the two desired products. These products were isolated and purified as described above.

α- and β-$Br(CO)_3Mn$(Triphos)$M(CO)_5$ (M = Cr, Mo). First, the $M(CO)_5$THF complexes were prepared *in situ* by irradiation of a tetrahydrofuran (THF) solution (100 ml) of $M(CO)_6$ (10 mmol) with a 100 W Hanovia UV lamp for 12 h^6. *fac*-$Mn(CO)_3$(Triphos)Br (0.12 mmol) was then added to the yellow solutions and the mixtures were stirred for 12 h (M = Cr, at room temperature; M = Mo, at 60°). After filtration, solvent was removed from the reaction mixtures on a rotary evaporator. Excess metal hexacarbonyl was removed from the crude products by sublimation (0.01 mmHg/40°). Elution with benzene on silica gel thin layer chromatography plates gave the required products which were then recrystallized from dichloromethane/n-hexane mixtures.

The reaction of *fac*-$Mn(CO)_3$(Triphos)Br with $Cr(CO)_4(C_7H_8)$[7] in dichloromethane solution also yielded the bimetallic complexes but in very small amounts (< 5%). However, reaction of *fac*-$Mn(CO)_3$(Triphos)Br with $Cr(CO)_6$ in chloroform solution at 60° for 24 h gave no new products.

α- and β-I(CO)$_3$Mn(Triphos)Mo(CO)$_5$. *fac*-$Mn(CO)_3$(Triphos)I (0.2 mmol) was added to a tetrahydrofuran solution of $Mo(CO)_5$THF (prepared as above). This mixture was stirred for 12 h at 60°. Following filtration, the solvent was removed under reduced pressure. Excess $Mo(CO)_6$ was removed from the solid residue by sublimation (0.01 mmHg/40°). The crude product was chromatographed on a silica gel column using a 1/1 acetone/n-hexane mixture as eluent. Two complexes were separated; the one with the smaller R_f value (β-isomer) was only obtained in milligram quantities and so only its IR spectrum could be recorded. The other complex (α-isomer) was recrystallized from a dichloromethane/n-hexane mixture.

The reaction of *fac*-$Mn(CO)_3$(Triphos)I with $Cr(CO)_5$THF was investigated on a spectroscopic scale under the same experimental conditions described above. The two resulting isomers were characterized by their IR spectra in the CO stretching region and their movement on a thin layer plate.

α- and β-Br(CO)$_3$Mn(Triphos)Mn(π-C$_5$H$_5$)(CO)$_2$. A mixture of π-$C_5H_5Mn(CO)_2(C_8H_{14})$ (0.3 mmol) and *fac*-$Mn(CO)_3$(Triphos)Br (0.25 mmol) in chloroform (15 ml) was refluxed for 12 h. The resulting solution was filtered and the solvent was removed under reduced pressure. The crude product remaining was chromatographed on silica gel thin layer plates with benzene as eluent. The two products obtained were recrystallized from dichloromethane/n-hexane mixtures.

fac-Mn(CO)$_3$(Triphos=O)X (X = Br, I). *fac*-$Mn(CO)_3$(Triphos)X (1 mmol) was dissolved in dichloromethane (15 ml) and ozone (1.5 mmol) was bubbled through the solution. The solvent was then removed under reduced pressure and the resulting yellow material was chromatographed on a preparative silicia gel thin layer plate with chloroform as eluent. The products obtained were recrystallized from dichloromethane/n-hexane mixtures.

Br(CO)$_2$[P(OMe)$_3$]Mn(Triphos)Cr(CO)$_5$. $Cr(CO)_5$THF was prepared *in situ* by irradiation of $Cr(CO)_6$ (10 mmol) in tetrahydrofuran (100 ml) with a Hanovia 100 W UV lamp for 3 h[6]. The halodicarbonyl complex, $Mn(CO)_2[P(OMe)_3]$(Triphos)Br, (0.2 mmol) was added to the solution and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure and the crude product was eluted on thin layer chromatography plates with a 1/2 acetone/n-hexane mixture. The two products which separated were recrystallized from a dichloromethane/n-hexane mixture.

Preparation of Diphos complexes

Two previously unreported Diphos complexes were prepared for spectral comparative purposes.

fac-Mn(CO)$_3$(Diphos)Cl. A dichloromethane solution (20 ml) containing $Mn(CO)_5Cl$ (1 mmol) and Diphos (1.2 mmol) was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure and the resulting yellow crystals were washed with n-hexane. Recrystallization from a dichloromethane/n-hexane mixture afforded the pure product.

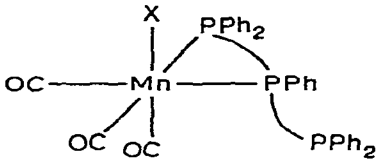
cis-[Mn(CO)$_4$Br]$_2$(Diphos). A mixture of $Mn(CO)_5Br$ (2 mmol) and Diphos (1 mmol) in dichloromethane (20 ml) was refluxed for 1 h. Removal of solvent under reduced pressure afforded the crude product which was then chromatographed on a silica gel column using benzene as eluent. Two products were separated; the one with the smaller R_f value was *fac*-Mn(CO)$_3$(Diphos)Br (identified by comparison of its IR spectrum with that of an authentic sample), the other was the desired product which was then recrystallized from a chloroform/n-hexane mixture.

RESULTS AND DISCUSSION

The halopentacarbonylmanganese(I) complexes, $Mn(CO)_5X$ (X=Cl, Br, I), react with Triphos in refluxing chloroform solution to produce Mn(CO)$_3$(Triphos)X in good yield. The potentially tridentate Triphos ligand is believed to be coordinated to the manganese atom in these complexes through only two of its three phosphorus atoms. The appearance of three strong CO stretching absorptions in their IR spectra (Table 2) strongly suggests a *facial* stereochemistry for the three CO groups[8].

As expected, monitoring the reactions by IR spectroscopy indicated that they proceed via the formation of a tetracarbonyl intermediate. In the case of the iodo complex, it was possible to isolate in milligram amounts a complex of the type [Mn(CO)$_4$I]$_n$(Triphos) (n=1 or 2) whose IR spectrum in the CO stretching region corresponded closely to that of [Mn(CO)$_4$Br]$_2$(Diphos). All attempts to isolate any other reaction intermediates failed. The IR spectra of the final halotricarbonyl products are virtually identical to that of *fac*-Mn(CO)$_3$(Diphos)Cl.

The reactions most probably proceed by the initial replacement of one CO group in $Mn(CO)_5X$ by Triphos followed by chelate formation and the expulsion of another CO group. So, the most likely structure for *fac*-Mn(CO)$_3$(Triphos)X is as shown below (the methylene groups of the Triphos ligand have been omitted for the sake of clarity).



Thin layer chromatography of the *fac*-Mn(CO)$_3$(Triphos)X complexes revealed that they were mixtures of two compounds. Although complete separation of the compounds was achieved for the iodo complex, the separations for the chloro and bromo complexes proved difficult. Elemental analyses for the various compounds are in accord with the molecular formula, Mn(CO)$_3$(Triphos)X (Table 1). Moreover, the IR spectra (Table 2) are almost identical. In view of these results, it is felt that each pair of compounds are in fact isomers of *fac*-Mn(CO)$_3$(Triphos)X. Molecular models indicate that there are two diastereomers possible for *fac*-Mn(CO)$_3$(Triphos)X which differ only in the orientation of the phenyl group attached to the central phosphorus atom of the Triphos ligand with respect to X. In one case this phenyl group can be regarded as *trans* to X while in the other it is *cis*. A somewhat related type of isomerism has been described recently for platinum and palladium complexes of Me(Ph)AsCH$_2$CH$_2$As(Ph)Me[9].

The *fac*-Mn(CO)$_3$(Triphos)X complexes can be regarded as potentially "monodentate phosphine ligands" and should therefore undergo typical substitution reactions with metal carbonyls. Indeed, reaction of the isomeric mixtures of the *fac*-Mn(CO)$_3$(Triphos)X complexes with Cr(CO)$_5$THF, Mo(CO)$_5$THF, Mn(CO)$_5$X, and π-C$_5$H$_5$Mn(CO)$_2$(C$_8$H$_{14}$) gave rise to a new series of bimetallic complexes, *viz*., X(CO)$_3$Mn(Triphos)Cr(CO)$_5$, X(CO)$_3$Mn(Triphos)Mo(CO)$_5$, X(CO)$_3$Mn(Triphos)-Mn(CO)$_4$X, and X(CO)$_3$Mn(Triphos)Mn(π-C$_5$H$_5$)(CO)$_2$, respectively. It should be emphasized here that these reactions were carried out under *mild* conditions so that there was no chance of forming the halodicarbonyl complexes, Mn(CO)$_2$(Triphos)X[1].

As anticipated, the new bimetallic complexes are in fact mixtures of two isomers which can readily be separated by thin layer chromatography. The IR spectra in the CO stretching region of each pair of isomers are very similar (Table 2) and are essentially superpositions of the spectra of *fac*-Mn(CO)$_3$(Triphos)X and the appropriate metal carbonyl starting material. Again it is felt that the stereochemistry of the phenyl group on the central phosphorus atom of the Triphos ligand is responsible for the formation of two different isomers. In the case of α- and β-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$, recent X-ray diffraction studies[10,11] have shown this to be true. The phenyl group in the α-isomer is *trans* to Br while it is *cis* in the β-isomer*. Moreover, in both cases, the three CO groups in the Br(CO)$_3$Mn(Triphos) moiety adopt a *facial* stereochemistry, as would be expected if the original Mn(CO)$_3$(Triphos)Br species has the same stereochemistry, as was suggested earlier.

The ultimate stereochemistry of the unique phenyl group when the Triphos ligand is coordinated to the manganese atom in *fac*-Mn(CO)$_3$(Triphos)X appears to play a role in the relative yields of the two isomers of these complexes. For example, reaction of Mn(CO)$_5$Br with Triphos affords an approximately 50/50 mixture of α- and β-*fac*-Mn(CO)$_3$(Triphos)Br; however, with Mn(CO)$_5$I, an 85/15 mixture of the α- and β-isomers is obtained. Presumably, steric interaction between the bulky iodine and phenyl groups renders formation of the β-isomer less likely.

It is of interest that when α-*fac*-Mn(CO)$_3$(Triphos)Br is treated with Cr(CO)$_5$-THF only α-Br(CO)$_3$Mn(Triphos)Cr(CO)$_5$ is produced (identified by its IR spectrum and its thin layer chromatography R_f value). This result suggests that there is no isomerization to the corresponding β-isomers taking place.

Reaction of the isomeric mixtures of *fac*-Mn(CO)$_3$(Triphos)X (X = Br, I) with O$_2$ (or preferably O$_3$ because of the cleaner reaction) gave the phosphine oxide complexes, Mn(CO)$_3$ (Triphos=O)X**, (characterized easily by the appearance of new absorptions due to ν(P=O) modes in the 1200–1100 cm^{-1} region). Apparently, the *facial* stereochemistry of the three CO groups in the original complexes is maintained because there are still three strong CO stretching absorptions observed. The non-ionic

---

* Throughout this paper, the faster moving of two isomers on a thin layer chromatography plate is referred to as the α-isomer while the other is the β-isomer.

** The uncoordinated P atom has been oxidized to P=O.

formulation of the complexes is supported by the low molar conductance ($2.5\ cm^{-1} \cdot \Omega^{-1} \cdot M^{-1}$) of the bromo complex in nitromethane solution at 21°.

Although two diastereomers of the *fac*-$Mn(CO)_3$(Triphos=O)X complexes were expected, only one compound could be separated by thin layer chromatography. Reaction of *fac*-$Mn(CO)_3$(Triphos=O)Br with $Mn(CO)_5Br$ did not afford any identifable products.

In an earlier paper[1], we reported the synthesis of $Mn(CO)_2$(Triphos)LX (L = tertiary phosphite; X = Cl, Br). The Triphos ligand in these "mixed ligand" complexes is acting as a bidentate ligand. Consequently, these complexes should also exist in two diastereomeric forms. However, thin layer chromatography using various solvents as eluents showed the presence of only one compound. Nevertheless, reaction of $Mn(CO)_2[P(OMe)_3]$(Triphos)Br with $Cr(CO)_5THF$ yielded a mixture of products which could be separated. Since the $P(OMe)_3$ group can be either *cis* or *trans* to the central phosphorus atom of the Triphos ligand, four different diastereomers are theoretically possible. However, we were only able to isolate two of these expected products, *viz.*, α- and β-$Br(CO)_2[P(OMe)_3]Mn$(Triphos)$Cr(CO)_5$ (the α-isomer having the larger R_f value in 1/2 acetone/n-hexane). In this case both the IR spectra and the decomposition points are virtually identical. Again the IR spectra are essentially superpositions of the spectra of the two starting materials.

CONCLUSION

It is apparent that the chemistry of poly-tertiary phosphines such as Triphos is far more complex than was heretofore realized. Not only are the expected substitution products formed with metal carbonyls, but in many cases the existence of diastereomers can be demonstrated. Moreover, these diastereomers arise because of the different stereochemical coordination abilities of particular phosphorus atoms.

ACKNOWLEDGEMENTS

The award of scholarships to N.J.C. by McGill University (Alexander McFee Scholarship, 1969–1970) and the National Research Council of Canada (1970–present) is gratefully acknowledged. This research was generously supported by a grant from the National Research Council of Canada.

REFERENCES

1 I. S. Butler, N. J. Coville and H. K. Spendjian, *J. Organometal. Chem.*, 43 (1972) 185.
2 R. B. King, *J. Coord. Chem.*, 1 (1971) 67.
3 E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, (1959) 1501.
4 E. O. Brimm, M. A. Lynch, Jr. and W. S. Sesny, *J. Amer. Chem. Soc.*, 76 (1954) 3831.
5 E. O. Fischer and M. Heberhold, *Essays in Coordination Chemistry*, Brinkhauser, Basel, 1964.
6 W. Strohmeier and R. Muller, *Z. Phys. Chem.* (Frankfurt) [N.S.], 28 (1961) 112.
7 R. B. King, *Organometallic Syntheses*, Academic, New York, 1965.
8 F. A. Cotton, *Inorg. Chem.*, 3 (1964) 702.
9 A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, (1971) 3549.
10 M. L. Schneider, N. J. Coville and I. S. Butler, *J. Chem. Soc., Chem. Commun.*, (1972) 799.
11 P. Bird, N. J. Coville, I. S. Butler and M. L. Schneider, in preparation.
12 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part. A*, 24 (1968) 845.
13 I. S. Butler and A. E. Fenster, *Inorg. Chim. Acta*, in press.