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TRANSITION METAL CARBONYLS

IV*. SUBSTITUTION REACTIONS OF RHENIUM PENTACARBONYL BROMIDE

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SUMMARY

Treatment of $Re(CO)_5Br$ with an excess of L has given *mer-cis*-$[Re(CO)_2L_3Br]$ for a wide range of tertiary phosphine and phosphite ligands. There was a marked temperature effect on these reactions. The disubstituted products *fac*- and *mer-trans*-$[Re(CO)_3L_2Br]$ have also been characterised. The carbonylations of *mer-cis*-$[Re(CO)_2L_3Br]$ to give *mer-trans*-$[Re(CO)_3L_2Br]$ have been shown to be dependent only upon the size of the ligand L. Qualitative studies on the reactions of *fac*- and *mer-trans*-$[Re(CO)_3L_2Br]$, $[L = P(OPh)_3$ and $PEt_2Ph]$ have inferred that *mer-cis*-$[Re(CO)_2L_3Br]$ only forms from the *mer-trans*-disubstituted isomer. The IR and ^1H NMR data for these complexes are discussed.

INTRODUCTION

Pentacarbonyl halide complexes of manganese and rhenium show a marked similarity in their substitution reactions with pyridine[2], phosphines and phosphites[1-4] as well as with bidentate ligands[4-8]. We have recently systematically studied[1] the substitution reactions of $Mn(CO)_5Br$ with monodentate phosphines and phosphites, L, and shown that trisubstitution readily occurs to give *mer-cis*-$[Mn(CO)_2L_3Br]$ with sterically favourable ligands. Although the larger size of the rhenium atom should reduce resistance towards higher substitution with bulkier ligands, there have been in fact few reports[3,4] of the replacement of more than two carbonyl groups in rhenium carbonyl halide compounds with monodentate tertiary phosphorus ligands. We have thus undertaken a systematic study of the reactions of $Re(CO)_5Br$ with fifteen tertiary phosphine and phosphite ligands of varying electronic and steric properties and find the substitution requirements and pathway to parallel those of $Mn(CO)_5Br$. The larger size of the rhenium atom also facilitated the formation of the trisubstituted

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complexes *mer-cis*-[$Re(CO)_2L_3Br$] for a much wider range of ligands than was possible for the analogous manganese species.

Preparation of $Re(CO)_{5-x}L_xBr$, ($x=2$ *or* 3) *complexes*

Treatment of a solution of $Re(CO)_5Br$ in a mixture of benzene/petroleum ether (b.p. 100–120°) with an excess of the ligands L [L = PMe_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $P(OEt)Ph_2$, $P(OMe)_2Ph$, $P(OEt)_2Ph$ and $P(OR)_3$, (R = Ph, Me, Et, Bu and i-Pr)] under reflux, readily afforded a total conversion to *mer-cis*-[$Re(CO)_2L_3Br$] (IIa) within 15 h. There was a marked temperature effect on these reactions, necessitating the presence of the higher boiling petroleum ether for the formation of (IIa). Higher boiling solvents, *e.g.* diglyme, further accelerate the formation of the trisubstituted product, but we found the use of the benzene/petroleum ether mixture to be very convenient as removal of the benzene under reduced pressure gave the required product in a crystalline form, with the exception of the phosphite compounds L = $P(OR)_3$, [R = Me, Et, Bu and i-Pr] which were obtained as oils and characterised only on IR data. The addition of sodium borohydride to the reaction solutions, in attempts to increase the substitution rate by carbonyl labilisation, was reasonably successful for some ligands, although generally the effect was small. This technique, however, seems to work well for similar substitution reactions of $M(CO)_6$, (M = Cr, Mo and W) with monodentate ligands[9], presumably through catalytic hydride formation.

Treatment of $Re(CO)_5Br$ with two molar equivalents of L [L = PMe_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $P(OMe)_2Ph$, $P(OEt)_2Ph$, $(POEt)Ph_2$ and $P(OPh)_3$] in refluxing benzene/petroleum ether (b.p. 100–120°) mixtures for 3 h readily gave *fac*-[$Re(CO)_3L_2Br$] (Ia) in high yield. Isomerisation of (Ia) to *mer-trans*-[$Re(CO)_3L_2Br$] (Ib) was effected in the same solvent mixture after 15 h usually with the addition of sodium borohydride. The isomerisations of (Ia) to (Ib) were generally slower for the smaller ligands and in preparing *mer-trans*-[$Re(CO)_3(PMe_3)_2Br$] from the *fac*-isomer, it was necessary to heat the *fac*-isomer in a sealed evacuated tube at 150° for 10 h. The compounds (Ib) were also prepared by the carbonylation of (IIa) in refluxing benzene solution, with the exception of L = $P(OEt)_2Ph$, PMe_2Ph, $P(OMe)_2Ph$ and PMe_3 which form equilibrium mixtures of (Ib) and (IIa).

The complexes (Ia), (Ib) and (IIa) are all colourless, stable in air and soluble in a variety of polar and non-polar solvents. They all have a high degree of thermal stability.

The IR and ^1H NMR data for all these compounds are summarised in Tables 1 and 2. The infrared spectra of (Ia) contain three strong carbonyl bands allowing an unequivocal[10] assignment of (Ia) as the *fac*-isomer of C_s symmetry $(2A'+A'')$. The carbonyl spectra of the second isomer of $Re(CO)_3L_2Br$ also show three absorptions, but the band at highest frequency is weak, and although these spectra can be interpreted in terms of either of two possible *mer*-conformations, we have assigned these complexes the *mer-trans*-configuration (Ib) of C_{2v} symmetry $(2A_1+B_1)$ as this does not involve substitution of the carbonyl group *trans* to the halogen, which is unknown in $M(CO)_5X$, (M = Mn or Re; X = halogen) reactions. The trisubstituted complexes exhibit two strong carbonyl bands in the IR spectra, consistent[11] with either *mer-cis* or *fac* configuration, both of C_s symmetry [$(2A')$ and $(A'+A'')$, respectively]. We have chosen the *mer-cis*-isomer (IIa), with a CO group *trans* to the halide, as the most likely conformer, again on carbonyl substitution precedents[3,11] and also on the supplement-

TABLE 1

MELTING POINTS, ANALYTICAL AND INFRARED SPECTROSCOPIC DATA FOR SOME SUBSTITUTED RHENIUM CARBONYL BROMIDE COMPOUNDS

Compound[a]		*Melting point (°C)*	*Analyses found (calcd.) (%)*			*C–O Stretching frequencies*[d] *(cm^{-1})*
			C	*H*	*Br*	
fac-[Re(CO)$_3$L$_2$Br] (Ia)	L = PMe$_3$	182–184[c]	21.6 (21.5)	3.6 (3.6)	15.8 (15.9)	2033 s, 1952 s, 1898 s
	PMe$_2$Ph	143	36.6 (36.4)	3.5 (3.5)	12.7 (12.8)	2034 s, 1955 s, 1899 s
	P(OEt)Ph$_2$	189–192	46.0 (45.9)	3.9 (3.7)	10.0 (9.9)	2044 s, 1970 s, 1914 s
	PEt$_2$Ph	104–107	40.7 (40.4)	4.4 (4.4)	12.0 (11.7)	2033 s, 1948 s, 1896 s
	P(OMe)$_2$Ph	94	33.3 (33.0)	3.2 (3.2)	11.7 (11.6)	2055 s, 1984 s, 1917 s
	P(OEt)$_2$Ph	96	36.8 (36.9)	4.0 (4.0)	10.6 (10.7)	2052 s, 1978 s, 1924 s
	P(OPh)$_3$	145–148	48.2 (48.2)	3.2 (3.1)	8.5 (8.2)	2067 s, 1998 s, 1938 s
	PMePh$_2$	158	46.1 (46.3)	3.4 (3.5)	10.7 (10.7)	2038 s, 1961 s, 1900 s
mer-trans-[Re(CO)$_3$L$_2$Br] (Ib)	L = PMe$_3$	158–160[c]	21.4 (21.5)	3.6 (3.6)	16.0 (15.9)	2035 w, 1949 s, 1893 m
	PMe$_2$Ph	126–129	36.4 (36.4)	3.6 (3.5)	12.5 (12.8)	2052 w, 1955 s, 1900 m
	P(OEt)Ph$_2$	177–182	45.9 (45.9)	3.7 (3.7)	9.8 (9.9)	2063 w, 1966 s, 1924 m
	PEt$_2$Ph	137	40.4 (40.4)	4.4 (4.4)	11.9 (11.7)	2052 w, 1955 s, 1888 m
	P(OMe)$_2$Ph	145–147	32.9 (33.0)	3.2 (3.2)	11.6 (11.6)	2072 w, 1978 s, 1923 m
	P(OEt)$_2$Ph	155	36.7 (36.9)	4.0 (4.0)	10.8 (10.7)	2070 w, 1974 s, 1918 m
	P(OPh)$_3$	158–163[b]	48.0 (48.2)	3.1 (3.1)	8.3 (8.2)	2088 w, 1995 s, 1945 m
	PMePh$_2$	151	46.3 (46.3)	3.5 (3.5)	10.9 (10.7)	2055 w, 1958 s, 1903 m
mer-cis-[Re(CO)$_2$L$_3$Br] (IIa)	L = PMe$_3$	175–178[c]	23.9 (24.0)	4.8 (4.9)	14.6 (14.5)	1942 s, 1842 s
	PMe$_2$Ph	156	42.1 (42.3)	4.4 (4.5)	10.7 (10.8)	1942 s, 1845 s
	P(OEt)Ph$_2$	142–145	52.0 (52.1)	4.5 (4.4)	7.9 (7.9)	1965 s, 1869 s
	PEt$_2$Ph	138–145	46.8 (46.8)	5.4 (5.5)	9.8 (9.7)	1934 s, 1836 s
	P(OMe)$_2$Ph	123	37.2 (37.5)	3.9 (3.8)	9.7 (9.6)	1986 s, 1882 s
	P(OEt)$_2$Ph	129	41.7 (41.9)	4.9 (4.9)	8.6 (8.7)	1982 s, 1878 s
	P(OPh)$_3$	133	53.5 (53.7)	3.6 (3.6)	6.4 (6.4)	2010 s, 1916 s
	PMePh$_2$	164–168	53.1 (53.3)	4.2 (4.2)	8.6 (8.7)	1948 s, 1850 s

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[a] All compounds are colourless, diamagnetic and non-electrolytes in acetone solution. [b] With decomposition. [c] Compound sublimes above 130°. [d] Measured in chloroform solution.

TABLE 2

^{1}H NMR SPECTROSCOPIC DATA[a] FOR SOME SUBSTITUTED RHENIUM CARBONYL BROMIDE COMPOUNDS

Compound		*$-CH_2-$ and $-OCH_2-$ Resonances (τ)*	*$-CH_3$ and $-OCH_3$ Resonances (τ) (J values in Hz)*
fac-$[Re(CO)_3L_2Br]$ (Ia)	L = PMe_3		8.32i; J^* = 8.4
	PMe_2Ph		8.24i; J^* = 13.5
	$P(OEt)Ph_2$	6.43 m	8.91t; J(H–H) = 7.0
	PEt_2Ph	7.92 m	9.10bm
	$P(OMe)_2Ph$		6.40i; J^* = 13.5
	$P(OEt)_2Ph$	6.03 m	8.70t; J(H–H) = 7.4
	$PMePh_2$		8.06i; J^* = 7.5
mer-trans-$[Re(CO)_3L_2Br]$ (Ib)	L = PMe_3		8.20t; J^* = 7.6
	PMe_2Ph		7.90i; J^* = 6.9
	$P(OEt)Ph_2$	6.23 m	8.75t; J(H–H) = 7.0
	PEt_2Ph	7.53 m	8.91bm
	$P(OMe)_2Ph$		6.27t; J^* = 11.5
	$P(OEt)_2Ph$	5.95 m	8.67t; J(H–H) = 7.1
	$PMePh_2$		7.60bs
mer-cis-$[Re(CO)_2L_3Br]$ (IIa)	L = PMe_3		8.30t (2); J^* = 6.9; 8.44d (1); J(P–H) = 7.4
	PMe_2Ph		8.12m (2); J^* = 13.2; 8.68d (1); J(P–H) = 7.5
	$P(OEt)Ph_2$	6.62 m	8.95m
	PEt_2Ph	7.64 m	9.16m
	$P(OMe)_2Ph$		6.46p
	$P(OEt)_2Ph$	6.08 m	8.74t (2); J(H–H) = 7.0; 8.79t (1); J(H–H) = 7.2
	$PMePh_2$		8.05p

[a] NMR data determined at 60 MHz and 37° in $CDCl_3$ solution; bs = broad singlet; d(n) = doublet of relative intensity n; t(n) = triplet; i = intermediate coupling pattern. m(n) = multiplet; bm = broad multiplet; p = overlapping multiplets. J^* = separation of the outer two peaks and represents $|^2J(P-H) + ^4J(P-H)|$, (see ref. 12).

ary ^{1}H NMR evidence for the compounds (IIa), ($L = PMe_2Ph$ and PMe_3). The methyl resonance pattern of $Re(CO)_2(PMe_2Ph)_3Br$ consists of a 1/2/2/2/1 multiplet of relative intensity 2 and 1/1 doublet of relative intensity 1. The multiplet can be interpreted in terms of two partially overlapping triplets, arising from the chemically non-equivalent methyl groups on the two phosphine ligands in mutually *trans* position and corresponding to a limiting case of an $[AM_3X_3]_2$[12] system in which $^2J(P–P) \gg |^2J(P–H) + ^4J(P–H)|$, whilst the doublet arises from the third, chemically non-equivalent phosphine. This establishes the compound as the *mer-cis*-isomer (IIa). A similar assignment could be made for $Re(CO)_2(PMe_3)_3Br$, from a methyl resonance pattern consisting of a 2/3/2 triplet and a doublet of relative intensities 2 and 1, respectively. No useful information was obtained from the NMR spectra of the other trisubstituted compounds, but all were assigned the *mer-cis*-configuration by analogy.

The NMR spectra of the disubstituted compounds (Ia) and (Ib) are less useful for structural assignments as all contain resonances characteristic of $[AM_3X_3]_2$ spectra, although for each ligand the spectra of (Ia) and (Ib) are distinct. Thus the *fac*-isomers (Ia), [$L = PMe_3$, $PMePh_2$ and $P(OMe)_2Ph$] exhibit distorted methyl triplets consisting of strong outer peaks with a broad central component indicative of intermediate $J(P–P)$ coupling. The appearance of phosphorus–phosphorus *cis* coupling in these and other *fac*-isomers could possibly be attributed to distortion of the P–Re–P angle from 90° by steric interaction. The methyl resonances in the spectra of (Ib) [$L = PMe_3$ and $P(OMe)_2Ph$] were observed as 1/2/1 triplets corresponding to strong $J(P–P)$ coupling. For $L = PMe_2Ph$ and $PMePh_2$, the observed methyl resonances are poorly resolved. All resonances corresponding to bonded ethyl groups were observed as broad, ill-defined multiplets.

EXPERIMENTAL

$Re(CO)_5Br$ was prepared by bromination of $Re_2(CO)_{10}$ in carbon tetrachloride solution at 30°. All ligands were obtained commercially. Melting points were determined on a Kofler hot-stage melting point apparatus and are corrected. The ^{1}H NMR spectra were recorded with a Varian A-60A instrument and IR spectra were recorded using a Perkin–Elmer Model 457 grating infrared spectrophotometer. Elemental analyses were performed by Mr. G. J. Roberts of this laboratory.

mer-cis-$\{Re(CO)_2[P(OPh)_3]_3Br\}$

$Re(CO)_5Br$ (1.0 g) was refluxed with triphenylphosphite (2.4 g, 3.15 molar equivalents) and sodium borohydride (0.3 g) in an equimolar mixture of petroleum ether (b.p. 100–120°) and benzene (15 ml) for 15 h. After filtration, the benzene was removed under reduced pressure and the white crystals obtained were recrystallised from dichloromethane/petroleum ether (b.p. 40–60°) to give the product as colourless needles (2.2 g).

Similarly prepared were *mer-cis*-[$Re(CO)_2L_3Br$], [$L = PMe_3$, PMe_2Ph, $P(OEt)Ph_2$, PEt_2Ph, $P(OMe)_2Ph$, $P(OEt)_2Ph$ and $PMePh_2$].

mer-trans-[$Re(CO)_3L_2Br$], [$L = PMe_2Ph$, $P(OEt)Ph_2$, PEt_2Ph, $P(OMe)_2Ph$, $P(OEt)_2Ph$, $P(OPh)_3$ and $PMePh_2$] were prepared by an analogous procedure using only 2 moles of L. In some cases, rapid removal of the benzene gave oily products, but these readily crystallised completely under pentane at 0°.

mer-trans-[$Re(CO)_3(PMe_3)_2Br$] was prepared by heating *fac-*[$Re(CO)_3(PMe_3)_2Br$] (0.40 g) to 150° for 10 h in a sealed evacuated tube immersed in an oil bath. After cooling, the crude product was recrystallised from dichloromethane/petroleum ether (b.p. 40–60°) to give the product as colourless prisms (0.33 g).

fac-[$Re(CO)_3L_2Br$], [L = PMe_3, PMe_2Ph, $P(OEt)Ph_2$, PEt_2Ph, $P(OMe)_2Ph$, $P(OEt)_2Ph$, $P(OPh)_3$ and $PMePh_2$] were prepared by the method described for *mer-cis-*{$Re(CO)_2[P(OPh)_3]_3Br$}, but without the addition of sodium borohydride to the reaction mixture and using 2 moles of L and reflux times of 3 h.

Carbonylation of mer-cis-[$Re(CO)_2L_3Br$] *compounds*

The compound (0.3 g) was dissolved in benzene (8 ml) and refluxed with CO gas bubbling through the solution. Infrared solution spectra were recorded directly from the reaction solution at regular intervals.

DISCUSSION

This systematic study of the substitution reactions of $Re(CO)_5Br$ to give the trisubstituted products *mer-cis-*[$Re(CO)_2L_3Br$] with a wide range of ligands has demonstrated the similarity of these reactions to those of $Mn(CO)_5Br$ in that the steric size of the incoming ligand, and not its π-characteristics, plays a dominant role in the formation of the product. The results are thus in accordance with those obtained previously[13] for the substitution reactions of $Ni(CO)_4$ with a wide range of phosphorus ligands. As expected, the larger rhenium atom has facilitated trisubstitution with a greater range of bulkier ligands than the manganese. Reactions of $Re(CO)_5Br$ with PEt_3 and $PEtPh_2$ have given only equilibrium mixtures of (Ib) and (IIa) as shown by infrared solution spectra of the reaction solutions and with PPh_3, (IIa) was not formed.

As with the corresponding manganese complexes, the compounds (IIa) readily react with CO at atmospheric pressure in benzene solution to give (Ib), though in contrast to the manganese analogues, reflux temperatures are required. These carbonylation reactions are rapid and a total conversion of (IIa) to (Ib) is obtained in under 10 min for the larger ligands of the series, *viz.* $P(OPh)_3$, $P(OEt)Ph_2$, $PMePh_2$ and PEt_2Ph, although for the smaller ligands an equilibrium between (Ib) and (IIa) is established. Thus for L = $P(OEt)_2Ph$ and PMe_2Ph, treatment of (IIa) for 4 h with CO in refluxing benzene gave only a 60% conversion to (Ib), as noted from infrared spectra of the reaction solution. As the ligand size decreases, the equilibrium at refluxing benzene temperature favours (IIa), *e.g.* for L = PMe_3 only 50% conversion and for L = $P(OMe)_2Ph$ 30%, after 4 h. These results show that the extent of carbonylation of (IIa) decreases with the ligand sequence $P(OPh)_3 \approx P(OEt)Ph_2 \approx PMePh_2 \approx PEt_2Ph > P(OEt)_2Ph \approx PMe_2Ph > PMe_3 > P(OMe)_2Ph$, and demonstrate clearly the dominant role played by steric effects in the carbonylation process, supplementing the similar results proposed for the analogous manganese reactions where the limited series available did not provide conclusive evidence.

It also seems that as the steric crowding in the molecule decreases the sterically controlled dissociative process for the bulky ligands is replaced by thermodynamically controlled equilibria. Interestingly, initial kinetic results on the system:

$$mer\text{-}trans\text{-}[Mn(CO)_3L_2Br] + L \rightleftarrows mer\text{-}cis\text{-}[Mn(CO)_2L_3Br] + CO$$

obtained by variations in the molar concentrations of L have also indicated that there is an equilibrium in this substitution process for the larger ligands. This, in fact, may now point to one of the reasons that though the complex $Re(CO)(PMe_2Ph)_4Cl$ can be formed[14] by refluxing $ReCl_3(PMe_2Ph)_3$ in 2-(diethylamino)ethanol, it cannot be prepared by carbonyl substitution reactions of $Re(CO)_5Cl$. We have treated $Re(CO)(PMe_2Ph)_4Cl$ with CO in refluxing benzene and observe an almost instantaneous carbonylation to give *mer-cis*-$[Re(CO)_2(PMe_2Ph)_3Cl]$.

We have performed comparative experiments on the reactivity of *fac*- and *mer-trans*-$[Re(CO)_3L_2Br]$, [$L = P(OPh)_3$ and PEt_2Ph] with an excess of L in refluxing benzene/petroleum ether mixtures and find that for $L = P(OPh)_3$, (Ib) is totally converted to (IIa) within 2 h whilst (Ia) gives only a 10% conversion to (IIa) in that time. For $L = PEt_2Ph$, (Ib) gives (IIa) after 12 h whilst (Ia) gives no reaction at all, even after extended refluxing. Thus the results are similar to those we obtained[1] for manganese carbonyl bromide substitution, which inferred that higher substitution will occur only after the formation of isomers with kinetically labilised *trans*-carbonyl groups. The poor reactivity of (Ia), [$L = P(OPh_3)$], under these conditions can be related to the known[15] retardation of the isomerisation rate of *fac*- to *mer-trans*-isomers of $Mn(CO)_3L_2Br$ in the presence of free ligand. Notably, in this work, no isomerisation from (IIa) to the *mer-trans* isomers of the trisubstituted compounds has been possible, which was shown to be crucial for further substitution in our manganese work, with the result that all attempts at further substitution of (IIa) have failed.

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