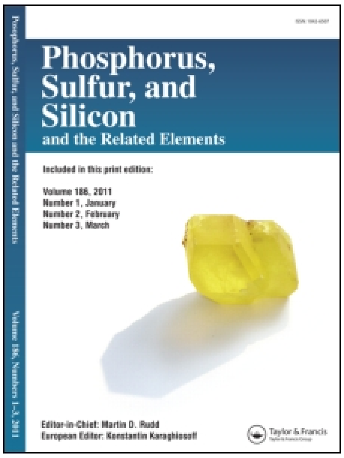

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STERIC AND STEREOCHEMICAL LIMITATIONS IN THE SUBSTITUTION REACTIONS OF MANGANESE AND RHENIUM CARBONYL BROMIDE WITH DIASTEREOMERIC DIAZAPHOSPHOLE LIGANDS

Graziano Baccolini[a]; Luigi Busetto[a]; Leonardo Contessa[a]; Vincenzo Albano[b]; Francesco Demartin[c]
[a] Facoltà di Chimica Industriale, Università, Bologna, Italy [b] Istituto Chimico "G. Ciamician," Facoltà di Scienze, Università, Bologna, Italy [c] Istituto Chimica Generale, Università, Milano, Italy

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STERIC AND STEREOCHEMICAL LIMITATIONS IN THE SUBSTITUTION REACTIONS OF MANGANESE AND RHENIUM CARBONYL BROMIDE WITH DIASTEREOMERIC DIAZAPHOSPHOLE LIGANDS

GRAZIANO BACCOLINI, LUIGI BUSETTO and
LEONARDO CONTESSA

*Facoltà di Chimica Industriale, Università, Viale Risorgimento 4, 40136
Bologna, Italy*

VINCENZO ALBANO

*Istituto Chimico "G. Ciamician," Facoltà di Scienze, Università, Via Selmi 2,
40126 Bologna, Italy*

FRANCESCO DEMARTIN

Istituto Chimica Generale, Università, Via Venezian 21, 20133 Milano, Italy

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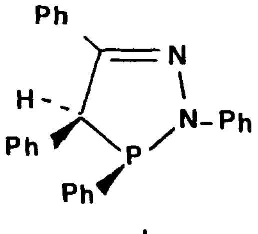
Thermal substitution reactions of $M(CO)_5Br$ (M = Mn, Re) with *cis* (L_c) and *trans* (L_t) diazaphosphole ligands (L = 3,4-dihydro-2,3,4,5-tetraphenyl-2H-1,2,3-diazaphosphole) have been studied. It has been found that L_c behaves as generally found for bulky phosphines affording to *cis*-$M(CO)_4(L_c)Br$, *mer*-$M(CO)_3(L_c)_2Br$ and *fac*-$Re(CO)_3(L_c)_2Br$ which has been thermally isomerized to *mer*-$Re(CO)_3(L_c)_2Br$. In contrast the corresponding reaction with the bulkier *trans* diazaphosphole isomer L_t have only afforded *cis*-$M(CO)_4(L_t)Br$ and *mer*-$M(CO)_3(L_t)_2Br$. All the different stereochemical results are rationalized on the basis of the size of the central metals and of the steric demand of the ligands. The nature of the complexes has been established essentially by IR spectra which, in the case of *cis*-$Re(CO)_4(L_c)Br$ presents in cyclohexane solution a doubling of all the characteristic $\nu(CO)$ bands expected for the C_{2v} local symmetry. This unexpected result has been tentatively discussed also on the light of an X-ray study which has confirmed the *cis* nature of this complex.

INTRODUCTION

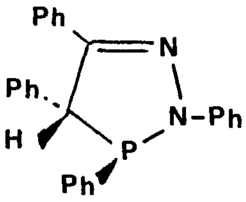
It is well known that steric and electronic factors play an important role in ligand substitution reactions of octahedral carbonyl derivatives and in particular steric effects have recently received considerable attention in these[1,2] and related processes.[3]

However the distinction between steric and electronic effects due to the phosphine ligands can be merely semantic when the different steric demand is achieved by changing the substituent on the phosphorus atom. Nevertheless this is not more *a priori* true when the ligand bulkiness variations are attributable only to diastereomeric forms.

We have recently investigated the complex forming properties[4,5] of two diastereomeric phosphines L_c and L_t having large and different cone angles but practically identical electronic properties. In particular we have found[5] that the substitution reactions of group 6B metal carbonyls give rise to different stereochemical results which have been explained by invoking fluxional five-coordinate intermediates in which only steric factors play a decisive role in determining the geometry and then the products distribution.



L_c



L_t

$$M(CO)_5L + L \rightarrow M(CO)_4L_2 + CO$$
$$(M = Cr, Mo, W;\ L = L_c \text{ or } L_t)$$

In order to obtain further evidences in this direction we have now investigated the reaction of $M(CO)_5Br$ (M = Mn, Re) with our diazaphosphole system L_c and L_t. We have found that the isomer distribution is not only influenced by the ligand size but also by the nature of the central metal.

An X-ray study on *cis*-$Re(CO)_4(L_c)Br$ is also reported.

RESULTS AND DISCUSSION

Bromopentacarbonylmanganese reacted in dichloromethane at refluxing temperature for about 1 hr with 1 mole of L_c to give *cis*-$Mn(CO)_4(L_c)Br$ which, with an additional mole of L_c under the same experimental condition, yielded after about 2 hrs only *mer*-$Mn(CO)_3(L_c)_2Br$ (see Scheme 1). All attempts at detecting the most electronically favoured facial isomer, also in the first time of reaction, failed. In addition we have found that heating *cis*-$Mn(CO)_4(L_c)Br$ in CH_2Cl_2 for about 2 hrs gave *mer*-$Mn(CO)_3(L_c)_2Br$ as the only tricarbonyl species. The latter complex was separated by column chromatography from a mixture containing also *cis*-$Mn(CO)_4(L_c)Br$ and $Mn(CO)_5Br$. These findings are in agreement with previously reported results on analogous reactions involving various phosphine ligands.[6]

The diastereomeric L_t form of the diazaphosphole system behaves differently from L_c in reacting with $Mn(CO)_5Br$. In fact no formation of *mer*-$Mn(CO)_3(L_t)_2Br$ is observed, but only the *cis*-$Mn(CO)_4(L_t)Br$ has been isolated after five days in refluxing CH_2Cl_2 or after 1 hr at 60°C in benzene. At higher temperature (refluxing benzene) and/or in the presence of an excess of L_t only small variable amounts (5–10%) of a red product containing carbonyl groups, not yet characterized, has been isolated.

The *cis*-$Re(CO)_4(L_c)Br$ has been obtained by refluxing equimolar quantities of L_c and $Re(CO)_5Br$ in chloroform for about 2 hrs; no formation of *trans* isomer[7] has been observed. In contrast to the behaviour of the analogous manganese derivatives

TABLE I

Carbonyl stretching frequencies[a] (CH_2Cl_2 solution)

Compd.	ν(CO), cm^{-1}			
cis-$Mn(CO)_4L_cBr$	2095 (m)	2005 (s)	2000 (vs)	1975 (s)
	[b] 2085 (m)	2020 (m)	2005 (vs)	1978 (s)
mer-$Mn(CO)_3L_{c_2}Br$	2040 (w)	1960 (vs)	1950 (m)	
cis-$Mn(CO)_4L_tBr$	2090 (m)	2020 (s)	2005 (vs)	1970 (s)
	[b] 2090 (m)	2025 (s)	2005 (vs)	1975 (vs)
cis-$Re(CO)_4L_cBr$	2100 (m)	2020 (s)	2005 (vs)	1955 (m)
	[b] 2110 (m) 2100 (m)	2030 (s) 2020 (m)	2005 (vs) 2000 (vs)	1970 (m) 1955 (s)
fac-$Re(CO)_3L_{c_2}Br$	2040 (s)	1960 (s)	1925 (s)	
mer-$Re(CO)_3L_{c_2}Br$	2040 (w)	1970 (vs)	1920 (m)	
cis-$Re(CO)_4L_tBr$	2110 (m)	2020 (s)	2010 (vs)	1960 (m)
	[b] 2110 (m)	2030 (s)	2010 (vs)	1965 (m)
mer-$Re(CO)_4L_{t_2}Br$	2060 (w)	1975 (vs)	1940 (m)	

[a] vs = very strong; s = strong; m = medium; w = weak.

[b] In cyclohexane solution.

the reaction with a further mole of L_c in refluxing $CHCl_3$ affords *fac*-$Re(CO)_3(L_c)_2Br$ which can be completely converted to the *mer*-isomer by refluxing a $CHCl_3$ or a *n*-hexane solution for 4 or 1 day respectively (see Scheme 1). The reactivity of L_c is similar to that found for other bulky phosphines[5] which give the same products distribution in reacting with $Re(CO)_5Br$. In contrast the *cis*-$Re(CO)_4(L_t)Br$, prepared by refluxing for about one day a $CHCl_3$ solution of equimolar amounts of $Re(CO)_5Br$ and L_t, produces only the *mer*-isomer in reacting with L_t in refluxing $CHCl_3$ for 4 days.

All the carbonyl complexes have been purified by column chromatography and their nature assigned by IR spectroscopy in CH_2Cl_2 solvent (Table I).

The results described above and collected on the following scheme may be rationalized on the basis of two main factors: (i) the size of the central metal; (ii) the steric demand of the ligands. The influence of the metal is well demonstrated by the lack of formation of the facial isomer of L_c in the case of the smaller manganese atom. The steric role of the phosphine is outlined in all the reactions which involve the L_t ligand. In fact whereas L_c behaves as a bulky phosphine[6] and its reactivity in

$$\textit{cis}\text{-}Mn(CO)_4(L_c)Br + L_c \rightarrow \textit{mer}\text{-}Mn(CO)_3(L_c)_2Br + CO$$

$$\textit{cis}\text{-}Mn(CO)_4(L_t)Br + L_t \rightarrow \text{no } \textit{mer} \text{ or } \textit{fac}\text{-isomers}$$

$$\textit{cis}\text{-}Re(CO)_4(L_c)Br + L_c \rightarrow \textit{fac}\text{-}Re(CO)_3(L_c)_2Br + CO$$

$$\textit{fac}\text{-}Re(CO)_3(L_c)_2Br \rightarrow \textit{mer}\text{-}Re(CO)_3(L_c)_2Br$$

$$\textit{cis}\text{-}Re(CO)_4(L_t)Br + L_t \rightarrow \textit{mer}\text{-}Re(CO)_3(L_t)_2Br + CO$$

SCHEME 1

substitution processes may be predictable on the basis of its cone angle which is about 145°, the L_t ligand owing to the larger cone angle (~ 190°)[8] do not display the same reactivity trend. Thus the steric limitation of L_t does not allow neither formation of *mer* and *fac* isomers in the case of Mn nor *fac* isomers in the case of the larger rhenium atom which generally accommodates phosphine ligands in facial positions. However the relief of steric inter-ligands interactions due to the increasing size of the central metal, permits the isolation of *mer*-$Re(CO)_3(L_t)_2Br$ in contrast with the behaviour of the manganese derivatives. It should be pointed out that all the conclusions described herein have been deduced without invoking electronic factors which can be ruled out by the diastereomeric nature of the phosphine ligands.

SPECTRAL DATA AND STRUCTURAL DETERMINATION

The results of infrared analyses of the *cis*, *mer* and *fac* carbonyl complexes are collected in Table I. The small differences observed in the ν(CO) absorptions in going from L_c derivatives to the corresponding ones containing L_t are an indication that the different steric properties of the two ligands do not induce significant electronic effects in these systems.

The infrared spectra of tricarbonyl complexes unequivocally distinguishes between facial and meridional isomers, showing three ν(CO) strong bands of similar intensity for *fac* and three bands of different intensity for *mer* species. However, IR spectra of *mer* derivatives do not permit the exact assignment of the two possible *mer*-isomers. We think, by analogy to previously reported examples[9] that the *mer-trans* is the more probable configuration for our complexes.

Unexpectedly the IR spectrum in cyclohexane of *cis*-$Re(CO)_4(L_c)Br$ in the ν(CO) region shows a doubling of the typical absorption pattern due to the C_{2v} local symmetry (see Table I). This result was not observed in the analogous $Re(CO)_4(L_t)Br$ and $Mn(CO)_4(L)Br$ which present the usual solvent effect observed in the ν(CO) of carbonyl complexes when the solvent is changed from CH_2Cl_2 to cyclohexane.[10,11] In addition the ^{13}C NMR spectra is in agreement with the *cis* configuration of the $Re(CO)_4(L_c)Br$.

For obtaining an unequivocal assignment of the proposed geometry a single crystal X-ray structural determination was performed. The results of this study indicates that the rhenium atom is octahedrally coordinated by four CO ligands, one bromine atom and the phosphorus atom of the L_c ligand as shown in Figure 1. The data for relevant bond distances and angles can be obtained from the authors. The bromine and the phosphorus atoms occupy cis positions and the rhenium coordination sphere has idealized C_s symmetry. The bulky ligand bearing the phosphorus donor atom does not significantly affect regular coordination at the metal atom. Due to the lack of symmetry of the L_c ligand the molecule is unsymmetrical. The crystal, however, is centric and contains equal amounts of enantiomeric molecules held together by van der Waals forces. As bonds parameters have been determined with limited accuracy they are not worth detailed discussion. The bond values in the L_c ligand are comparable with those found in the previous structural determination of *cis*-$Mo(CO)_4(L_c)_2$.[5]

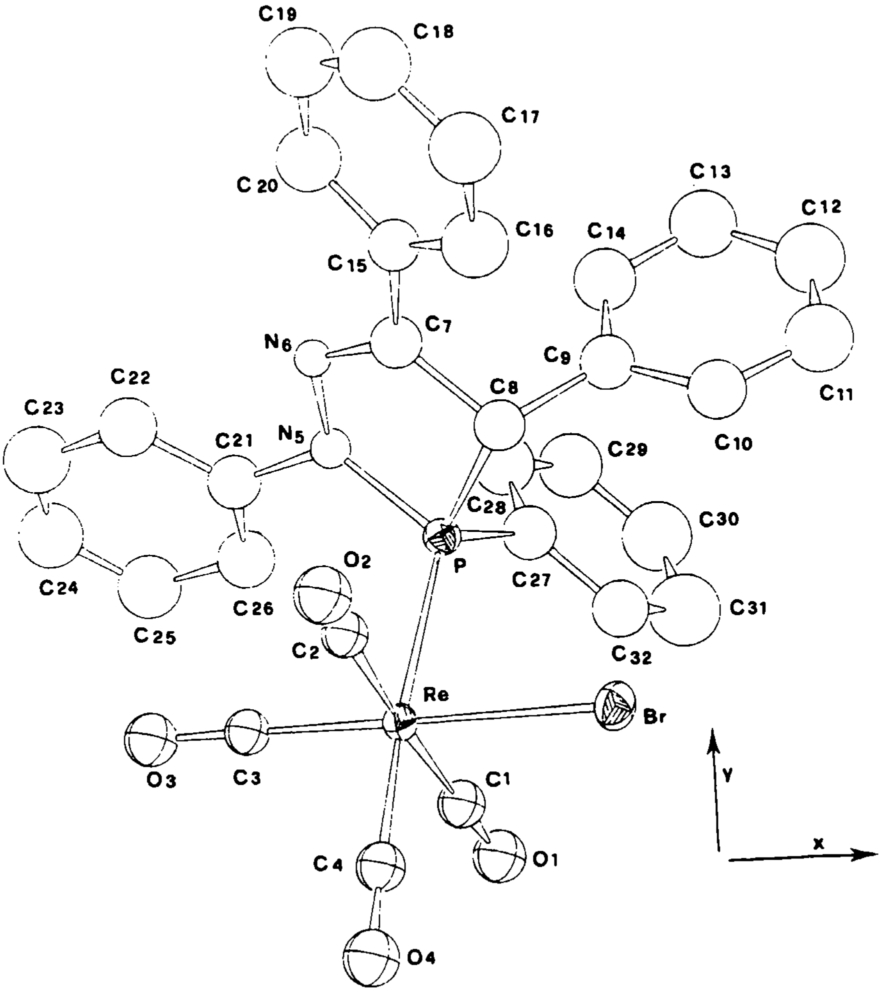


FIGURE 1 Molecular structure of *cis*-Re(CO)$_4$(L$_c$)Br.

The structural investigation confirms the *cis*-assignment of the Re(CO)$_4$L$_c$Br, but as expected does not give any information in order to explain the observed doubling of ν(CO) (see above). Nevertheless the results in our hand cannot exclude an explanation based on the presence of two or more conformers in solution because of the C_s coordination symmetry of the molecule. Moreover, the fact that this unusual IR pattern is displayed only in the case of *cis*-Re(CO)$_4$(L$_c$)Br indicates that cooperative motions of the ligands which give rise to conformers, are more favoured with the less bulky ligand L$_c$ and with larger rhenium atom. It follows that in the case where the steric compression between ligands is higher, as in complexes of the type Re(CO)$_3$(L$_c$)$_2$Br, it will be probably possible to separate conformers of the same coordination geometry.

Further studies are under way in this direction and will be reported later.

EXPERIMENTAL

All reactions were carried out on an atmosphere of oxygen-free nitrogen and all the solvents were dried according to established procedures. Infrared spectra were recorded on a Perkin-Elmer model 180 Spectrometer using 0.5 mm cells; ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 100, operating at 100 and 25.15 MHz respectively. Melting points are uncorrected. Diazaphosphole ligands L_c, L_t were prepared as described previously.[12] $Mn(CO)_5Br$[13] and $Re(CO)_5Br$[14] were prepared by published methods. Microanalyses were performed on pure complex isomers as well as on mixture of isomers: the results obtained were practically identical. Column chromatography was performed with silica gel of particle size 0.05–0.2 mm.

Preparation of cis-$Mn(CO)_4(L_c)Br$. Equimolar amounts of L_c (0.4 g, 1 mmol) and $Mn(CO)_5Br$ were refluxed in 100 ml of dichloromethane for 1 hr and the course of the reaction followed by t.l.c. after evaporation of the solvent, the reaction mixture was chromatographed on a silica gel column. Elution with a 35 : 2 : 2 mixture of *n*-hexane–benzene–diethyl ether gave the title complex (Rf. 0.35) in 75% yield, small amounts of the starting materials L_c (Rf. 0.50) and $Mn(CO)_5Br$ (Rf. 0.25). Crystallization of the tetracarbonyl complex from CH_2Cl_2–*n*-pentane afforded a pale yellow crystals with m.p. 163–165°C. Anal. Calcd. for $C_{30}H_{21}N_2O_4PBrMn$: C, 56.34; H, 3.24; N, 4.38. Found: C, 56.5; H, 3.1; N, 4.5.

Preparation of mer-$Mn(CO)_3(L_c)_2Br$. Equimolar quantities of $Mn(CO)_4(L_c)Br$ and L_c were refluxed in dichloromethane for 2 hrs, and the course of the reaction was followed by t.l.c. The reaction mixture was chromatographed on silica gel column and elution with the same mixture gave the title complex (Rf. 0.20) as the only product. Crystallization from CH_2Cl_2–*n*-hexane afforded yellow crystals with m.p. 148–150°C. Alternatively, when $Mn(CO)_4(L_c)Br$ was refluxed in dichloromethane, for 3 hrs, *mer*-$Mn(CO)_3(L_c)_2Br$ was obtained together with small amounts of tetracarbonyl complex and $Mn(CO)_5Br$. No formation of *fac*-$Mn(CO)_3(L_c)_2Br$ was observed in either case. Anal. Calcd. for $C_{55}H_{42}N_4O_3P_2BrMn$: C, 66.0; H, 4.19; N, 5.58. Found: C, 65.7; H, 4.1; N, 5.4.

Preparation of cis-$Mn(CO)_4(L_t)Br$. Diazaphosphole ligand L_t (0.4 g, 1 mmol) was added to a suspension of $Mn(CO)_5Br$ (1 mmol) in benzene, the mixture was allowed at 60°C for about 2 hrs and the course of reaction was followed by t.l.c. The title complex (Rf. 0.21) was separated by column chromatography using the same eluent and was crystallized (m.p. 138–140°C) from *n*-hexane. Anal. Calcd. for $C_{30}H_{21}N_2O_4PBrMn$: C, 56.34; H, 3.24; N, 4.38. Found: C, 55.9; H, 3.2; N, 4.8.

The reaction of *cis*-$Mn(CO)_4(L_t)Br$ with a further mole of L_t did not give $Mn(CO)_3(L_t)_2Br$ also after 3 days at refluxing benzene, but a new carbonyl complex was observed. This unstable complex was separated by column chromatography (Rf. 0.47) eluting with the same mixture and crystallized from *n*-hexane gave red impure crystals (m.p. 168–170°C). IR (cyclohexane): 2095 (w) 2010 (m) 2000 (vs) 1975 (m) 1950 (m) 1940 (m) cm^{-1}.

Preparation of cis-$Re(CO)_4(L_c)Br$. Equimolar amounts of L_c (0.4 g, 1 mmol) and $Re(CO)_5Br$ were refluxed in 100 ml of chloroform for 4 hrs and the course of the reaction followed by t.l.c. Chromatography of the resulting mixture on a silica gel column eluting with 30 : 2 : 1 solution of *n*-hexane–benzene–diethyl ether, afforded the title complex (Rf. 0.22) in 80% yield. Crystallization of this complex from CH_2Cl_2 and *n*-hexane gave white crystals, with m.p. 183–185°C. ^{13}C ($CDCl_3$): δ $C_{trans\text{-}Br}$, (d) 184.1 (J_{PC} 12 Hz); $C_{trans\text{-}P}$, (d) 181.0 (J_{PC} 60 Hz); $C_{cis\text{-}P}$, (m) 181.25. Anal. Calcd. for $C_{30}H_{21}N_2O_4PBrRe$: C, 46.75; H, 2.73; N, 3.64. Found: C, 46.5; H, 2.5; N, 3.5.

Preparation of fac-$Re(CO)_3(L_c)_2Br$. Equimolar quantities of *cis*-$Re(CO)_4(L_c)Br$ and L_c were refluxed in chloroform for a day and the course of the reaction was followed by t.l.c. The reaction mixture was chromatographed on silica gel column and elution with the above solution gave the title complex (Rf. 0.12) which by crystallization from *n*-hexane afforded white crystals, m.p. 165–170°C. From this reaction small amounts of *mer*-isomer (Rf. 0.10) were also obtained.

Isomerization of fac to mer-$Re(CO)_3(L_c)_2Br$. Refluxing a solution of *fac*-$Re(CO)_3(L_c)_2Br$ in chloroform for 4 days or in *n*-hexane for 1 day gave complete isomerization to *mer*-$Re(CO)_3(L_c)_2Br$. This complex (Rf. 0.10) was separated by column chromatography eluting with the above eluant and crystallized from *n*-hexane gave white plates, m.p. 158–160°C. Anal. Calcd. for $C_{55}H_{44}N_4O_3P_2BrRe$: C, 58.20; H, 3.70; N, 4.94. Found: C, 57.9; H, 3.5; N, 4.9.

Preparation of cis-$Re(CO)_4(L_t)Br$. Equimolar solution of $Re(CO)_5Br$ and L_t in chloroform was refluxed for about 1 day. Chromatography of the resulting mixture, eluting with the above solution, afforded the title complex (Rf. 0.35) which was crystallized from CH_2Cl_2–*n*-hexane giving white needles (m.p. 145–146°C). ^{13}C ($CDCl_3$): δ $C_{trans\text{-}Br}$, (d) 184.1 (J_{PC} 12 Hz); $C_{trans\text{-}P}$, (d) 180.75 (J_{PC} 60 Hz);

$C_{cis\text{-}P}$, (d) 179.3 (J_{PC} 12 Hz). Anal. Calcd. for $C_{30}H_{21}N_2O_4PBrRe$: C, 46.75; H, 2.73; N, 3.64. Found: C, 46.5; H, 2.7; N, 3.6.

Preparation of mer-Re(CO)$_3$(L$_c$)$_2$Br. Refluxing equimolar solution of *cis*-$Re(CO)_4(L_t)Br$ in chloroform for 4 days gave exclusively *mer*-$Re(CO)_3(L_t)_2Br$ which was isolated by chromatographic separation (Rf. 0.05) eluting with the same mixture. This complex, crystallized from *n*-hexane, had m.p. 178–180°C. No evidence of formation of *fac*-isomer was observed during this reaction. Anal. Calcd. for $C_{55}H_{42}N_4O_3P_2BrRe$: C, 58.20; H, 3.70; N, 4.94. Found: C, 58.1; H, 3.6; N, 4.9.

X-Ray Data Collection and Structure Determination. $C_{30}H_{21}BrN_2O_4PRe$, $M = 770.6$, colourless monoclinic prisms, space group P $2_{1/n}$, a = 15.671(2), b = 10.343(2), c = 18.927(3) Å, $\beta = 111.51(1)°$, $V = 2854$ Å^3, $Z = 4$, $D_c = 1.793$ g cm^{-3}, μ (Mo-K$_\alpha$) = 57.9 cm^{-1}. Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. Two octants of the reciprocal space were explored with the ω-scan technique in the 2θ range 6–50°C. The standard CAD-4 centering, indexing and data collection programs were used. An empirical absorption correction was made. 5142 reflection intensities were collected but only 1575 $|I > 3\sigma(I)|$ were used because of the poor quality of the crystal. The structure was solved by conventional Patterson and Fourier methods. The structure model was refined by full matrix least-squares calculations. Rhenium, bromine and phosphorus atoms were allowed to vibrate anisotropically; the other atoms isotropically. The hydrogen atoms were placed in their expected positions but not refined. The final conventional R and weighted R′ agreement indices were 0.046 and 0.050, respectively. A difference Fourier map computed after refinement did not reveal significant features. All the computations were carried out on a PDP 11/34 computer using the SDP package of crystallographic programs. The fractional coordinates of the structure model, the thermal parameters and the structure factors can be obtained on application to the authors.

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