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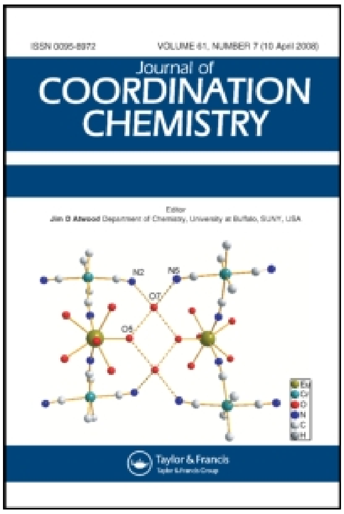

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RHENIUM(I) COMPLEXES OF BIS(DIFLUOROPHOSPHINO) METHYLAMINE. THE CRYSTAL AND MOLECULAR STRUCTURE OF HEXACARBONYLDI-μ-BROMO-μ-BIS (DIFLUOROPHOSPHINO) METHYLAMINEDIRHENIUM(I)

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RHENIUM(I) COMPLEXES OF BIS(DIFLUOROPHOSPHINO) METHYLAMINE. THE CRYSTAL AND MOLECULAR STRUCTURE OF HEXACARBONYLDI-μ-BROMO-μ-BIS (DIFLUOROPHOSPHINO) METHYLAMINEDIRHENIUM(I)

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Reaction of $ReBr(CO)_3(MeCN)_2$ with one-half an equivalent of $MeN(PF_2)_2$ forms $Re_2(CO)_6(\mu\text{--}Br)_2(\mu\text{-}MeN(PF_2)_2)$ (**1**) as the major product while with one equivalent of the phosphine, a mixture of **1**, $ReBr(CO)_3(\eta^2\text{-}MeN(PF_2)_2)$ (**2**) and $ReBr(CO)_3(\eta^1\text{-}MeN(PF_2)_2)(MeCN)$ (**3**) is produced. Complex **2** is more conveniently prepared from $ReBr(CO)_3(THF)_2$ and one equivalent of the phosphine. It reacts with $ReBr(CO)_3(MeCN)_2$ to form **1** and with acetonitrile to form **3**. The crystal and molecular structure of **1** has been determined. **1**: Triclinic, $P\bar{1}$; $a = 6.501(3)$, $b = 100.98(3)$, $c = 14.722(4)$Å, $\alpha = 94.32(2)$, $\beta = 100.93(3)$, $\gamma = 107.21(3)°$; $Z = 2$; $R = 0.042$, $R_w = 0.055$ for 3144 reflections ($I \geq 3\sigma(I)$).

KEYWORDS: rhenium, bis(difluorophosphino) methylamine, dimer

INTRODUCTION

We have previously reported that prolonged reaction of $ReBr(CO)_3(MeCN)_2$ with an excess of $MeN(PF_2)_2$ at room temperature forms *fac*-$ReBr(CO)_3(\eta^1\text{-}MeN(PF_2)_2)_2$ in high yield[1] but that under the same conditions, bis(dimethylphosphino)methane (dmpm) only forms *fac*-$ReBr(CO)_3(\eta^2\text{-dmpm})$.[2,3] Synthesis of *fac*-$ReBr(CO)_3(\eta^1\text{-dmpm})_2$ can be accomplished by running the reaction at elevated temperature.[2] The complexes *fac*-$ReBr(CO)_3(\eta^1\text{-}L_2)_2$ ($L_2 = MeN(PF_2)_2$,dmpm) have proved to be versatile synthons for the directed synthesis of heterobimetallic complexes.[1,2] In some reactions of one sample of *fac*-$ReBr(CO)_3(\eta^1\text{-}MeN(PF_2)_2)_2$, a small quantity of a species characterized as $Re_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}MeN(PF_2)_2)$ (**1**) was obtained. To ascertain the origin of **1** we have explored the reactions of $ReBr(CO)_3(MeCN)_2$ with $MeN(PF_2)_2$ in more detail.

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EXPERIMENTAL

All manipulations were carried out in an atmosphere of purified nitrogen using standard Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen prior to use. Literature methods were used to prepare ReBr(CO)$_5$[4],ReBr(CO)$_3$(MeCN)$_2$[5] and MeN(PF$_2$)$_2$[6]. Infrared spectra were obtained on a Mattson-Cygnus 100 Fourier transform instrument while ^{1}H and ^{31}P{^{1}H} NMR spectra were obtained on an IBM/Bruker AF-200 instrument at 200.132 and 81.015 MHz, respectively. Proton and phosphorus chemical shifts are referred, respectively, to external tetramethylsilane (δ 0.0) and 85% phosphoric acid (δ 0.0) with positive shifts downfield of the reference. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

Synthesis of Complexes

Re$_2$(CO)$_6$(μ-Br)$_2$(μ-MeN(PF$_2$)$_2$) (1)

To a solution of 0.16 g (0.37 mmol) of ReBr(CO)$_3$(MeCN)$_2$ in 2 mL of dichloromethane was added 0.031 g (0.185 mmol) of MeN(PF$_2$)$_2$ and the mixture was stirred overnight at room temperature. The solvent was removed in *vacuo* and the off-white residue extracted with 5 mL of diethyl ether. Concentration of the extract in *vacuo* to 2 mL and dilution with hexane afforded **1** in *ca.* 60% yield as pale yellow crystals after cooling overnight at −20° C. The supernatant was removed *via* syringe and the product was dried in *vacuo. Anal. Calcd* for $C_7H_3O_6NP_2F_4Br_2Re_2$(%): C, 9.90; H, 0.04. Found: C, 9.9; H < 0.5. IR (CH_2Cl_2): 2083(m), 2070(m), 1998(s), 1952(vs) cm^{-1} ($\nu_{c=o}$).[7] ^{1}H NMR ($CDCl_3$): δ 3.36 (*t*(J = 6.1 Hz), N-C*H*$_3$).[8] ^{31}P{^{1}H} NMR ($CDCl_3$): δ 130.7 (The A portion of an X$_2$AA'X'$_2$ pattern (see Figure 1)).

fac-ReBr(CO)$_3$(η^2-MeN(PF$_2$)$_2$) (2)

A solution of 0.30 g (0.74 mmol) of ReBr(CO)$_5$ in 15 mL of tetrahydrofuran was refluxed for 22 h after which time the infrared spectrum of the solution indicated complete conversion to ReBr(CO)$_3$(THF)$_2$.[9] Following concentration of the solution to *ca.* 8 mL under reduced pressure, 0.123 g (0.74 mmol) of MeN(PF$_2$)$_2$ was added and the mixture was stirred for 1 h at room temperature. The resulting solution was diluted with hexane and concentrated to *ca.* 0.5 mL under reduced pressure. The crude solid obtained was washed with 2 mL of hexane and the liquid removed *via* syringe. The solid was taken up in 5 mL of diethyl ether, filtered, diluted with an equal volume of hexane and the solution concentrated slowly in *vacuo* to afford the product as off-white crystals in *ca.* 75% isolated yield. *Anal.* Calcd for $C_4H_3NP_2O_3F_4BrRe$(%): C, 9.29; H, 0.58. Found: C, 8.6; H, 1.2. IR (CH_2Cl_2): 2083(vs), 2029(s), 1966(vs) cm^{-1} ($\nu_{c=o}$) ^{1}H NMR ($CDCl_3$): δ 2.94 (*t* (J(P-H) = 10.6 Hz), N-C*H*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 86.5 (The A portion of an X$_2$AA'X'$_2$ pattern).

X-ray Crystallography

A pale yellow needle of **1**, obtained by cooling a concentrated dichloromethane solution of the complex at −20°C., was cut to size, coated with a film of epoxy and

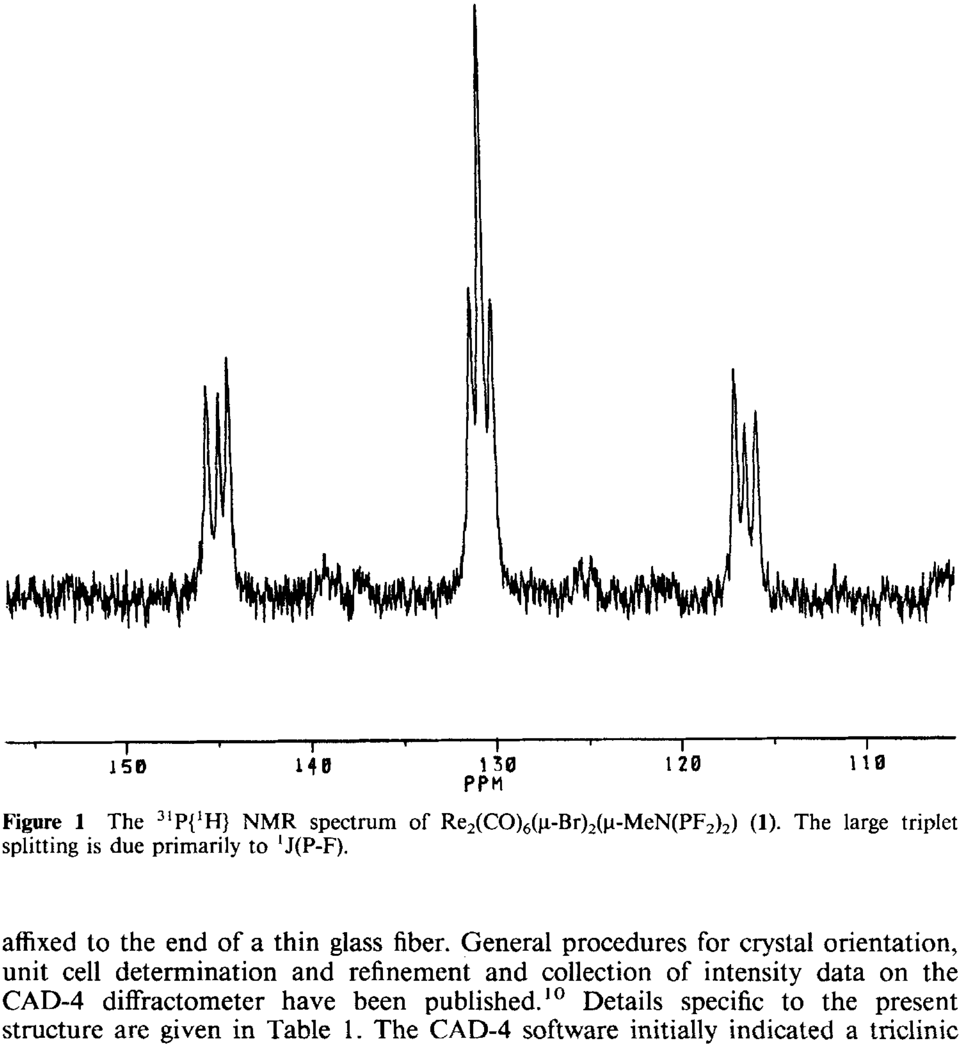

Figure 1 The $^{31}P\{^{1}H\}$ NMR spectrum of $Re_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}MeN(PF_2)_2)$ (**1**). The large triplet splitting is due primarily to $^{1}J(P\text{-}F)$.

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affixed to the end of a thin glass fiber. General procedures for crystal orientation, unit cell determination and refinement and collection of intensity data on the CAD-4 diffractometer have been published.[10] Details specific to the present structure are given in Table 1. The CAD-4 software initially indicated a triclinic unit cell and as no cell of higher symmetry could be found this was taken to be correct. A hemisphere (h, $\pm k$, $\pm l$) of data was collected and corrected for Lorentz and polarization effects as well as for absorption using ψ scans on three reflections with χ near 90°. The intensity monitors showed only statistical fluctuations obviating the need for a decay correction. The Re and Br atoms were located from an origin-removed Patterson map and the remainder of the structure developed by successive cycles of full-matrix, least-squares refinement followed by the calculation of $\Delta\rho$ maps. The initial assumption of $P\bar{1}$ as the space group was confirmed by the successful refinement. Location of a hydrogen atom on the methyl carbon (C(7)) permitted placement of the hydrogen atoms in idealized positions ($C-H = 0.95Å$) with fixed isotropic thermal parameters 20% larger than that of C(7). These were updated periodically. The final $\Delta\rho$ map was rather noisy but the largest peaks were all relatively close to the heavy atoms and are presumed to be artifacts of the

Table 1 Summary of crystallographic data

Formula	$C_7H_3F_4NO_6P_2Br_2Re_2$	Temp, K	295
fw	870.29	radtn	Mo Kα(Graphite Monochromated, $\lambda = 0.71073$ Å)
cryst size, mm	0.23 × 0.33 × 0.53	scan type	ω/2θ
cryst system	Triclinic	scan range, deg	0.8 + 2.0(tan θ)
space group	$P\bar{1}$(No.2)	2θ range, deg	1.0–50.0
A, Å	6.501(3)	total no. of refls	3452
B, Å	10.098(3)	no. unique refls	3144
C, Å	14.722(4)	R_{int}	0.037
α, deg	94.32(2)	no. obs data	2540 ($I \geq 3\sigma(I)$)
β, deg	100.93(3)	no. parameters	217
γ, deg	107.21(3)	$(\Delta/\sigma)_{max}$in last cycle	0.01
V,$Å^3$	898(2)	R^a	0.042
Z,	2	$R_w{}^b$	0.055
ρ_{calc}, g cm^{-3}	3.22	GOF^c	1.88
μ, cm^{-1}	183.1	Δp in final ΔF map, e/$Å^3$	1.60 to −2.69
range trans factors	0.5302–0.9986		

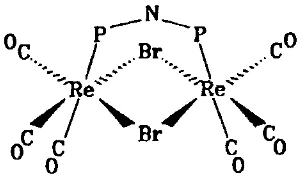
[a] $R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(\|F_o|-|F_c\|)^2/\Sigma w(|F_o|)^2]^{1/2}$ with $w = 1/(\sigma_F)^2$; $\sigma_F = \sigma(F^2)\ /2F$; $\sigma(F^2) = [(\sigma_I)^2 + (0.04F^2)^2]^{1/2}$. [c] $GOF = [\Sigma w(\|F_o|-|F_c\|)^2/(N_o-N_v)]^{1/2}$ where N_o and N_v are, respectively, the number of observations and variables.

empirical absorption correction. The neutral atom scattering factors used include corrections for the real and imaginary components of the effects of anomalous dispersion.[11] All calculations were performed on a VAXstation 3100 with the MolEN[12] suite of programs. Final refined atomic coordinates are given in Table 2 with additional crystallographic data provided as supplementary material.

RESULTS AND DISCUSSION

Synthesis and Chemistry

Reaction of $ReBr(CO)_3(MeCN)_2$ with one-half an equivalent of $MeN(PF_2)_2$ at room temperature in dichloromethane for 15 h affords pale yellow crystals analyzing as $Re_2Br_2(CO)_6(MeN(PF_2)_2)$ (**1**). The spectroscopic data given in the Experimental Section are consistent with formulation of **1** as $Re_2(CO)_6(\mu\text{-Br})_2(\mu\text{-MeN}(PF_2)_2)$ and this has been confirmed by an X-ray structure determination.



1

Somewhat surprisingly, reaction of $ReBr(CO)_3(MeCN)_2$ with an equimolar quantity of $MeN(PF_2)_2$ did not give a single product (*vide infra*), but if $ReBr(CO)_3(THF)_2$ is used instead, good yields of an off-white, crystalline material

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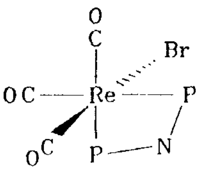
Table 2 Positional parameters (esd) for $(Re_2(CO)_6\ (\mu\text{-}Br)_2\ (\mu\text{-}MeN(PF_2)_2)$ (1)

Atom	x	y	z	$B_{eq}(Å^2)$
Re(1)	0.10128(7)	0.37144(4)	0.20921(3)	2.229(9)
Re(2)	-0.10112(8)	-0.02782(4)	0.20637(3)	2.55(1)
Br(1)	0.1237(2)	0.1497(1)	0.11004(8)	2.83(2)
Br(2)	-0.2334(2)	0.1860(1)	0.25312(9)	3.19(3)
P(1)	0.3308(6)	0.3464(3)	0.3448(2)	3.07(7)
P(2)	0.1935(5)	0.0394(3)	0.3369(2)	3.10(7)
F(1)	0.295(2)	0.4181(9)	0.4346(6)	6.0(2)
F(2)	0.576(1)	0.4332(9)	0.3580(7)	5.4(2)
F(3)	0.125(2)	-0.015(1)	0.4273(7)	6.2(3)
F(4)	0.373(1)	-0.357(8)	0.3344(7)	5.5(2)
O(1)	-0.208(2)	0.429(1)	0.0372(7)	5.2(3)
O(2)	0.056(2)	0.6215(8)	0.3260(7)	4.8(2)
O(3)	0.507(2)	0.562(1)	0.1500(8)	5.4(3)
O(4)	-0.517(2)	-0.139(1)	0.0397(9)	6.7(4)
O(5)	-0.356(2)	-0.222(1)	0.3254(8)	5.4(3)
O(6)	0.070(2)	-0.255(1)	0.1342(8)	6.5(3)
N	0.361(2)	0.202(1)	0.3805(7)	3.4(2)
C(1)	-0.097(2)	0.406(1)	0.1000(9)	3.0(3)
C(2)	0.072(2)	0.529(1)	0.2795(9)	3.8(3)
C(3)	-0.353(2)	0.493(1)	0.1734(9)	3.4(3)
C(4)	-0.368(2)	-0.097(1)	0.097(1)	4.4(4)
C(5)	-0.263(2)	-0.147(1)	0.2795(9)	4.0(3)
C(6)	0.001(2)	-0.171(1)	0.159(1)	4.2(3)
C(7)	0.540(3)	0.223(2)	0.469(1)	5.1(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i \bullet a_j$

can be obtained which is spectroscopically pure by ^{1}H and ^{31}P NMR and which analyzes reasonably well as $ReBr(CO)_3(MeN(PF_2)_2)$ (**2**). The three band pattern in the infrared spectrum of **2** is quite similar to that seen previously for *fac*-$ReBr(CO)_3(\eta^1\text{-}MeN(PF_2)_2)_2$ and a number of its derivatives that have been structurally characterized[1] indicating **2** contains the {*fac*-$Re(CO)_3$} unit. The $^{31}P\{^1H\}$ NMR spectrum (Figure 2) is a single, complex resonance of similar appearance to that of the free $MeN(PF_2)_2$ ligand. Its significant upfield shift compared with that for **1** indicates the ligand is chelated[13] to rhenium leading to formulation of **2** as *fac*-$ReBr(CO)_3(\eta^2\text{-}MeN(PF_2)_2)$.



2

Monitoring of the reaction of $ReBr(CO)_3(MeCN)_2$ with one-half an equivalent of $MeN(PF_2)_2$ by ^{31}P NMR shows that after 1–2 h the major species present is **2** together with lesser amounts of **1** and a new species **3**. If the reaction is continued overnight, virtually all the **2** and **3** initially present are consumed and **1** is now the

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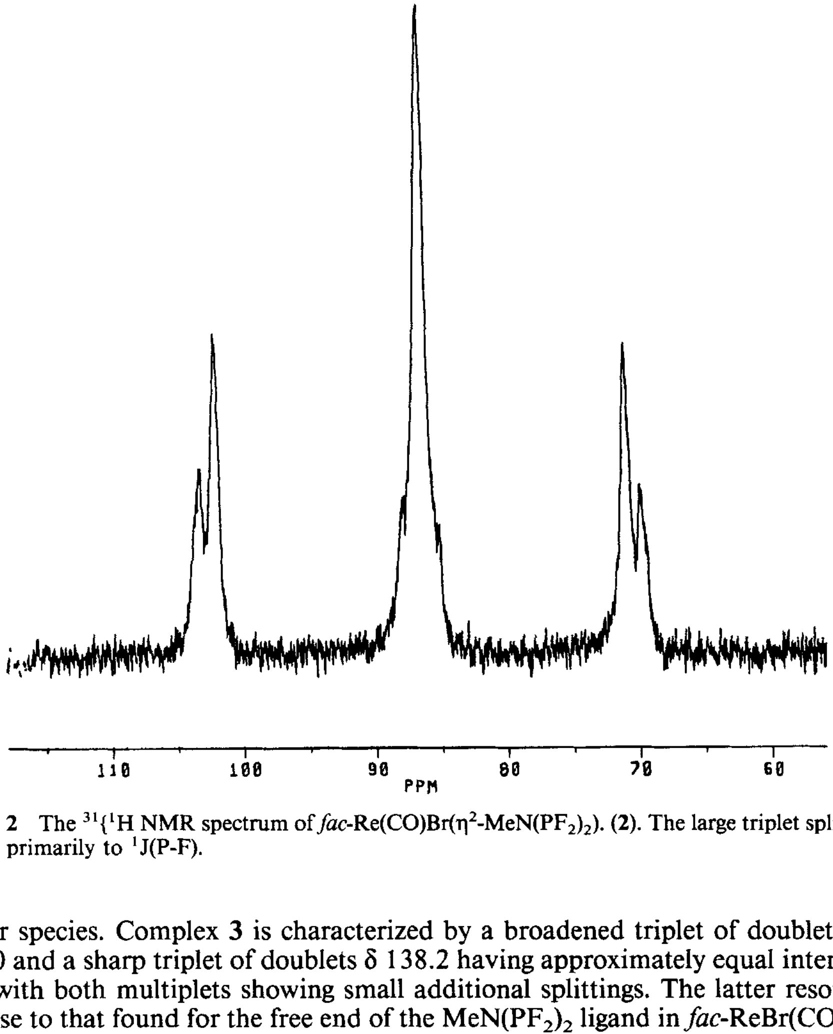
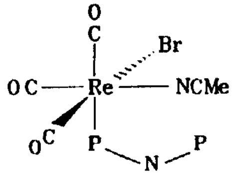


Figure 2 The $^{31}\{^{1}H$ NMR spectrum of *fac*-Re(CO)Br(η^2-MeN($PF_2)_2)_2$). (**2**). The large triplet splitting is due primarily to $^{1}J(P\text{-}F)$.

major species. Complex **3** is characterized by a broadened triplet of doublets at δ 129.0 and a sharp triplet of doublets δ 138.2 having approximately equal intensities and with both multiplets showing small additional splittings. The latter resonance is close to that found for the free end of the MeN($PF_2)_2$ ligand in *fac*-ReBr$(CO)_3$(η^1-MeN($PF_2)_2)_2$[1] while the former is very close to that for **1** suggesting that **3** contains monodentate MeN($PF_2)_2$. On this basis we suggest that a reasonable formulation for **3** is ReBr$(CO)_3$(η^1-MeN($PF_2)_2$)(MeCN) and this is supported by the observation that the spectrum attributed to **3** is generated by addition of a small quantity of



3

acetonitrile to a deuterochloroform solution of **2**. The *fac* stereochemistry about rhenium is assumed based on the fact that all the other species in this system have this geometry. The doublet splittng (*ca.* 170 Hz) which appears in both resonances is presumably due primarily to $^2J(P\text{-}P)$, although, since the spectrum is clearly second order, this splitting may include other couplings as well. In a separate experiment, equimolar quantities of **2** and $ReBr(CO)_3(MeCN)_2$ react in dichloromethane at room temperature overnight to form a substantial amount of **1** indicating that this is likely to be the process by which **2** is consumed in the previous reaction. Under the same conditions, there is no reaction between **1** and $MeN(PF_2)_2$ even after two days.

As noted above, the reaction of equimolar quantities of $ReBr(CO)_3(MeCN)_2$ and $MeN(PF_2)_2$ in dichloromethane does not cleanly proceed to **2**. Even after 15 h, an in *situ* ^{31}P NMR spectrum shows modest amounts of **1** and **3** to be present. This is not surprising given that **2** reacts with acetonitrile to form **3** (*vide supra*) and that, to the extent that **2** is formed initially, there will be free acetonitrile present. The fact that **1** can be formed even when there is more than a 1:2 ratio of $MeN(PF_2)_2$ to rhenium present and that **1** is resistant to further reaction with $MeN(PF_2)_2$ indicates that **1** is a potential side product in the synthesis of *fac*-$ReBr(CO)_3(\eta^1\text{-}MeN(PF_2)_2)_2$, particularly if care is not taken to use a significant excess of $MeN(PF_2)_2$ in the synthesis of the latter complex.

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Description of the Structure

A perspective view of **1** is shown in Figure 3 while pertinent bond distances and interbond angles appear in Table 3. There are no unusual intermolecular contacts in the solid. The structure can be compared with those of $Re_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}L_2)$ ($L_2 = Ph_4P_2$ **(4)**[14], *cyclo*-$(MePNBu^t)_2$ **(5)**[15], $Cp_2Mo_2(CO)_4(\mu\text{-}P_2)$ **(6)**[16]), all of which

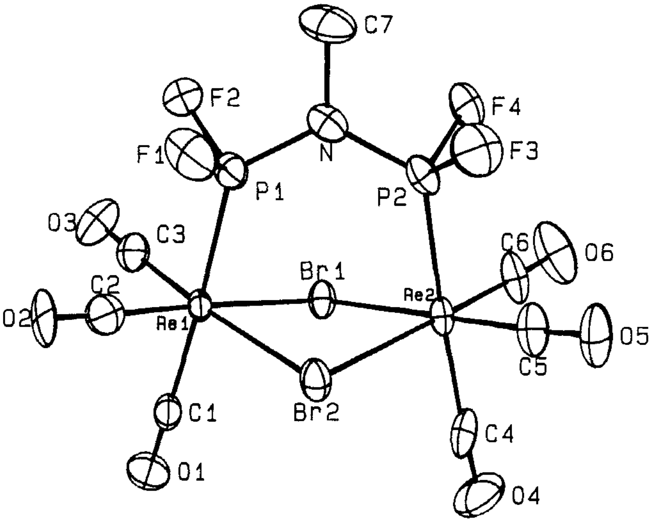

Figure 3 A perspective view of $Re_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}MeN(PF_2)_2)$ (**1**). Thermal ellipsoids are drawn at the 50% contour level and hydrogen atoms are omitted.

Table 3 Selected bond distances (Å) and interbond angles (°) for $(Re_2(CO)_6$ $(\mu\text{-}Br)_2(\mu\text{-}MeN(PF_2)_2$ (1)

Distances			
Re(1) - Br(1)	2.636(1)	Re(2)-Br(1)	2.642(1)
Re(1) - Br(2)	2.639(1)	Re(2)-Br(2)	2.641(1)
Re(1) - P(1)	2.334(3)	Re(2)- P(2)	2.337(4)
Re(1) - C(1)	1.98(1)	Re(2)- C(4)	2.04(2)
Re(1) - C(2)	1.91(2)	Re(2)- C(5)	1.89(1)
Re(1) - C(3)	1.92(1)	Re(2)- C(6)	1.90(1)

Angles			
Br(1)-Re(1)-Br(2)	82.94(4)	Br(1)-Re(2)-P(2)	92.08(9)
Br(1)-Re(1)-P(1)	94.33(9)	Br(1)-Re(2)-C(4)	91.7(4)
Br(1)-Re(1)-C(1)	90.3(4)	Br(1)-Re(2)-C(5)	176.9(4)
Br(1)-Re(1)-C(2)	177.6(4)	Br(1)-Re(2)-C(6)	90.6(4)
Br(1)-Re(1)-C(3)	92.9(4)	Br(2)-Re(2)-P(2)	91.79(9)
Br(2)-Re(1)-P(1)	88.9(1)	Br(2)-Re(2)-C(4)	89.3(5)
Br(2)-Re(1)-C(1)	91.3(4)	Br(2)-Re(2)-C(5)	94.4(4)
Br(2)-Re(1)-C(2)	95.3(4)	Br(2)-Re(2)-C(6)	172.8(4)
Br(2)-Re(1)-C(3)	175.0(4)	P(2)-Re(2)-C(4)	176.2(4)
P(1)-Re(1)-C(1)	175.3(4)	P(2)-Re(2)-C(5)	86.9(5)
P(1)-Re(1)-C(2)	87.2(4)	P(2)-Re(2)-C(6)	91.4(6)
P(1)-Re(1)-C(3)	90.0(4)	C(4)-Re(2)-C(5)	89.4(6)
C(1)-Re(1)-C(2)	88.2(6)	C(4)-Re(2)-C(6)	87.9(7)
C(1)-Re(1)-C(3)	90.1(6)	C(5)-Re(2)-C(6)	92.3(6)
C(1)-Re(1)-C(2)	89.6(6)	Re(1)-Br(1)-Re(2)	93.61(4)
Br(1)-Re(2)-Br(2)	82.78(4)	Re(1)-Br(2)-Re(2)	93.56(4)

contain the $\{Re_2(CO)_6(\mu\text{-}Br)_2\}$ moiety with a *fac* arrangement of carbonyl ligands and are folded about the Br—Br axis. A comparison of the geometries of the $\{Re_2(\mu\text{-}Br)_2P_2\}$ core in **1** and **4–6** is given in Table 4. Despite having the largest P—P separation, **1** has the shortest Re—Re distance and a "fold" angle about the Br—Br axis intermediate between those exhibited by the other complexes. This is probably the result of the shorter Re-Br and Re-P distances seen in **1** as compared with those in **4–6**. The short Re-P distance can be attributed to the strong π-acid character of the $MeN(PF_2)_2$ ligand. It has been noted with some apparent surprise that the "fold" angle in **5** is larger than that in **4** despite the larger P—P separation in the former.[15] This is evidently the result of a stretching of the $\{Re_2(\mu\text{-}Br)_2\}$ unit along the Re—Re axis as seen from the Re-Br-Re and Br-Re-Br angles which are, respectively, the largest and smallest of those found

Table 4 Geometries of the $\{Re_2(\mu\text{-}Br)_2P_2\}$ Unit in (1) and elated complexes

Complex	6	4	5	1
P–P(Å)	2.093(8)	2.308(6)	2.449(3)	2.974(3)
Re–Re(Å)	3.878(1)	3.890(1)	3.952(1)	3.8475(5)
Fold Angle(°)	37.9	23.4	35.7	27.10(6)
Re-Br(Å)[a]	2.662(1)	2.650(18)	2.670(3)	2.640(1)
Re-P(Å)	2.490(4)	2.478(5)	2.435(2)[a]	2.335(4)[a]
Br-Re-Br(°)[a]	79.2(1)	82.69(6)	77.92(3)	82.86(4)
Re-Br-Re(°)[a]	93.5(1)	93.47(6)	95.50(3)	93.58(4)

[a] Average value.

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for this series of complexes. Clearly the "fold" angle cannot be determined by the P–P separation alone.

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References

1. J.T. Mague and Z. Lin, *Organometallics* **13**, 3027 (1994).
2. J.T. Mague, *Inorg. Chem.* **31**, 4261 (1994).
3. J.T. Mague, *Acta Crystallogr.* (in press).
4. S.P. Schmidt, W.C. Trogler and F. Basolo, *Inorg. Synth.*, **23**, 41 (1985).
5. M.F. Farona and Kraus, K. F., *Inorg. Chem.* **9**, 1700 (1970).
6. R.B. King and J. Gimeno, *Inorg. Chem.* **17**, 2390 (1978)
7. Key to infrared band intensities: vs, very strong; s, strong; m, medium.
8. Key to NMR peak multiplicities: *t*, triplet.
9. D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, **102**, 587 (1972).
10. J.T. Mague and C.L. Lloyd *Organometallics*, **7**, 963 (1988).
11. a) D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol IV, (The Kynoch Press, Birmingham, England, 1974), Table 2.2B. b) D.T. Cromer, *Ibid*, Table 3.2.1.
12. C.K. Fair, **MolEN**, *An Interactive Intelligent System for Crystal Structure Analysis*, (Enraf-Nonius, Delft, The Netherlands 1990).
13. P.E. Garrou, *Chem. Rev.* **81**, 229 (1981).
14. J.L. Atwood, J.K. Newell, W.E. Hunter, I. Bernal. F. Calderazzo, I.P. Mavani and D. Vitali, *J. Chem. Soc., Dalton Trans.* 1189 (1978).
15. O.J. Scherer, R. Anselmann and W.S. Sheldrick, *J. Organomet. Chem.* **263**, C26 (1984).
16. O.J. Scherer, H. Sitzmann and G. Wolmershäuser, *Angew. Chem. Int. Ed. Engl.*, **23**, 968 (1984).

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