Polyhedron Vol. 8, No. 7, pp. 959–967, 1989
Printed in Great Britain

0277–5387/89 $3.00+.00

NEUTRAL AND CATIONIC OXO-METHYL COMPLEXES OF RHENIUM(V); X-RAY STRUCTURE OF $ReOMe_2Cl(PMe_3)_2$

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(*Received* 27 *August* 1988; *accepted* 9 *November* 1988)

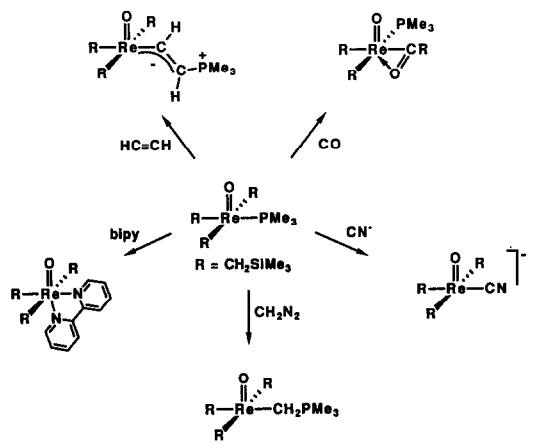
Abstract—Reaction of $ReO(OEt)Cl_2(py)_2$ with 1 equivalent of $AlMe_3$ in the presence of 2 equivalents of PMe_3 or PMe_2Ph produces $ReOMe_2Cl(PMe_2R)_2$ (R = Me or Ph) and reaction of $ReOMe_2Cl(PMe_2R)_2$ with dmpe gives $ReOMe_2Cl(dmpe)$. Spectroscopic studies and an X-ray structure of the PMe_3 derivative show that the compounds are octahedral with a *trans*-[Cl—Re═O] group and *cis*-methyl ligands. Reactions of an excess of $ZnMe_2$ with $ReOMe_2Cl(PMe_2R)_2$ and $ReOMe_2Cl(dmpe)$ give square-pyramidal $ReOMe_3(PMe_2R)$ (R = Me and Ph) and octahedral $ReOMe_3(dmpe)$, respectively. The trimethyl complexes are unstable at room temperature ($t_{1/2} \approx 3$ h for $ReOMe_3(PMe_3)$ in C_6D_6). The complexes $ReOMe_2Cl(PMe_2R)_2$ and $ReOMe_2Cl(dmpe)$ react with $[Ag(CH_3CN)_2][BF_4]$ to give $[ReOMe_2(PMe_2R)_2(CH_3CN)][BF_4]$ (R = Me and Ph) and $[ReOMe_2(dmpe)(CH_3CN)[BF_4]$, respectively. The cations are octahedral and contain a *trans*-$[CH_3CN—Re═O]$ moiety. Both the PMe_3 and PMe_2Ph derivatives exist in solution as a mixture of *cis*- and *trans*-phosphine isomers; variable temperature NMR studies show that the *trans* isomer predominates at low temperatures.

We have established that d^2 square-pyramidal $ReO(CH_2SiMe_3)_3(PMe_3)$ reacts with a variety of small molecules, including CO,[1] HCCH,[2] CN^-, CH_2N_2 and bipyridine (bipy),[3] Scheme 1. Surprisingly, however, $ReO(CH_2SiMe_3)_3(PMe_3)$ does not react with ethylene.[1] This may be due to the large steric bulk of the trimethylsilylmethyl ligand. These observations prompted us to prepare d^2 oxo-methyl complexes in order to test the reactivity of the less hindered complexes with ethylene and other small organic molecules. Reported here are the results of our initial synthetic work which includes the preparation of $ReOMe_2Cl(PMe_2R)_2$ (R = Me and Ph); $ReOMe_2Cl(dmpe)$ (dmpe = $Me_2PCH_2CH_2PMe_2$); $ReOMe_3(PMe_2R)$ (R = Me and Ph); $ReOMe_3(dmpe)$; $ReOMe_3(bipy)$; $[ReOMe_2(CH_3CN)(PMe_2R)_2]^+$ (R = Me and Ph); and $[ReOMe_2(CH_3CN)(dmpe)]^+$.

RESULTS AND DISCUSSION

Neutral oxo-dimethyl rhenium(V) *complexes*

The reaction of $ReO(OEt)Cl_2(py)_2$ (**1**)[4] with 1 equivalent of $AlMe_3$ in the presence of 2 equivalents of trimethylphosphine or dimethylphenylphosphine gives $ReOMe_2Cl(PMe_3)_2$ (**2a**, yield 62%) and $ReOMe_2Cl(PMe_2Ph)_2$ (**2b**, yield 56%), respectively [eq. (1)]. If 1/3 equivalent of $AlMe_3$ is used in reaction (1), a mixture of starting material, and mono- and dimethylated products is obtained. Reaction of **1** with 1 equivalent of $AlMe_3$ in the absence of phosphine, or with 2 or 3 equivalents of $AlMe_3$ in presence of PMe_2Ph or PMe_3, gives paramagnetic products which have not yet been characterized.



Scheme 1.

* Author to whom correspondence should be addressed.

These are presumably oxo-free complexes.

$$\underset{(\mathbf{1})}{ReO(OEt)Cl_2(py)_2} + AlMe_3 + 2PMe_2R \xrightarrow[CH_2Cl_2]{75°C\,12\,h}$$

$$ReOMe_2Cl(PMe_2R)_2 + Al(OEt)ClMe + 2py. \quad (1)$$

[R = Me (**2a**) and Ph (**2b**)]

Reaction of **2a** or **2b** with dmpe at room temperature gives $ReOMe_2Cl(dmpe)$ (**2c**) quantitatively by ^1H NMR (vs internal standard) and in 62 and 73% isolated yields, respectively [eq. (2)]. Surprisingly, the reaction of **1** with $AlMe_3$ and dmpe [cf. eq. (1)] does not give **2c**.

$$ReOMe_2Cl(PMe_2R)_2 + dmpe \xrightarrow[1\,h]{Toluene}$$

$$\underset{(\mathbf{2c})}{ReOMe_2Cl(dmpe)} + 2PMe_2R. \quad (2)$$

The compounds **2a**, **2b** and **2c** are red–brown crystalline solids, which are sparingly soluble in hexane and soluble in toluene and CH_2Cl_2. They are moderately air-sensitive, more so in solution than in the solid state.

The structure of **2a** has been determined by an X-ray crystallographic study; an ORTEP plot of the molecule is given in Fig. 1. Bond lengths and angles are presented in Table 1. The molecular geometry of **2a** is distorted octahedral. The Re=O,[1,2,5] Re—CH_3,[6] and Re—P[1,7] distances are normal, but the Re—Cl distance (2.607(3) Å) is long [e.g. it is 0.17 and 0.16 Å longer than the Re—Cl distances (Cl *trans* to Re=O) in $ReOCl_3(CNBu^t)_2$ and $ReOCl_3(PEt_2Ph)_2$, respectively].[5b,c] A possible explanation for the longer than normal Re—Cl distance is that electron donation from the strongly σ donating methyl groups makes an electron contribution from the chloride unnecessary and, given this, that steric interactions are minimized by pushing chlorine away from the rhenium centre.

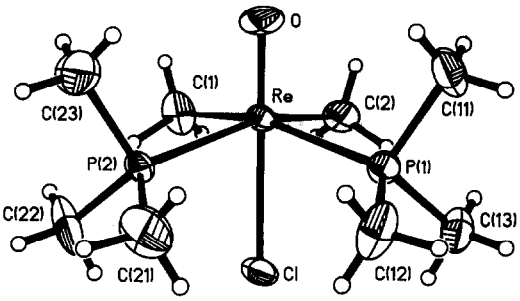


Fig. 1. ORTEP plot of $ReOMe_2Cl(PMe_3)_2$ (**2a**) showing the atom numbering scheme (50% probability level).

In **2a** the methyl groups are closer to the rhenium than the phosphines ($d_{Re-P} - d_{Re-C} = 0.25$ Å) and, because of this, the oxo and chloride ligands are repelled more by the methyl groups than the phos-

Table 1. Complete listing of bond lengths (Å) and angles (°) for $ReOMe_2Cl(PMe_3)_2$ (**2a**)

Bond distances			
Re—O	1.673(6)	P(1)—C(11)	1.828(11)
Re—C(1)	2.184(9)	P(1)—C(12)	1.813(11)
Re—C(2)	2.193(9)	P(1)—C(13)	1.809(10)
Re—Cl	2.607(3)	P(2)—C(21)	1.805(11)
Re—P(1)	2.459(3)	P(2)—C(22)	1.780(10)
Re—P(2)	2.449(3)	P(2)—C(23)	1.800(12)
Angles			
O—Re—C(1)	102.0(3)	P(2)—Re—Cl	76.6(1)
O—Re—C(2)	103.3(3)	Re—P(1)—C(11)	108.0(3)
O—Re—P(1)	96.6(2)	Re—P(1)—C(12)	122.1(3)
O—Re—P(2)	97.0(2)	Re—P(1)—C(13)	118.0(3)
O—Re—Cl	169.9(2)	C(11)—P(1)—C(12)	101.4(5)
C(1)—Re—C(2)	81.5(3)	C(11)—P(1)—C(13)	103.4(5)
C(1)—Re—P(1)	159.5(3)	C(12)—P(1)—C(13)	101.5(4)
C(1)—Re—P(2)	84.9(2)	Re—P(2)—C(21)	122.2(4)
C(1)—Re—Cl	85.4(3)	Re—P(2)—C(22)	117.0(4)
C(2)—Re—P(1)	86.0(2)	Re—P(2)—C(23)	108.3(4)
C(2)—Re—P(2)	157.5(2)	C(21)—P(2)—C(22)	102.3(5)
C(2)—Re—Cl	84.5(2)	C(21)—P(2)—C(23)	99.8(5)
P(1)—Re—P(2)	101.4(1)	C(22)—P(2)—C(23)	104.8(5)
P(1)—Re—Cl	77.3(1)		

phine ligands, even though the phosphines are larger. This is indicated in the structure by angular distortions from an octahedral geometry. For instance, the O—Re—C angles [102.0(3) and 103.3(3)°] are slightly larger than the O—Re—P angles [96.6(2) and 97.0(2)°]. Also, the O—Re—Cl angle is 10° from linear and bent in the direction of a line bisecting the P—Re—P angle.

Spectroscopic data for **2a**, **2b** and **2c** are similar and consistent with the solid state structure of **2a**. For instance, in **2a** the protons of the Re—*Me* groups appear as a doublet in the ^{1}H NMR spectrum, and the carbons appear as a doublet of a doublet in the $^{13}C\{^1H\}$ NMR spectrum ($^2J_{CP}$ = 48 and 8 Hz). By analogy to what has been reported for $ReO(CH_2SiMe_3)_3(PMe_3)$,[1] the $^{31}P—^1H$ coupling observed for **2a** is attributed to the *cis*-[P—Re—CH_3] groups, and the large and small $^2J_{PC}$ values are assigned to the *trans*- and *cis*-[P—Re—CH_3] moieties, respectively. The methyl protons of the PMe_3 ligands in **2a** give rise to a doublet in the ^{1}H NMR spectrum, but the carbons appear as a complex multiplet in the $^{13}C\{^1H\}$ spectrum. To a first approximation the latter can be interpreted as one half of an AA′XX′ spectrum, but in order to simulate the spectrum successfully it is necessary to use an AXY spin system (Fig. 2). This takes into account that $ReO(^{12}CH_3)_2Cl[^{31}P(^{13}CH_3)(^{12}CH_3)_2][^{31}P(^{12}CH_3)_3]$ is the isotopomer actually observed by $^{13}C\{^1H\}$ NMR. A complete listing of all coupling constants is given in the Experimental.

^{18}O labelling studies show that the Re=O stretching bands for **2a**, **2b** and **2c** occur at 1004, 999 and 1000 cm^{-1}, respectively. These are normal values for neutral rhenium(V) mono-oxo complexes.[8] The ^{18}O labelled compounds were prepared by stirring the unlabelled complexes with an excess of degassed $H_2{}^{18}O$ (100 equivalents) for 24 h in toluene.

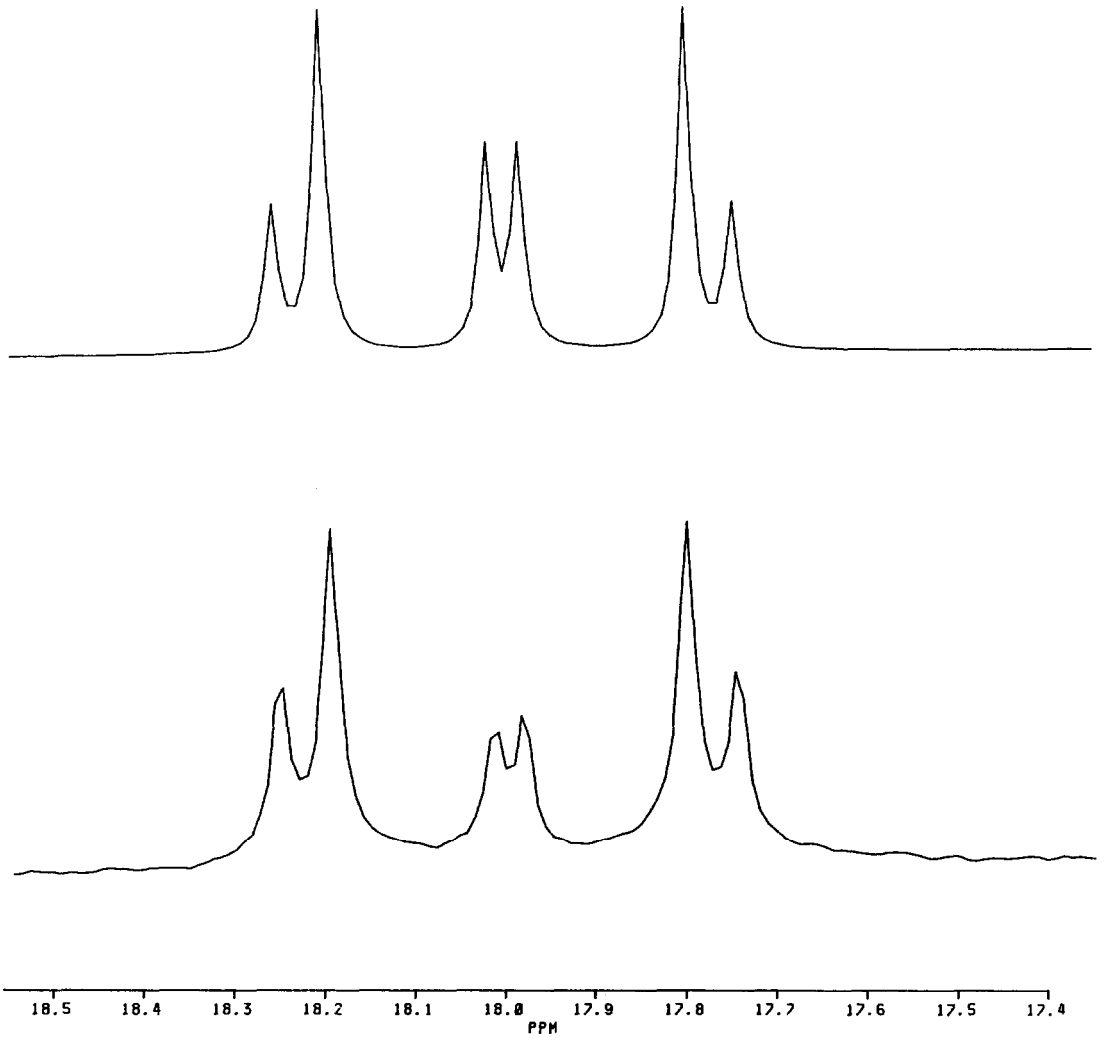
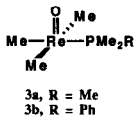


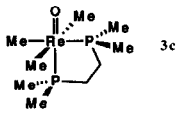
Fig. 2. Simulated (top) and experimental (bottom) $P(CH_3)_3$ region of the 75.5 MHz $^{13}C\{^1H\}$ spectrum for $ReOMe_2Cl(PMe_3)_2$ (**2a**).

Neutral oxo-trimethyl rhenium(V) complexes

Reactions of **2a**, **2b** and **2c** with an excess of $ZnMe_2$ at 0°C give the corresponding trimethyl derivatives, $ReOMe_3(PMe_2R)$ [R = Me (**3a**) and Ph (**3b**)] and $ReOMe_3$(dmpe) (**3c**), eqs (3) and (4). Reactions (3) and (4) are quantitative by ^1H NMR (vs internal standard), and the isolated yields are 47, 51 and 31% for **3a**, **3b** and **3c**, respectively.



3a, R = Me
3b, R = Ph



3c

Complex **3b** can also be prepared by the reaction of $Re_2(\mu\text{-}O)O_2Me_6$[6a,c] with PMe_2Ph [eq. (5)], and complex **3c** by the reactions of dmpe with **3a** or **3b**.

$$ReOMe_2Cl(PMe_2R)_2 + ZnMe_2 \xrightarrow[\text{Toluene}]{0°C} ReOMe_3(PMe_2R) + ZnMeCl + PMe_2R \quad (3)$$

[R = Me (**3a**) and Ph (**3b**)]

$$ReOMe_2Cl(\text{dmpe}) + ZnMe_2 \xrightarrow[\text{Toluene}]{0°C} ReOMe_3(\text{dmpe}) + ZnMeCl \quad (4)$$

(**3c**)

$$Re_2(\mu\text{-}O)O_2Me_6 + 3PMe_2Ph \longrightarrow 2ReOMe_3(PMe_2Ph) + P(O)Me_2Ph. \quad (5)$$

Compounds **3a** and **3b** are green oils, and **3c** is a red solid. All of the compounds decompose at room temperature ($t_{1/2} \approx 3$ h for **3a** in C_6D_6) to give as yet, uncharacterized products. The decomposition rates depend qualitatively on the phosphine ligand, with the dmpe ligand complex being the slowest to decompose and the PMe_3 complex being fastest.

The facile decomposition of **3a**, **3b** and **3c** has hampered their complete characterization. In particular, chemical analyses could not be obtained for any of the compounds and reliable IR data have been collected only for **3c** (ν(Re=O) 1018 cm^{-1}). NMR data sets have been obtained for all three compounds, however, and they are consistent with the structures shown. The proposed structures for **3a** and **3b** are analogous to the structure reported for $ReO(CH_2SiMe_3)_3(PMe_3)$.[1]

Compounds **3a** and **3b** are fluxional on the NMR time scale at room temperature. In low temperature limiting ^1H NMR spectra recorded at −66°C, the methyl ligands in **3a** give rise to a doublet, which by the integral intensity is assigned to the methyl ligands *cis* to PMe_3, and a singlet (methyl ligand *trans* to PMe_3). The observation of P—H coupling due to the *cis*-[P—Re—CH_3] and not the *trans*-[P—Re—CH_3] groups is consistent with an earlier study of $ReO(CH_2SiMe_3)_3(PMe_3)$.[1]

In contrast to compounds **3a** and **3b**, **3c** is not fluxional on the NMR time scale. In the $^{31}P\{^1H\}$ NMR spectrum recorded for **3c**, two doublets are observed indicating that the phosphorus atoms are in different chemical environments and are both bound to the metal. The ^1H NMR spectrum also shows evidence for two bound phosphorus atoms in that each methyl ligand (2:1 integral ratio) appears as a doublet of a doublet. Doublet of doublet resonances are also observed for the carbons of the methyl ligands in the $^{13}C\{^1H\}$ NMR spectrum.

In addition to $ReO(CH_2SiMe_3)_3(PMe_3)$, two other compounds related to **3a**, **3b** and **3c**, $Re(NPh)Me_3(PMe_3)_2$[9] and $ReOEt_3(PPh_3)_2$,[10] have been reported in the literature. The existence of these two compounds, each containing two phosphine ligands, suggested to us that the bis-phosphine complexes $ReOMe_3(PMe_2R)_2$, R = Me and Ph, should exist.

In an effort to observe a bis-phosphine adduct, we recorded a low-temperature limiting ^1H NMR spectrum (−73°C, $C_6D_5CD_3$) for a mixture of **3a** and 5 equivalents of PMe_3. This spectrum was consistent with the presence of *cis,mer*-$ReOMe_3(PMe_3)_2$ and free PMe_3 in solution. An attempt to isolate the bisphosphine complex by reacting an excess of PMe_3 with **3a** on a large scale, however, resulted in recovery of only **3a** after work-up. Thus, two phosphine ligands do coordinate to **3a** at low temperature in solution, but the isolable species contains only *one* phosphine ligand. Obviously, two phosphine centres coordinate in **3c** because of the chelate effect, but it is unclear why two phosphines coordinate in $Re(NPh)Me_3(PMe_3)_2$ and $ReOEt_3(PPh_3)_2$, whereas only one coordinates in **3a** and **3b**.

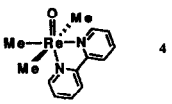
In addition to the NMR studies, there is also indirect evidence that the mono-phosphine formulation of **3b** is correct. The reaction of **3b** with bipyridine, carried out in an NMR tube and monitored by ^1H NMR, gave *one* free phosphine molecule and $ReOMe_3$(bipy) (**4**) [eq. (6), 80% yield by integration vs internal standard]. A large-scale reaction produced **4** in 35% isolated yield.

$$ReOMe_3(PMe_2Ph) + \text{bipy} \xrightarrow{C_6D_6} ReOMe_3(\text{bipy}) + PMe_2Ph. \quad (6)$$

(**4**)

Complex **4** is a blue crystalline solid which is air-stable in solution and in the solid state. The IR spectrum has a strong band at 970 cm^{-1} which can be assigned to the Re=O stretch. The ^1H NMR

spectrum reveals two methyl resonances in the integral ratio 2:1 as well as eight different resonances attributable to coordinated bipyridine. These data are consistent with the structure shown below.



4

Cationic oxo-methyl rhenium(V) *complexes*

Reactions of **2a**, **2b** and **2c** with $[Ag(CH_3CN)_2][BF_4]$ in acetonitrile give the cationic rhenium(V) complexes $[ReOMe_2(PMe_2R)_2(CH_3CN)]$ [R = Me (**5a**, yield 71%) and R = Ph (**5b**, yield 65%)], eq. (7) and $[ReOMe_2(dmpe)(CH_3CN)][BF_4]$ (**5c**, yield 68%), eq. (8), respectively. The cationic complexes are thermally stable red oils or oily solids which are insoluble in hydrocarbon solvents.

$$ReOMe_2Cl(PMe_2R)_2 + [Ag(CH_3CN)_2][BF_4] \xrightarrow{CH_3CN} [ReOMe_2(PMe_2R)_2(CH_3CN)][BF_4] + AgCl \quad (7)$$

[R = Me (**5a**) and Ph (**5b**)]

$$ReOMe_2Cl(dmpe) + [Ag(CH_3CN)_2][BF_4] \xrightarrow{CH_3CN} [ReOMe_2(dmpe)(CH_3CN)][BF_4] + AgCl. \quad (8)$$

(**5c**)

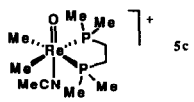
Variable temperature ^1H and ^{13}C NMR studies (CD_3COCD_3) reveal that **5a** and **5b** exist in solution as an equilibrium mixture of the *cis*- and *trans*-phosphine isomers shown below. For **5a** at 23°C, the ratio of *cis* to *trans* isomers (*cis–trans*) is approximately 1:1. At −33°C the *trans* isomer is dominant (1:6) and at +39°C the *cis* isomer is slightly favoured (1.7:1). The spectral changes are fully reversible. The solution behaviour of **5b** is similar to that of **5a** but, as expected on steric grounds, PMe_2Ph has a greater preference to be *trans* to PMe_2Ph (as opposed to *cis*) in comparison to the PMe_3 case.

5a, R = Me
5b, R = Ph

If the variable temperature ^1H NMR studies of **5a** and **5b** are repeated using CD_3CN as a solvent, the *cis–trans* ratio remains constant at temperatures below 23°C. This suggests that the isomerization is a two-step process involving acetonitrile dissociation followed by an intramolecular rearrangement of the resulting five-coordinate intermediate.

The *cis*- and *trans*-phosphine isomers of **5a** and **5b** are readily distinguished in ^1H NMR spectra. For instance, the *cis* isomer of **5a** gives rise to a doublet of a doublet for $ReCH_3$ and a doublet for the PMe_3 protons, whereas the *trans* isomer gives a triplet for $ReCH_3$ and a virtual triplet for the PMe_3 protons.

In contrast to **5a** and **5b**, NMR spectra recorded for **5c** are invariant with temperature. Two separate proton resonances for the dmpe methyl groups and only one ^{31}P resonance are observed for **5c**, and the ^1H NMR spectrum in the Re*Me* region resembles the spectra of *cis* **5a** and **5b**. These findings, as well as $^{13}C\{^1H\}$ NMR data, are consistent with the structure shown below.



5c

IR spectra recorded for **5a**, **5b** and **5c** show broad overlapping bands in the 950–1050 cm^{-1} region. This has prevented a definitive identification by labelling studies of the bands arising from the Re=O stretches. Oxo ligands are present, however, because the cations can be converted in the absence of air or water to their respective neutral compounds (**2a**, **2b** and **2c**) via reactions (9) and (10). It is noteworthy that only *cis*-dimethyl *cis*-diphosphine $ReOMe_2Cl(PMe_2R)_2$ complexes are obtained from eq. (9).

$$[ReOMe_2(PMe_2R)_2(CH_3CN)][BF_4] + NaCl \xrightarrow[1\,h]{CH_3CN} ReOMe_2Cl(PMe_2R)_2 + NaBF_4 \quad (9)$$

$$[ReOMe_2(dmpe)(CH_3CN)][BF_4] + NaCl \xrightarrow[1\,h]{CH_3CN} ReOMe_2Cl(dmpe) + NaBF_4. \quad (10)$$

CONCLUSION

We have prepared the neutral rhenium oxo-methyl complexes $ReOMe_2Cl(PMe_2R)_2$ (R = Me, Ph) and $ReOMe_2Cl(dmpe)$, and the cationic rhenium oxo-methyl complexes $[ReOMe_2(PMe_2R)_2(CH_3CN)]^+$ (R = Me, Ph) and $[ReOMe_2(dmpe)(CH_3CN)]^+$, in moderate yields. The latter compounds are the first examples of rhenium(V) mono-oxo cations.

The original synthetic targets of this study, $ReOMe_3(PMe_2R)$ compounds, are thermally unstable. This is in contrast to $ReO(CH_2SiMe_3)_3(PMe_3)$, which is stable at 23°C in the absence of air for months.[1] A related compound, $ReOEt_3(PPh_3)_2$, is also reported to be unstable at room temperature, but in this case the instability is

probably due to the presence of β-hydrogens in the molecule.[10] We are studying the decomposition reactions of $ReOMe_3(PMe_2R)$ in order to determine the ultimate products. Reactivity studies using $ReOMe_3(PMe_2R)$, which can be generated quantitatively *in situ*, are also in progress.

EXPERIMENTAL

Microanalyses were performed by Dornis and Kolbe, F.R.G. IR data were collected on a Perkin–Elmer 598 spectrophotometer (Nujol mulls (cm^{-1}), referenced externally to the 1601 cm^{-1} band of polystyrene). NMR data were collected using Bruker AM-500, AM-300, AM-250 and WM-300-WB (^{31}P NMR) spectrometers. ^1H NMR spectra were referenced to the ^1H impurities in the deuterated solvents (benezene-d_6, δ 7.15; acetonitrile-d_3, δ 1.93), ^{13}C NMR spectra to the ^{13}C triplet of benzene-d_6 (δ 128.0) or the septet of acetonitrile-d_3 (δ 1.3), and ^{31}P spectra to external H_3PO_4, with upfield shifts taken as negative. Molecular weights were determined by isothermal distillation (vs ferrocene).[11]

All operations were performed under oxygen-free nitrogen, argon or *in vacuo*. Solvents were purified by standard techniques and were dry and oxygen-free.

$^{13}C\{^1H\}$ NMR spectra obtained for the carbons of the phosphine ligands in **2a**, **2b**, **2c**, **3c**, **5a**, **5b** and **5c** were simulated using the program PANIC (Bruker). Initial ^{13}C coupling constants for **2a**, **2b**, **2c**, **5a**, **5b** and **5c** were obtained analytically by approximating the spin systems as AA′XX′ ($J_{CC'} = 0$).[12] Simulations with PANIC were carried out using an AXY spin system. In all cases, simulated and analytically determined coupling constants were in close agreement. The methyl region of the ^1H NMR spectrum of $ReOMe_3$(dmpe) (**3c**) was simulated as well.

(1) *Chlorodimethyloxobis(trimethylphosphine)rhenium*(V), $ReOMe_2Cl(PMe_3)_2$ (**2a**)

To a cold solution (−78°C) of $ReO(OEt)Cl_2(py)_2$ (1.50 g, 3.15 mmol) in methylene chloride (75 cm^3) $AlMe_3$ (1.6 cm^3, 3.20 mmol, 2.0 mol dm^{-3} in toluene) was added dropwise. The resulting green solution was frozen (−196°C) and the flask evacuated. PMe_3 (6.50 mmol) was then condensed into the flask via a calibrated vacuum manifold. After the mixture was allowed to warm to room temperature, the blue solution was heated (**Caution**: closed flask heating) at 75°C for 12 h. The volatiles were then removed *in vacuo*, and the residue was extracted with toluene (4 × 75 cm^3); the extracts were filtered and then evaporated to dryness *in vacuo*, and the residue was extracted with warm hexane (6 × 75 cm^3, 45°C). The hexane solution was filtered, reduced in volume, and cooled to −60°C to give red blocks. If necessary, the compound can be recrystallized from toluene. (Yield 0.82 g, 1.97 mmol, 62%.) Found: C, 23.1; H, 5.9; mol. wt (CH_2Cl_2) 404(30). Calc. for $ReClP_2OC_8H_{24}$: C, 22.9; H, 5.8%; mol. wt calc. 419.9.

^1H NMR (C_6D_6): δ 3.8 (d, 6, *cis*-J_{PH} = 7.4 Hz, Re*Me*), 1.6 (d, 18, J_{PH} = 9.2 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.4 (dd, 2, *trans*-J_{CP} = 48 Hz, *cis*-J_{CP} = 8 Hz, Re*Me*), 18.0 (AXY, J_{CP} = 27.3, $^3J_{CP}$ = 2.7, J_{PP} = −11.4 Hz, $\Delta P_X - \Delta P_Y$ = 1.9 Hz, P*Me*$_3$). $^{31}P\{^1H\}$ (C_6D_6): δ −47.1 (s). IR: ν(Re═O) 1004 s [ν(Re═^{18}O) 949], 1433(sh), 1420(m), 1368(sh), 1305(m), 1281(s), 958(s), 944(s), 859(m), 850(m), 747(s), 671(m), 510(m), 500(m), 351(w), 301(w), 268(w).

(2) *Chlorodimethyloxobis(dimethylphenylphosphine) rhenium*(V), $ReOMe_2Cl(PMe_2Ph)_2$ (**2b**)

This compound was prepared by a procedure analogous to the one used for the preparation of $ReOMe_2Cl(PMe_3)_2$. (Yield 54%.) Found: C, 39.4; H, 4.9; mol. wt (benzene) 520(30). Calc. for $ReClP_2OC_{18}H_{28}$: C, 39.7; H, 5.2%; mol. wt calc. 544.0.

^1H NMR (C_6D_6): δ 7.33 (m, 4, PMe_2*Ph*), 7.00 (m, 6, PMe_2*Ph*), 4.05 (d, 6, *cis*-J_{PH} = 7.1 Hz, Re*Me*), 1.47 (d, 6, J_{PH} = 8.9 Hz, P*Me*$_a$Me$_b$Ph), 1.41 (d, 6, J_{PH} = 9.5 Hz, PMe$_a$*Me*$_b$Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 131.50 (d, 1, J_{CP} = 3.3 Hz, PMe_2*Ph*), 131.47 (d, 1, J_{CP} = 3.3 Hz, PMe_2*Ph*), 130.9 (s, 1, PMe_2*Ph*), 129.54 (d, 1, J_{CP} = 3.3 Hz, PMe_2*Ph*), 129.51 (d, 1, J_{CP} = 3.3 Hz, PMe_2*Ph*), 18.7 (dd, 2, *trans*-J_{CP} = 44 Hz, *cis*-J_{CP} = 7 Hz, Re*Me*), 15.7 (AXY, J_{CP} = 33.7 Hz, $^3J_{CP}$ = 4.9 Hz, J_{PP} = −6.9 Hz, $\Delta P_X - \Delta P_Y$ = 1.7 Hz, P*Me*$_a$Me$_b$Ph), 14.5 (AXY, J_{CP} = 36.2 Hz, $^3J_{CP}$ = 4.5 Hz, J_{PP} = −5.0 Hz, $\Delta P_X - \Delta P_Y$ = 2.4 Hz, PMe$_a$*Me*$_b$Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −39.5 (s). IR: ν(Re═O) 999(s) [ν(Re═^{18}O) 948], 1438(m), 1419(w), 1370(w), 1315(w), 1307(w), 1290(m), 1279(w), 1239(w), 1161(w), 1109(m), 987(sh), 948(s), 912(sh), 907(s), 839(m), 752(m), 741(s), 711(w), 697(m), 679(w), 679(w), 510(w), 502(w), 489(m), 417(m), 404(m), 345(w), 327(w), 311(w), 301(w).

(3) *Chlorodimethyloxo(bis(dimethylphosphino)ethane)rhenium*(V), $ReOMe_2Cl(Me_2PCH_2CH_2PMe_2)$ (**2c**)

To a solution of $ReOMe_2Cl(PMe_2Ph)_2$ (0.275 g, 0.51 mmol) in toluene (25 cm^3) dmpe (0.106 cm^3,

0.58 mmol) was added via syringe. The brown solution was stirred (1 h), filtered and concentrated *in vacuo* (to *ca* 3 cm^3). Cooling (−20°C) produced brown crystals. (Yield 0.162 g, 0.39 mmol, 76%.) This compound was also prepared from $ReOMe_2Cl(PMe_3)_2$ in 62% yield by an analogous procedure. A satisfactory carbon analysis was not obtained. Found: C, 25.5; H, 5.4. Calc. for $ReClP_2OC_8H_{22}$: C, 23.0; H, 5.3%.

^1H NMR (C_6D_6): δ 3.76 (d, 6, *cis*-J_{PH} = 6.8 Hz, Re*Me*), 1.79 (m, 2, —C*H*$_2$PMe$_2$), 1.40 (d, 6, J_{PH} = 11.4 Hz, —CH$_2$P*Me*$_2$), 1.07 (d, 6, J_{PH} = 8.0 Hz, —CH$_2$P*Me*$_2$), 0.93 (m, 2, —C*H*$_2$PMe$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.9 (AXY, 2, J_{CP} = 41.0 Hz, $^3J_{CP}$ = 3.3 Hz, J_{PP} = −12 Hz, —*C*H$_2$PMe$_2$), 16.7 (AXY, 2, J_{CP} = 28.2 Hz, $^3J_{CP}$ = 10.1 Hz, J_{PP} = −4.3 Hz, $\Delta P_X - \Delta P_Y$ = 3.4 Hz, —CH$_2$P*Me*$_2$), 11.8 (AXY, 2, J_{CP} = 39.8 Hz, $^3J_{CP}$ = 7.1 Hz, J_{PP} = −5 Hz, $\Delta P_X - \Delta P_Y$ = 1.9 Hz, —CH$_2$P*Me*$_2$), 11.35 (AXY, 2, *trans*-J_{CP} = 37.5 Hz, *cis*-J_{CP} = 12.5 Hz, J_{PP} = −3.4 Hz, Re*Me*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.1 (s). IR: ν(Re═O) 1000(s) [ν(Re═^{18}O) 948], 1827(w), 1799(m), 1420(w), 1409(w), 1302(sh), 1288(m), 1246(w), 1180(br), 1107(w), 940(s), 919(w), 901(m), 867(w), 844(w), 748(m), 713(m), 650(m), 636(m), 510(m), 453(w), 362(w), 349(w).

(4) *Trimethyloxo(trimethylphosphine)rhenium*(V), $ReOMe_3(PMe_3)$ (**3a**)

To a cold solution (0°C) of $ReOMe_2Cl(PMe_2Ph)_2$ (0.050 g, 0.12 mmol) in toluene (20 cm^3) a toluene solution (5 cm^3) of $ZnMe_2$ (0.020 cm^3, 0.21 mmol) was added dropwise via an addition funnel over a period of 10 min. The solvent was then removed at 0°C under reduced pressure. The residue was extracted with cold pentane. Removal of the pentane under reduced pressure yielded a green oil. The yield was quantitative by ^1H NMR vs internal standard. The isolated yield was 47%. The material decomposed within days when stored at −20°C.

^1H NMR (C_7D_8, −57°C): 3.56 (s, 3, Re*Me*), 2.57 (d, 6, J_{PH} = 8.2 Hz, Re*Me*), 0.61 (d, 9, J_{PH} = 8.2 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_7D_8, −66°C): 32.2 (d, 1, J_{CP} = 25.3 Hz, Re*Me*), 18.0 (s, 2, Re*Me*), 12.6 (d, 2, J_{CP} = 31.3 Hz, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (C_7D_8, −23°C): δ −0.7 (s).

(5) *Trimethyloxo(dimethylphenylphosphine)rhenium*(V), $ReOMe_3(PMe_2Ph)$ (**3b**)

This compound was prepared by a procedure analogous to the one used for the preparation of $ReOMe_3(PMe_3)$. The yield was quantitative by ^1H NMR vs internal standard. The isolated yield was 51%.

^1H NMR (C_7D_8, −66°C): δ 7.26 (m, 2, PMe$_2$*Ph*), 7.04 (m, 3, PMe$_2$*Ph*), 3.66 (s, 3, Re*Me*), 2.62 (d, 6, J_{PH} = 8.7 Hz, Re*Me*), 0.85 (d, 6, J_{PH} = 9.1 Hz, P*Me*$_2$Ph). $^{13}C\{^1H\}$ NMR (C_7D_8, −66°C): δ 131.6 (d, 2, J_{CP} = 10.7 Hz, PMe$_2$*Ph*), 130.8 (s, 1, PMe$_2$*Ph*), 129.1 (2, PMe$_2$*Ph*), 31.8 (d, 1, J_{CP} = 24.9 Hz, Re*Me*), 18.9 (s, 2, Re*Me*), 12.5 (d, 2, J_{CP} = 30.7 Hz, P*Me*$_2$Ph). $^{31}P\{^1H\}$ NMR (C_7D_8, 23°C): δ −0.8 (s).

(6) *Trimethyloxo(bis(dimethylphosphino)ethane) rhenium*(V), $ReOMe_3$(dmpe) (**3c**)

This compound was prepared by a procedure similar to the one used for the preparation of $ReOMe_3(PMe_3)$. The compound is a red solid. (Yield 31%.)

^1H NMR (C_6D_6): δ 3.25 (dd, 3, J_{P_XH} = 7.8 Hz, J_{P_YH} = 6.6 Hz, Re*Me*), 2.94 (dd, 6, J_{P_XH} = 13.7 Hz, J_{P_YH} = 5.7 Hz, Re*Me*), 1.39 (d, 6, J_{PH} = 9.9 Hz, —CH$_2$P*Me*$_2$), 1.02 (m, 2, —C*H*$_2$PMe$_2$), 0.55 (m, 2, —C*H*$_2$PMe$_2$), 0.20 (d, 6, J_{PH} = 7.5 Hz, —CH$_2$P*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 28.8 (m, 1, —*C*H$_2$PMe$_2$), 25.9 (dd, 1, J_{CP_X} = 20.5 Hz, J_{CP_Y} = 17.5 Hz, Re*Me*), 24.7 (m, 1, —*C*H$_2$PMe$_2$), 17.2 (m, 2, CH$_2$P*Me*$_2$), 17.0 (dd, 2, J_{CP_X} = 17.5 Hz, J_{CP_Y} = 12.5 Hz, Re*Me*), 7.7 (m, 2, CH$_2$P*Me*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −3.0 (d, J_{PP} = 29 Hz), −34.7 (d, J_{PP} = 29 Hz). IR: ν(Re═O) 1018(s), 1419(m), 1360(sh), 1299(m), 1283(m), 1239(m), 1252(m), 1221(m), 980(m), 938(s), 927(sh), 910(m), 894(m), 835(m), 793(w), 703(m), 649(w).

(7) *Trimethyloxo(bipyridine)rhenium*(V), $ReOMe_3$(bipy) (**4**)

To a cold (0°C) solution of $ReOMe_2Cl(PMe_2Ph)_2$ (0.050 g, 0.09 mmol) in toluene (30 cm^3) a toluene solution (5 cm^3) of $ZnMe_2$ (0.020 cm^3, 0.21 mmol) was added dropwise via an addition funnel. After the addition was complete, the solvent was removed at 0°C *in vacuo*. The residue was extracted with cold pentane, and the pentane solution added to a flask containing an excess of bipy (0.050 g, 0.32 mmol). The mixture slowly changed colour from green to blue (2 h). Solvent and the excess bipy were then removed *in vacuo*. Crystallization from pentane (−50°C) gave blue crystals. (Yield 0.013 g, 0.03 mmol, 35%.)

^1H NMR (C_6D_6): δ 8.81 (m, 1, *bipy*), 7.77 (d, 1, bipy), 7.25 (m, 1, bipy), 6.79 (d, 1, bipy), 6.50 (dt, 1, bipy), 6.23 (dq, 2, bipy), 5.34 (m, 1, bipy), 3.92 (s, 3, Re*Me*), 2.83 (s, 6, Re*Me*). IR: ν(Re═O) 970(s), 1602(m), 1588(m), 1579(sh), 1562(w), 1419(sh),

1312(m), 1260(m), 1239(m), 1150(w), 1010(w), 990(w), 957(sh), 900(m), 752(s), 511(w).

(8) *Dimethyloxo(acetonitrile)bis(trimethylphosphine) rhenium*V) *tetrafluoroborate*, $[ReOMe_2(PMe_3)_2(CH_3CN)][BF_4]$ (**5a**)

To a mixture of $ReOMe_2Cl(PMe_3)_2$ (0.100 g, 0.24 mmol) and $[Ag(CH_3CN)_2][BF_4]$ (0.065 g, 0.24 mmol) cold acetonitrile (25 cm^3, 0°C) was added. A white powder formed immediately. The solution was stirred (1 h), filtered, and then the solvent removed *in vacuo* to yield a red oil. (Yield 0.086 g, 0.17 mmol, 71%.) Two isomers were observed in solution (the *cis–trans* ratio at 24°C in CD_3CN is 3:1). Found: C, 23.4; H, 5.1; N, 2.9. Calc. for $ReP_2F_4ONC_{10}BH_{27}$: C, 23.4; H, 5.3; N, 2.7%.

IR: 2287(w), 1314(sh), 1292(m), 1235(s), 1120(br), 1030(br), 1010(m), 950(m), 905(m), 848(w), 761(w).

cis isomer. ^1H NMR (CD_3CN): δ 3.0 (dd, 6, *cis*-J_{PH} = 7.3 Hz, *trans*-$J_{P'H}$ = 2.3 Hz, Re*Me*), 1.9 (s, 3, C*H*$_3$CN), 1.83 (d, 18, J_{PH} = 10.3 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 18.0 (AXY, 2, J_{CP} = 23 Hz, $^3J_{CP}$ = 10.5 Hz, J_{PP} = −17 Hz, $\Delta P_X - \Delta P_Y$ = 1.9 Hz, P*Me*$_3$), 14.4 (dd, 2, *trans*-J_{CP} = 15 Hz, *cis*-J_{CP} = 9 Hz, Re*Me*). $^{31}P\{^1H\}$: δ −36.1 (s).

trans isomer. ^1H NMR (CD_3CN): δ 3.73 (t, 6, J_{PH} = 6.3 Hz, Re*Me*), 1.95 (s, 3, C*H*$_3$CN), 1.73 (virtual triplet, 18, $J_{PH} = J_{P'H}$ = 5.1 Hz, P*Me*$_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): 14.72 (virtual triplet, 6, $J_{CP} = {}^3J_{CP}$ = 17 Hz, P*Me*$_3$), −6.1 (t, 2, J_{CP} = 5 Hz, Re*Me*). $^{31}P\{^1H\}$ (CD_3CN): δ −32.9 (s).

(9) *Dimethyloxo(acetonitrile)bis(dimethylphenylphosphine)rhenium*(V) *tetrafluoroborate*, $[ReOMe_2(PMe_2Ph)_2(CH_3CN)][BF_4]$ (**5b**)

This compound was prepared by a procedure similar to the one used for the preparation of $[ReOMe_2(PMe_3)_2(CH_3CN)][BF_4]$. The compound was isolated as a red–orange oil. (Yield 65%.) Two isomers were observed in solution (the *cis–trans* ratio at 24°C in CD_3CN is 2:1).

IR: 2255(w), 2240(m), 1440(sh), 1308(m), 1289(w), 1236(m), 1060(vbr), 980(br), 956(w), 895(m), 870(sh), 838(w), 740(s), 690(m), 675(w), 518(m), 483(s), 412(m), 397(sh).

cis isomer. ^1H NMR (CD_3CN): δ 7.62 (m, 2, PMe_2*Ph*), 7.51 (m, 3, PMe_2*Ph*), 3.08 (dd, 6, *cis*-J_{PH} = 9.4 Hz, *trans*-$J_{P'H}$ = 2.0 Hz, Re*Me*), 1.95 (s, 3, C*H*$_3$CN), 1.90 (d, 6, J_{PH} = 10 Hz, P*Me*$_2$Ph), 1.85 (d, 6, J_{PH} = 9.9 Hz, P*Me*$_2$Ph). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 132.1 (s, 2, PMe_2*Ph*), 131.82 (d, 2, J_{PC} = 3.5 Hz, PMe_2*Ph*), 131.77 (d, 2, J_{CP} = 3.5 Hz, PMe_2*Ph*), 131.46 (d, 2, J_{CP} = 3.7 Hz, PMe_2*Ph*), 131.41 (d, 2, J_{CP} = 3.7 Hz, PMe_2*Ph*), 130.15 (d, 2, J_{CP} = 4.5 Hz, PMe_2*Ph*), 16.25 (AXY, 2, J_{CP} = 30 Hz, $^3J_{CP}$ = 2.2 Hz, J_{PP} = −12.2 Hz, $\Delta P_X - \Delta P_Y$ = 2.0 Hz, P*Me*$_a$Me$_b$Ph), 14.96 (AXY, 2, J_{CP} = 32.2 Hz, $^3J_{CP}$ = 1.3 Hz, J_{PP} = −12.2 Hz, $\Delta P_X - \Delta P_Y$ = 2.4 Hz, PMe$_a$*Me*$_b$Ph), 16.5 (dd, 2, *trans*-J_{CP} = 16 Hz, *cis*-J_{CP} = 2 Hz, Re*Me*). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −28.1 (s).

trans isomer. ^1H NMR (CD_3CN): δ 7.62 (m, 2, PMe_2*Ph*), 7.51 (m, 3, PMe_2*Ph*), 3.65 (t, 6, J_{PH} = 6.4 Hz, Re*Me*), 2.02 (virtual triplet, 12, $J_{P'H} = J_{PH}$ = 4.6 Hz, P*Me*$_2$Ph), 1.95 (s, 3, C*H*$_3$CN). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 132.1 (s, 2, PMe_2*Ph*), 131.82 (d, 2, J_{PC} = 3.5 Hz, PMe_2*Ph*), 131.77 (d, 2, J_{PC} = 3.5 Hz, PMe_2*Ph*), 131.46 (d, 2, J_{PC} = 3.7 Hz, PMe_2*Ph*), 131.41 (d, 2, J_{PC} = 3.7 Hz, PMe_2*Ph*), 130.0 (t, 2, J_{PC} = 4.5 Hz, PMe_2*Ph*), 13.87 (virtual triplet, 4, $J_{CP} = {}^3J_{CP}$ = 17.2, P*Me*$_2$Ph), −3.1 (t, 2, J_{CP} = 4.5 Hz, Re*Me*). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −23.4 (s).

(10) *Dimethyloxo(acetonitrile)(bis(dimethylphosphino)ethane)rhenium*(V) *tetrafluoroborate*, $[ReOMe_2(Me_2PCH_2CH_2PMe_2)(CH_3CN)][BF_4]$ (**5c**)

This compound was prepared by a procedure similar to the one used for the preparation of $[ReOMe_2(PMe_3)_2(CH_3CN)][BF_4]$. The compound was isolated as a red–brown solid. (Yield 68%.) Found: C, 23.6; H, 5.1; N, 2.5. Calc. for $ReP_2F_4ONC_{10}BH_{25}$; C, 23.5; H, 4.9; N, 2.7%.

^1H NMR (CD_3CN): δ 2.96 (dd, 6, *cis*-J_{PH} = 5.8 Hz, *trans*-$J_{P'H}$ = 2.5 Hz, Re*Me*), 2.20 (m, 4, —C*H*$_2$PMe$_2$), 1.91 (d, 6, J_{PH} = 11.5 Hz, —CH$_2$ P*Me*$_2$), 1.69 (d, 6, J_{PH} = 11.5 Hz, —CH$_2$P*Me*$_2$). $^{13}C\{^1H\}$: δ 31.5 (AXY, 2, J_{CP} = 42 Hz, $^3J_{CP}$ = 1 Hz, J_{PP} = −16 Hz, $\Delta P_X - \Delta P_Y$ = 1.7 Hz, —*C*H$_2$ PMe$_2$), 15.8 (AXY, 2, J_{PC} = 27.2 Hz, $^3J_{CP}$ = 1 Hz, J_{PP} = −10.8 Hz, $\Delta P_X - \Delta P_Y$ = 3.3 Hz, —CH$_2$ P*Me*$_a$Me$_b$), 10.6 (AXY, 2, J_{CP} = 36 Hz, $^3J_{CP}$ = 2.3 Hz, J_{PP} = −12.8 Hz, $\Delta P_X - \Delta P_Y$ = 3.7 Hz, —CH$_2$PMe$_a$*Me*$_b$), 4.9 (m, 2, Re*Me*). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 22.6 (s). IR: 1421(sh), 1302(m), 1297(m), 1250(w), 1210(w), 1186(w), 1135(sh), 1095(s), 1055(s), 1040(s), 1010(s), 955(s), 940(s), 921(sh), 906(sh), 870(s), 851(m), 793(w), 755(m), 651(m), 520(m), 500(sh), 450(m), 355(w), 335(w).

Crystallographic studies

Crystal data. $ReOClMe_2(PMe_3)_2$ at −80(1)°C: M = 419.9; monoclinic, space group $P2_1/n$, a = 6.632(4), b = 12.729(4), c = 17.495(6) Å, β = 93.08(4)°, Z = 4, D_c = 1.891 g cm^{-3}, μ(Mo-K_α) = 87.21 cm^{-1}.

Data collection. X-ray data were collected on a

Nicolet R3 four-circle diffractometer equipped with a LT-1 low-temperature device. Data collection was controlled using the Nicolet program P3. Raw diffractometer data were processed using the program XDISK. An empirical absorption correction was performed with the program PSICOR. $4 \leqslant 2\theta \leqslant 45°$, $T = 193$ K, 4366 data measured, 1930 unique, 1741 observed [$F_o > 6\sigma(F_o)$].

Structure solution and refinement. The structure was solved and refined using the SHELXTL-PLUS (microVax II) packages of programs. The rhenium atom was found by use of a Patterson synthesis. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed approximately one half of the hydrogen positions. The hydrogen atoms were therefore placed in calculated positions on the appropriate carbon atoms ($U_{iso}(H) = 1.2U_{iso}(C)$; d_{C-H} 0.96 Å) for refinement. Refinement was performed to convergence [$\Delta/\sigma(\max) < 0.001$] with this model. The values of R, R_w were 0.0335 and 0.0401, respectively, and the weighting scheme was $w = [\sigma^2(F) + 0.0018F^2]^{-1}$. The final difference map contained two peaks (1.63 and 1.44 eÅ^{-3}) within 1.00 Å of the rhenium. All other peaks were less than 0.90 eÅ^{-3}.

Final atomic coordinates, a table of anisotropic thermal parameters and a F_o/F_c listing have been deposited with the Editor as supplementary material.

Acknowledgement—The authors thank the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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