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Synthesis and structures of technetium(I) and rhenium(I) tricarbonyl complexes with bis(diphenylthiophosphoryl)amide, $\{M(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ (M = Tc, Re)

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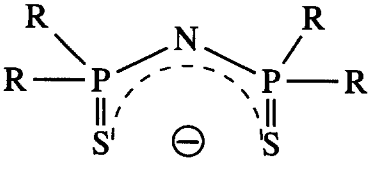
Abstract—Complexes of the general formula $\{M(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ (M = Tc, Re) have been prepared by the reaction of $(Et_4N)_2[M(CO)_3X_3]$ (M = Tc, Re; X = Cl, Br) with sodium bis(diphenylthiophosphoryl)amide, $Na[(Ph_2PS)_2N]$, in acetonitrile. The metal is six-coordinate with facially arranged carbonyl ligands. Bis(diphenylthiophosphoryl)amide is deprotonated and bonded as S,S′-chelate with Tc—S distances of 2.526(3) and 2.546(3) Å. Acetonitrile occupies the sixth coordination position. The rhenium compound is isomorphous and the bonding situation in $\{Re(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ is similar to that in its technetium analogue. $(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$ crystallizes from a hot acetonitrile solution of $(Et_4N)_2[Re(CO)_3Br_3]$ despite the fact that in solution only $[Re(CO)_3(CH_3CN)_3]^+$ can be detected spectroscopically. It has a facial arrangement of CO groups in an octahedral co-ordination geometry. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: technetium; rhenium; carbonyl complexes; sulphur donor ligands; X-ray structures.

Bis(dialkylthiophosphoryl)amides and bis(diarylthiophosphoryl)amides (**I**) have been shown to be a versatile class of ligands which can easily be substituted to meet the specific requirements of the metals to be co-ordinated or of potential applications of the products [1,2]. Complexes with the tetraphenyl substituted amide have been discussed as models for the co-ordination sites of metalloenzymes [1]. Tetrahedral bis-co-ordinated complexes with divalent metal ions have been confirmed for Ni^{II} and Cu^{II} by X-ray crystallography and EPR spectroscopy [3,4].



I

The capabilities of the ligands to adopt the specific co-ordination requirements of the metals makes them interesting for the chemistry of technetium and rhenium which is of interest for diagnostic (^{99m}Tc: γ-emitter, half-life: 6 h) or therapeutic (^{186}Re, β^--emitter) nuclear medicine [5,6]. Rossi *et al.* [7,8] studied the co-ordination behaviour of $Ph_2P(X)NH(X)PPh_2$

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(X = O or S) and K[$Ph_2P(Se)N(Se)PPh_2$] towards the [ReO]$^{3+}$ core and reported a considerable tendency for the products to decompose with loss of chalcogen donor atoms. It has been found more recently that the nitrogen containing [ReN]$^{2+}$ and [ReNMe]$^{3+}$ cores are more suitable to stabilize complexes with the "soft" sulphur donor sites of [$(Ph_2PS)_2N$]$^-$ than the oxorhenium(V) centre [9,10]

In the present paper, synthesis and structures of technetium(I) (using the long-lived isotope ^{99}Tc which is a weak β^--emitter with $t_{1/2} = 2.12 \times 10^5$ years) and rhenium(I) tricarbonyl complexes are described which demostrate that bis(diphenylthiophosphoryl)amide is also able to stabilize monomeric, low-valent metal complexes.

EXPERIMENTAL

The starting complexes $(Et_4N)_2[Tc(CO)_3Cl_3]$ and $(Et_4N)_2[Re(CO)_3Br_3]$ have been prepared by procedures reported previously [11,12]. $(Ph_2PS)_2NH$ was prepared from PPh_2Cl, $NH(SiMe_3)_2$ and sulphur as outlined in ref. 13 and converted into the sodium salt by the reaction with NaOMe. IR spectra were recorded as KBr pellets on a Perkin-Elmer Specord 75 IR. Mass spectra were recorded on a MAT TSQ-70 spectrometer (Finnigan). For FAB measurements xenon was used as primary beam gas. The ion gun was operated at 8 kV and 100 μA (probe temperature: 30°C) nitrobenzylalcohol was used as the matrix. ^{99}Tc and ^{31}P NMR spectra were recorded on Varian Gemini 2000 (300 MHz) and JEOL EX-270 spectrometers with H_3PO_4 and NH_4TcO_4 as references.
CAUTION! ^{99}Tc is a weak β-emitter. Although radiation from small amounts of material is completely absorbed by the glass walls, all operations have been carried out in a specially equipped laboratory under well ventilated hoods to avoid contamination or ingestion.

{$Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)$}

55 mg (0.1 mmol) $(Et_4N)_2[Tc(CO)_3Cl_3]$ were dissolved in 10 ml acetonitrile and a solution of 51 mg (0.11 mmol) Na[$(Ph_2PS)_2N$] in 5 ml CH_3CN was added dropwise. The colourless reaction mixture was heated under reflux for 1.5 h and the volume was reduced to about 3 ml. After standing overnight, colourless crystals formed which were filtered off and washed with a small amount of cold methanol. Recrystallization from CH_3CN. Yield: 80%. Found: Tc, 15.7%; $C_{29}H_{23}N_2O_3P_2S_2Tc$ requires: Tc, 15.3%. IR: ν(CO) 1925, 1953, 2035 cm^{-1} (st), ν(CN) 2362 cm^{-1} (w). ^{99}Tc-NMR: −1266 ppm (s).

{$Re(CO)_3[(Ph_2PS)_2N](CH_3CN)$}

The complex was prepared as the technetium analogue starting from 77 mg (0.1 mmol) $(Et_4N)_2[Re(CO)_3Br_3]$ and 51 mg (0.11 mmol) Na[$(Ph_2PS)_2N$] in acetonitrile. Colourless crystals. Yield: 75%. Found: C, 44.65; H, 3.23; N, 3.91; S, 8.15%; $C_{29}H_{23}N_2O_3P_2S_2Re$ requires: C, 45.79; H, 3.03; N, 3.68; S, 8.42%. IR: ν(CO) 1919, 1948, 2043 cm^{-1} (st), ν(CN) 2362 cm^{-1} (w). ^{31}P-NMR: 38.7 ppm (s). FAB$^+$ MS: $m/z = 760$ ([M]$^+$, 5% B), $m/z = 719$ {$(Re(CO)_3[(Ph_2PS)_2N]$}$^+$, 100% B), $m/z = 691$ {$(Re(CO)_2[(Ph_2PS)_2N]$}$^+$, 45% B), $m/z = 663$ {$(Re(CO)[(Ph_2PS)_2N]$}$^+$, 20% B).

{$Re(CO)_3[(Ph_2PS)_2N](py)$}

76 mg (0.1 mmol) {$Re(CO)_3[(Ph_2PS)_2](CH_3CN)$} were dissolved in 10 ml $CHCl_3$ and a few drops of pyridine were added. The mixture was heated on reflux for 10 min and allowed to cool to room temperature. Upon slow evaporation of the solvent a colourless solid precipitated which was removed by filtration and rinsed with a minimum amount of cold methanol. Yield 65%. Found: C, 47.92; H, 3.10; N, 3.19%; $C_{32}H_{25}N_2O_3P_2S_2Re$ requires C, 48.12; H, 3.13; N, 3.51%. IR: ν(CO) 1924, 1962, 2020 cm^{-1} (st). ^{31}P-NMR: 38.5 ppm (s). FAB$^+$ MS: $m/z = 798$ ([M]$^+$, 5% B), $m/z = 719$ ({$Re(CO)_3[(Ph_2PS)_2N]$}$^+$, 100% B), $m/z = 691$ ({$Re(CO)_2[(Ph_2PS)_2N]$}$^+$, 25% B), $m/z = 663$ ({$Re(CO)[(Ph_2PS)_2N]$}$^+$, 20% B).

$(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$

77 mg (0.1 mmol) $(Et_4N)_2[Re(CO)_3Br_3]$ were dissolved in 10 ml acetonitrile and refluxed for 1 h. Upon slow evaporation of the solvent colourless crystals formed which were collected and rinsed with a minimum amount of cold water to remove $(Et_4N)Br$. Yield: almost quantitative. Found: C, 25.85; H, 3.91; N, 4.31%; $C_{13}H_{23}N_2O_3Br_2Re$ requires: C, 25.91; H, 3.82; N, 4.65%. IR: ν(CO) 1945, 1971, 2055 cm^{-1} (st), ν(CN) 2360 cm^{-1} (w). FAB$^-$ MS: $m/z = 472$ ([M]$^-$, 7% B), $m/z = 431$ ([$Re(CO)_3Br_2$]$^-$, 100% B), $m/z = 403$ ([$Re(CO)_2Br_2$]$^-$, 15% B), $m/z = 475$ ([$Re(CO)Br_2$]$^-$, 20% B), $m/z = 350$ ([$Re(CO)_3Br$]$^-$, 60% B).

X-Ray structure determinations

The intensities for the X-ray determinations were collected on an automated single crystal diffractometer of the type CAD4 (Enraf-Nonius, Delft) using Mo-K_α radiation with ω-scans. The unit cell dimensions were determined from the angular settings of 25 high-angle reflections. The structures were solved by Patterson synthesis using SHELXS86 [14]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL93 [15]. The hydrogen atoms were included at calculated positions and refined using the "riding model" option of

SHELXL93. Crystal data and more details of the data collections and refinements are contained in Table 1. Additional information on the structure determinations has been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Recently, we reported on the synthesis of $(Et_4N)_2[M(CO)_3X_3]$ complexes (M = Tc, Re; X = Cl, Br) starting directly from the tetrabutylammonium permetallates and applying 1 atm of CO [11,12]. Dissolution of the complexes in co-ordinating solvents results in the replacement of only the weakly bound halide ligands and the formation of solvent complexes of the composition $[M(CO)_3(solv)_3]^+$. The course of the ligand exchange can easily be followed by IR spectroscopy [11]. After removing X^- by silver ions the addition of PF_6^- results in precipitation of the solvent complexes. Thus, the dissolution of $(Et_4N)_2[Re(CO)_3Br_3]$ or $(Et_4N)_2[Tc(CO)_3Cl_3]$ in acetonitrile and addition of $AgPF_6$ represents high yield syntheses of the well known complexes $[M(CO)_3(CH_3CN)_3]PF_6$. For further ligand exchange reactions, however, the readily soluble solvent complexes can be used without isolation. In particular, chelating ligands and good π-acceptors easily replace the weakly bound solvent ligands from the electron-rich metal centre. Upon dissolution of $(Et_4N)_2[Re(CO)_3Br_3]$ in acetonitrile and slow evaporation of the solution without removing the bromide anions $(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$ can be isolated.

The reactions of the *in situ* generated $[M(CO)_3(CH_3CN)_3]^+$ cations with approximately equimolar amounts of sodium bis(diphenylthiophosphoryl) amide (I) in acetonitrile, give the neutral complexes $\{M(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ in good yields. Co-ordination of a second molecule $(Ph_2PS)_2N^-$ could not be observed, even when a large excess of ligand was used. In the latter case, however, the formation of considerable amounts of $(Ph_2PS)_2NH$ is observed when the solvent has not been tried very carefully prior to use. This causes serious problems in the isolation of pure $\{M(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ complexes and can be avoided by an $(Et_4N)_2[M(CO)_3X_3]/Na[(Ph_2PS)_2N]$ ratio not exceeding 1 : 1.1.

$\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ is a colourless solid which crystallizes as large plates directly from the reaction mixture. The compound is soluble in warm acetonitrile, only sparingly soluble in alcohols and nearly insoluble in hydrocarbons. No decomposition could be detected in the solid state over a period of 4 weeks. In coordinating solvents (e.g. thf or pyridine), however, a ligand exchange acetonitrile vs solvent can be observed. This is a route for the synthesis of further derivatives containing the $\{Tc(CO)_3[(Ph_2PS)_2N]\}$ moiety.

The infrared spectrum of $\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ in KBr shows a typical "*fac*-$Tc(CO)_3$" pattern for a slightly distorted C_{3v} symmetry with intense bands at 2035 (A_1), 1953 and 1925 (E) cm^{-1}. The coordinated acetonitrile shows a weak band at 2362 cm^{-1}. The ^{99}Tc resonance of the diamagnetic technetium(I) complex ($4d^6$) can be observed at −1266 ppm vs TcO_4^-. This value agrees well with those found for other neutral technetium(I) tricarbonyls. Cationic compounds of comparable structures show significantly highfield shifted ^{99}Tc NMR signals [18–20].

$\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ crystallizes triclinic in the space group $P\bar{1}$. An ORTEP representation [21] of the molecular structure along with the atomic numbering scheme is given in Fig. 1. Selected bond lengths and angles are summarized in Table 2. The metal has a distorted octahedral coordination sphere with facially arranged carbonyls. The Tc—S bond lengths of 2.526(3) and 2.546(2) Å are longer by about 0.1 Å than those in the five-coordinate bis-chelate $\{Tc^VN[(Ph_2PS)_2N]_2\}$ [10]. This can easily be understood by the strong *trans* influence of the carbonyls. A similar tendency has been observed at Tc^V complexes when phosphines are co-ordinated *trans* to $(Ph_2PS)_2N^-$ [22]. The P—S distances are lengthened by a mean value of 0.07 Å and the P—N distances shortened by 0.09 Å with regard to the pro-ligand [23]. This relates to delocalization of electron density in the chelate rings although the six-membered ring is not planar. The pairs of P—S and P—N distances are almost equal as is expected for a chelate ring with delocalized electron density. The same situation has been observed in the structures of Re^V with $[(Ph_2PS)_2N]^-$ [7–10]. In contrast to that, the indium(III) complex $\{In[(Ph_2PS)_2N]_2Cl\}$ shows a "non-symmetric" co-ordination of the ligand with different S—P and P—N bond lengths in the chelate rings suggesting co-ordination with distinct "thiolate" and "phosphorus sulphide" donor sites [24].

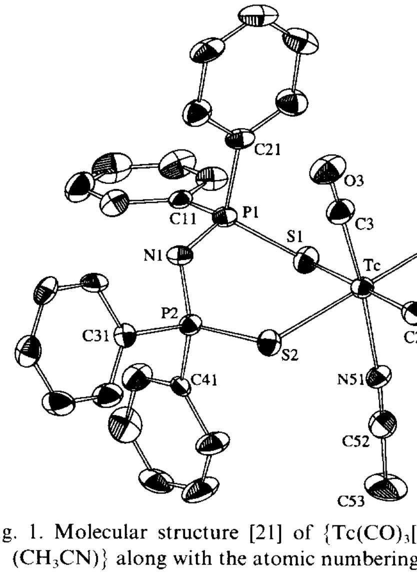

Fig. 1. Molecular structure [21] of $\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ along with the atomic numbering scheme.

Table 1. X-ray structure data collection and refinement parameters

	$\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$	$\{Re(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$	$(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$
Crystal dimensions (mm^3)	0.3·0.1·0.1	0.25·0.15·0.05	0.5·0.3·0.2
Formula	$C_{29}H_{23}N_2O_3P_2S_2Tc$	$C_{29}H_{23}N_2O_3P_2S_2Re$	$C_{13}H_{23}N_2O_3Br_2Re$
M	671.55	759.75	601.35
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell	a = 10.693(9) Å b = 11.18(1) Å c = 12.96(1) Å α = 76.19(7)° β = 75.11(7)° γ = 86.95(6)°	a = 10.709(4) Å b = 11.176(4) Å c = 12.901(4) Å α = 76.34(3)° β = 75.33(3)° γ = 87.45(2)°	a = 8.440(4) Å b = 10.177(5) Å c = 11.740(7) Å α = 91.87(3)° β = 111.04(3)° γ = 91.69(3)°
V ($Å^3$)	1454(2)	1451.3(9)	939.8(9)
Z	2	2	2
D_c ($g\ cm^{-3}$)	1.533	1.739	2.125
Linear absorption coefficient (mm^{-1})	0.782	4.475	10.726
Absorption correction	None	DIFABS [16]	DIFABS [16]
T_{min}		0.417	0.402
T_{max}		1.000	1.000
Weighting scheme ($P = (F_o^2+2F_c^2)/3$)	$w = 1/[\sigma^2(F_o^2)+(0.0272P)^2]$	$w = 1/[\sigma^2(F_o^2)+(0.0635P)^2]$	$w = 1/[\sigma^2(F_o^2)+(0.0677P)^2+3.6223P]$
Measured reflections	6017	5368	3879
Independent reflections	5119	4548	3283
Independent reflections ($I > 2\sigma(I)$)	3114	3841	2975
Refined parameters	352	352	202
$R_1(F)/wR2(F^2)$	0.055/0.0857	0.039/0.093	0.034/0.093
GooF	1.002	1.038	1.038
Programs used	SHELXS86 [14], SHELXL93 [15], PLATON, HELENA [17]	SHELXS86 [14], SHELXL93 [15], PLATON, HELENA [17]	SHELXS86 [14], SHELXL93 [15], PLATON, HELENA [17]

Table 2. Selected bond lengths and angles in $\{Tc(CO)_3[Ph_2PS)_2N](CH_3CN)\}$ and $\{Re(CO)_3[Ph_2PS)_2N](CH_3CN)\}$

	$\{Tc(CO)_3[Ph_2PS)_2N](CH_3CN)\}$	$\{Re(CO)_3[Ph_2PS)_2N](CH_3CN)\}$
M—C(1)	1.893(7)	1.913(9)
M—C(2)	1.900(7)	1.914(8)
M—C(3)	1.920(7)	1.933(7)
M—S(1)	2.546(3)	2.528(2)
M—S(2)	2.526(3)	2.544(2)
M—N(51)	2.155(6)	2.147(6)
N(51)—C(52)	1.124(7)	1.125(10)
C(1)—O(1)	1.147(7)	1.145(9)
C(2)—O(2)	1.155(7)	1.126(9)
C(3)—O(3)	1.142(7)	1.133(9)
S(1)—P(1)	2.012(3)	2.021(3)
P(1)—N(1)	1.590(5)	1.600(6)
P(2)—N(1)	1.592(5)	1.582(6)
S(2)—P(2)	2.013(3)	2.017(3)
C(1)—M—C(2)	88.8(3)	88.9(3)
C(1)—M—C(3)	90.5(3)	88.3(3)
C(1)—M—S(1)	85.9(2)	89.6(2)
C(1)—M—S(2)	177.3(2)	170.6(2)
C(1)—M—N(51)	95.6(2)	91.7(3)
C(2)—M—C(3)	88.0(3)	90.4(3)
C(2)—M—S(1)	171.3(2)	178.3(2)
C(2)—M—S(2)	88.9(2)	85.7(2)
C(3)—M—S(1)	98.9(2)	88.9(2)
C(3)—M—S(2)	87.9(2)	99.5(2)
C(3)—M—N(51)	173.9(3)	173.9(3)
S(1)—M—S(2)	96.52(9)	95.87(7)
S(1)—M—N(51)	82.0(2)	85.0(2)
S(2)—M—N(51)	85.9(2)	81.1(2)
M—C(1)—O(1)	176.8(6)	176.7(6)
M—C(2)—O(2)	175.8(6)	177.5(7)
M—C(3)—O(3)	174.9(6)	174.8(8)
M—S(1)—P(1)	104.7(1)	109.2(1)
S(1)—P(1)—N(1)	117.6(2)	119.2(3)
N(1)—P(2)—S(2)	119.7(2)	117.5(2)
M—S(2)—P(2)	108.8(1)	104.72(9)
M—N(51)—C(52)	173.6(5)	174.0(7)

Deviations from an idealized octahedron can be observed for the first co-ordination sphere of technetium in $\{Tc(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ (*cis* angles between 82.0 and 98.9°). The Tc—C bond *trans* to CH_3CN is slightly longer than the others suggesting a somewhat stronger *trans* influence of the acetonitrile ligand compared with the sulphur donor sites.

The bonding situation in $\{Re(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ is very similar to that in the technetium analogue. Therefore, the corresponding bond lengths and angles are compared in Table 2. An ellipsoid representation of the rhenium complex is given in Fig. 2. In both complexes M—N bond to the acetonitrile ligand is long by 2.155(6) and 2.147(6) Å, respectively. The suggested lability of this position is confirmed by the chemical behaviour of the complexes.

Dissolution of $\{Re(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ in $CHCl_3$ and addition of pyridine results in the for-

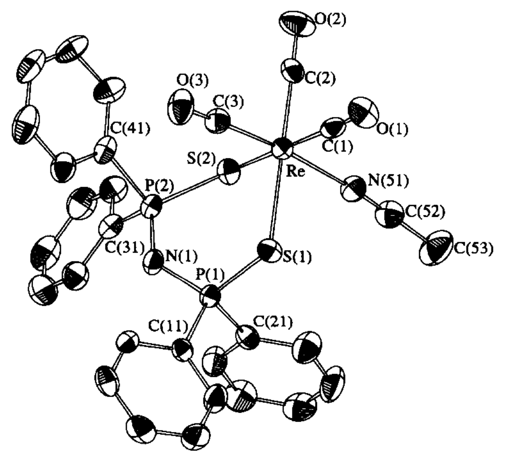

Fig. 2. Molecular structure [21] of $\{Re(CO)_3[(Ph_2PS)2N](CH_3CN)\}$ along with the atomic numbering scheme.

mation of $\{Re(CO)_3[(Ph_2PS)_2N](py)\}$ which can be isolated upon evaporation of the solvent. The colourless solid has been characterized spectroscopically.

The lability of acetonitrile ligands in rhenium tricarbonyl complexes can also be demonstrated by evaporation of a CH_3CN solution of $[Re(CO)_3(CH_3CN)_3]^+$ which has been prepared by dissolution of $[Re(CO)_3Br_3]^{2-}$ without removing the bromide ions by addition of a silver salt. Despite the infrared spectrum of such a solution, it is clearly identical to those of isolated $[Re(CO)_3(CH_3CN)_3]^+$ and solutions from which Br^- has been completely removed [11] and a ligand re-exchange CH_3CN vs Br^- can be observed upon concentration and colourless crystals of the $(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$ deposit.

$(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$ crystallizes triclinic in the space group $P\bar{1}$. Figure 3 shows an ORTEP plot of the complex anion. Table 3 contains selected bond lengths and angles. The facially arranged carbonyl ligands induce long Re—Br bond lengths of 2.623(2) and 2.632(2) Å, respectively. These values are in agreement with other Re—Br bonds in rhenium(I) complexes and in *trans* position to CO (2.633(1)–2.662(1) Å in $[Re(CO)_3Br_3]^{2-}$ [12], 2.638(1) Å in [Re2(CO)6Br_2(tetraphos)] [12], 2.624(1)–2.647(2) Å in rhenium(I) tricarbonyl complexes with thiourea derivatives [25]), but longer than in the rhenium(III) complex *cis*-$[Re(CO)_2Br4]^-$, where the Re—Br bond *trans* to CO is 2.542(1) Å [26]. As observed in the $\{Re(CO)_3[(Ph_2PS)_2N](CH_3CN)\}$ complexes, the Re—(CO) bond *trans* to acetonitrile is slightly longer than the others (0.04 Å in $[Re(CO)_3Br_2(CH_3CN)]^-$). The co-ordination geometry of rhenium comes close to an idealized octahedron with *cis* angles between 86.1(2) and 93.6(2)° and *trans* angles between 177.2(2) and 179.1(3)°.

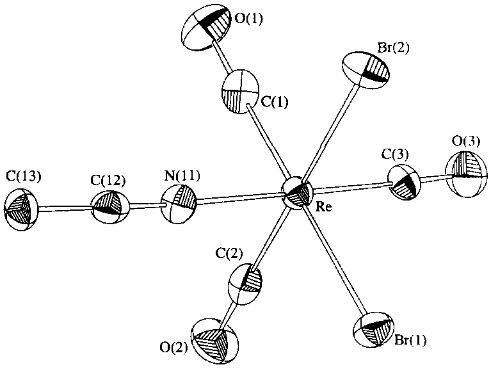

Fig. 3. Structure [21] of the complex anion in $(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$ along with the atomic numbering scheme.

CONCLUSIONS

$[M(CO)_3X_3]^{2-}$ complexes (M=Tc, Re; X=Cl, Br) can be used as reactive starting materials for the synthesis of further rhenium(I) and technetium(I) tricarbonyl complexes. The halide ligands are only weakly bound and readily substituted by co-ordinating solvents. Addition of chelating ligands like $[(Ph_2PS)_2N]^-$ results in neutral, monomeric metal(I) tricarbonyl complexes with one remaining co-ordinated solvent molecule. The *in situ* produced $[Re(CO)_3(solvent)_3]^+$ complexes show a ligand rearrangement (solvent vs halide) upon concentration of their solutions.

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Table 3. Selected bond lengths and angles in $(Et_4N)[Re(CO)_3Br_2(CH_3CN)]$

Re—C(1)	1.881(8)	N(11)—C(12)	1.14(1)
Re—C(2)	1.884(8)	C(12)—C(13)	1.45(1)
Re—C(3)	1.922(7)	C(1)—O(1)	1.17(1)
Re—Br(1)	2.623(2)	C(2)—O(2)	1.17(1)
Re—Br(2)	2.632(2)	C(3)—O(3)	1.124(9)
Re—N(11)	2.150(6)		

C(1)—Re—C(2)	91.6(2)	C(3)—Re—Br(2)	93.1(2)
C(1)—Re—C(3)	88.0(3)	C(3)—Re—N(11)	179.1(3)
C(1)—Re—Br(1)	177.4(2)	Br(1)—Re—Br(2)	87.89(5)
C(1)—Re—Br(2)	90.0(2)	Br(1)—Re—N(11)	86.1(2)
C(1)—Re—N(11)	92.2(3)	Br(2)—Re—N(11)	86.1(2)
C(2)—Re—C(3)	89.2(3)	Re—C(1)—O(1)	179.5(7)
C(2)—Re—Br(1)	90.4(2)	Re—C(2)—O(2)	178.5(7)
C(2)—Re—Br(2)	177.2(2)	Re—C(3)—O(3)	178.7(7)
C(2)—Re—N(11)	91.7(3)	Re—N(11)—C(12)	173.6(6)
C(3)—Re—Br(1)	93.6(2)		

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