ELSEVIER

Journal of Organometallic Chemistry 492 (1995) 217–224

Journal of Organo metallic Chemistry

Metal carbonyl syntheses
XXII. [☆] Low-pressure carbonylation of $[MOCl_4]^-$ and $[MO_4]^-$. The technetium(I) and rhenium(I) complexes $[NEt_4]_2[MCl_3(CO)_3]$

Roger Alberto [a,*], Roger Schibli [a], André Egli [a], P. August Schubiger [a,*], Wolfgang A. Herrmann [b,*], Georg Artus [b], Ulrich Abram [c], Thomas A. Kaden [d]

[a] *Division of Radiopharmacy, Paul Scherrer Insitut, CH-5232 Villigen, Switzerland*
[b] *Anorganisch-chemisches Institut, Lichtenbergstrasse 4, D-85747 Garching b. München, Germany*
[c] *Institut für Anorganische Chemie, Auf der Morgenstelle 18, D-72076 Tübingen, Germany*
[d] *Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel, Switzerland*

Received 29 September 1994; in revised form 11 November 1994

Abstract

Low pressure carbonylation (1 atm) of $[MOCl_4]^-$ or $[MO_4]^-$ in the presence of BH_3/THF and halides X^- results in the clean formation of $[NEt_4]_2[MX_3(CO)_3]$ containing monovalent rhenium or technetium (M = Re, Tc, X = Cl, Br). In the case of the radioactive element technetium this low pressure synthesis is an important progress since the potential hazards of traditional high-pressure carbonylations are thus avoided. The complex $[NEt_4]_2[ReBr_3(CO)_3]$ crystallizes in the space group *P*-1 with $a = 10.166(2)$, $b = 16.393(4)$, $c = 17.243(5)$ Å, and $\alpha = 69.27(2)$, $\beta = 86.42(2)$, $\gamma = 88.61(2)°$, $Z = 4$, and $V = 2682(1)$ Å^3. $[NEt_4]_2[MX_3(CO)_3]$ is a versatile precursor compound of other Re(I) and Tc(I) complexes: substitution of the halide ligands by a variety of σ-donor ligands is facile even under mild conditions. Examples include reactions with CN-^{t}Bu to yield quantitatively $TcCl(CN\text{-}^tBu)_2(CO)_3$ and with a tetradentate phosphine ligand to yield the dinuclear complex $[Re_2Br_2(CO)_6(\text{tetraphos})]$. The X-ray structures of both compounds were determined. Dissolution of $[NEt_4]_2[MX_3(CO)_3]$ in water under aerobic conditions results in the unusual organometallic aqua cation $[M(OH_2)_3(CO)_3]^+$, which species is stable in water for days (IR spectroscopy).

Keywords: Rhenium; Technetium; Low-pressure Carbonylation; Metal Carbonyls; Structure

---

1. Introduction

The two nuclides Tc-99m and Re-186 have found extended application for nuclear medical purposes [2–4]. Various tissue-specific technetium complexes are presently utilized for radio (immuno) diagnosis, while rhenium is used for palliative treatment of cancer and for radioimmunotherapy [5,6]. Ideally, the goal is to develop identical pharmaceutical kits for both diagnosis and therapy, since the chemical reactivity of the two elements is believed to be relatively similar. This assessment, however, does not take into consideration the increase in kinetic stability of rhenium over technetium. This is particularly true for complexes in low oxidation states.

For this reason we are specifically interested in the development of Tc(I) or Re(I) compounds containing the "*fac*-$M(CO)_3$" moiety. Compounds of the general formula $[LRe(CO)_3]^+$ where L stands for a *facial* coordinating tridentate ligand, are usually very stable in aqueous media [7,8]. Thus there is a good chance to apply such compounds in nuclear medicine; L could, for example, represent a bifunctional ligand for the labelling of proteins. Traditionally, "*fac*-$LM(CO)_3$" complexes are prepared from $M_2(CO)_{10}$, which is available by high-pressure carbonylation. However, this method is not practical for radioactive materials at tracer or non-tracer levels [9,10] due to the potential hazards involved. Thus the development of a low-pressure route to a reactive M(I)-complex that provides the "*fac*-$M(CO)_3$" moiety and three substitutionally labile

---

[☆] XXI. Communication of this series, see Ref. [1].
[*] Corresponding authors.

0022-328X/95/$09.50
SSDI 0022-328X(94)05319-7

ligands was investigated. Here we describe a convenient, high yield, low-pressure synthesis (1 atm) of the complexes $[NEt_4]_2[MX_3(CO)_3]$ (M = Re, Tc) and their substitution chemistry with S-, P- and C-donating ligands under mild reaction conditions.

2. Experimental details

Caution: Tc-99 emits low energy β^- particles with a half-life of 2.12×10^5 years. Shielding is not necessary when amounts as applied for this investigation are used, since β^- particles do not penetrate glasswalls. However, special care in the manipulation of radioactive materials is required to avoid contamination and incorporation. In this paper Tc refers only to the isotope Tc-99.

2.1. Abbreviations

The following abbreviations have been used in this article: TBA = tetra(*n*-butyl)ammonium. Et = ethyl. M = rhenium, technetium. X = chloride, bromide. 9-aneS3 = 1,4,7-trithiacyclononane. tetraphos = $P[CH_2CH_2P(C_6H_5)_2]_3$.

2.2. Reagents

All chemicals were of reagent-grade and used without further purification. $BH_3 \cdot THF$ was purchased as a 1 M THF solution from Aldrich. All other reagents were received from Fluka AG. $NH_4[TcO_4]$ was received as a 0.4 M solution from Oak Ridge National Laboratory $TBA[TcO_4]$ and $TBA[ReO_4]$ were prepared by precipitation from aqueous solution using [TBA]Br. $TBA[TcOCl_4]$ was prepared as described elsewhere [11] while for $TBA[ReOCl_4]$ a new modified high-yield synthesis described below was used.

2.3. Synthesis of tetra(n-butyl)ammonium-[tetrachlorooxorhenate(V)]

$TBA[ReO_4]$ (1.1 g, 2.2 mmol) was dissolved in 20 cm^3 of ethanol. HCl was bubbled slowly through the solution so that the temperature did not rise (dissolution of HCl (g) is very exothermic). The solution initially turned intensely yellow. After saturation the reaction was stirred for two hours. The volume was reduced to 50% with a stream of N_2, and the solution was then chilled to −30 °C. After 10 h large yellow crystals of analytically pure $TBA[ReOCl_4]$ were collected by filtration. The process is repeated several times, and 1.2 g (92%) of product are thus collected. Anal.: Found, C, 33.05; H, 6.34; N, 2.47. Calc. for $[C_{16}H_{36}Cl_4NORe]$: C, 32.77; H, 6.19; N, 2.39%. IR (KBr, cm^{-1}): 2962(st), 2874(sh), 1468(st), 1380(m), 1168(w), 1030(m), 1014(m), 884(w), 736(w).

2.4. Synthesis of bis(tetraethylammonium)-[tricarbonyltrichlorotechnetate(I)]

2.4.1. Method a

$TBA[TcOCl_4]$ (158 mg, 0.32 mmol) was dissolved in 15 cm^3 of dry diglyme under an atmosphere of pure CO. 2 cm^3 of a 1 M $BH_3 \cdot THF$ solution was added dropwise. The solution turned deep green and was heated to 110 °C during which time the color changed to yellow. CO was bubbled through the solution for 5 h. The clear, slightly yellow mixture was cooled to room temperature, and [TBA]Cl (266 mg, 0.96 mmol) was then added. $[TBA]_2[TcCl_6]$ readily precipitated as a bright yellow powder and the solution became colorless. $[TBA]_2[TcCl_6]$ was filtered and $[NEt_4]Cl$ (530 mg, 3.2 mmol) was added to the filtrate. The diglyme solution was stirred at 50 °C for some hours while the activity remaining in solution was checked by liquid scintillation. The precipitate was filtered, washed with Et_2O and dried. To remove excess $[NEt_4]Cl$, the collected solid was stirred in 4 cm^3 of cold EtOH and filtered to yield analytically pure $[NEt_4]_2[TcCl_3(CO)_3]$, 110 mg (67%). Anal.: Found, Tc, 17.73; Cl, 20.08. Calc. for $[C_{19}H_{40}Cl_3O_3Tc]$: Tc, 18.02; Cl, 19.35%. IR (KBr, cm^{-1}): 2989(w), 2028(sh), 1902(vs), 1458(m), 1184(w), 798(w), 668(w), 638(w), 500(w).

2.4.2. Method b

$TBA[TcO_4]$ (117 mg, 0.3 mmol) was dissolved in 2 cm^3 of THF. [TBA]Cl (150 mg, 1.2 mmol) was dissolved in 10 cm^3 of diglyme under an atmosphere of N_2 and CO was bubbled through the solution. A 1 M solution of $BH_3 \cdot THF$ was added until H_2 evolution resulting from the neutralization of water in [TBA]Cl was no longer observed. An additional 2 cm^3 of $BH_3 \cdot THF$ was added, and the pertechnetate solution was added over a period of 2 h in several small portions at 40–50 °C. The temperature was raised to 100 °C. After 10 h the color changed from intense yellow to almost colorless. Diglyme was evaporated in vacuo, and the residue was washed with toluene and ether. The resulting solid was dissolved in 10 cm^3 of CH_2Cl_2 and 500 mg of $[NEt_4]Cl$ was then added. The solution was stirred for 3 h and CH_2Cl_2 evaporated under a stream of N_2. The residue was dried and a small amount of cold ethanol was added. The suspension was stirred for 2 minutes after filtration and the solid was washed with cold ethanol to yield pure $[NEt_4]_2[TcCl_3(CO)_3]$, 75 mg (45%). Analytical data as above.

2.5. *Synthesis of bis(tetraethylammonium)-[tricarbonyltrichlororhenate(I)]*

2.5.1 *Method a*

TBA[$ReOCl_4$] (510 mg, 0.87 mmol) was dissolved in 20 cm^3 of dry diglyme under an atmosphere of N_2 and [TBA]Cl (257 mg, 0.87 mmol) was added. 6 cm^3 of a 1 M $BH_3 \cdot THF$ solution was added over a period of 20 minutes and H_2 evolution was observed due to the reaction with water present in the [TBA]Cl. The solution turned dark green and the oily precipitate which formed during addition of $BH_3 \cdot THF$ disappeared. CO is bubbled through the solution and the reaction was heated to 115 °C for 10 h. After this time the reaction solution was nearly colorless. The solution was cooled to 40 °C, [NEt_4]Cl (285 mg, 1.73 mmol) was added and the reaction was stirred for an additional 12 h. The mixture was filtered and the solid was washed with Et_2O and dried. To remove the resulting boric acid and excess [NEt_4]Cl the resulting solid was stirred in cold EtOH and filtered again to yield analytically pure $[NEt_4]_2[ReCl_3(CO)_3]$, 405 mg (73%). Anal.: Found, C, 36.15; H, 6.07; N, 4.39. Calc. for [$C_{19}H_{40}Cl_3O_3Re$]: C, 35.82; H, 6.33; N, 4.40%. IR (KBr, cm^{-1}): 2988(m), 2008(sh), 1886(vs), 1458(m), 1400(m), 1372(w), 1180(m), 1030(w), 1004(m), 790(m), 652(w), 510(m).

2.6.2. *Method b*

TBA[ReO_4] (220 mg, 0.45 mmol) was dissolved in 15 cm^3 diglyme under an atmosphere of CO. [TBA]Cl (820 mg, 2.45 mmol) was then added. A 6 cm^3 solution of 1 M $BH_3 \cdot THF$ was added over a period of 30 minutes, with H_2 evolution occuring due to the reduction of water present in the [TBA]Cl. The solution turned slightly yellow, and CO was bubbled through the solution. The reaction solution was heated to 110 °C for 10 h during which time it became nearly colorless. The reaction was cooled to 50 °C, [NEt_4]Cl (900 mg, 5 mmol) was added, and the reaction stirred for 1–2 h. The suspension was filtered. The white powder was treated in a similar manner as described for technetium to yield $[NEt_4]_2[ReCl_3(CO)_3]$, 215 mg (75%). Additional product can be collected by evaporating diglyme in vacuo and stirring the resulting oily residue in THF. $[NEt_4]_2[ReCl_3(CO)_3]$ is nearly insoluble and can be filtered and treated as described above.

2.6. *Synthesis of bis(tert-butylisocyanide)tricarbonylchlorotechnetium(I)*

$[NEt_4]_2[TcCl_3(CO)_3]$ (83 mg, 0.15 mmol) was suspended in 5 cm^3 of dry THF and CN-^{t}Bu (60 mg, 0.72 mmol) was added. The mixture was stirred at room temperature for 4 h and was then filtered. The collected white powder was [NEt_4]Cl. THF was evaporated in vacuo and the residue was dissolved in Et_2O. A large excess of hexane was layered above the Et_2O solution, and the solution was left undisturbed for 7 days. X-ray quality crystals of [$TcCl(CN\text{-}^tBu)_2(CO)_3$], 53 mg (91%), were obtained. Anal.: Found, Tc, 25.03. Calc. for [$C_8H_9ClO_3Tc$]: Tc, 25.78%. IR (KBr, cm^{-1}): 2985(w), 2208(m), 2190(m), 2049(sh), 1977(sh), 1909(sh), 1369(w), 1262(w), 1199(m), 800(m), 635(m), 588(m), 554(m).

2.7. *Synthesis of dibromohexacarbonyl{tris[2-diphenylphosphino)ethyl] phosphane}dirhenium(I)*

$[NEt_4]_2[ReBr_3(CO)_3]$ (77 mg 0.1 mmol) was dissolved in 10 cm^3 of dry ethanol and an ethanol solution (30 cm^3) containing tetraphos (200 mg, 0.3 mmol) was added. The mixture was refluxed for 5 h and the volume was reduced by 50%. Upon cooling a colouress powder of [$Re_2(CO)_6Br_2$(tetraphos)] precipitated. This solid was filtered and recrystallized from a CH_2Cl_2/ethylacetat (1/1 v/v) mixture to give colourless prisms. Anal.: Found, C, 42.10; H, 3.69; Br, 10.96. Calc. for [$C_{52}H_{50}Br_2O_8P_4Re_2$]: C, 42.74; H, 3.42; Br, 10.96%. IR (KBr, cm^{-1}): 3060(m), 2990(w), 2045(vs), 1972(sh), 1945(vs), 1918(sh), 1910(vs), 1883(s), 1742(s), 1588(w), 1572(w), 1485(m), 1434(w), 1410(sh), 1372(m), 1333(w), 1310(w), 1272(m), 1254(s), 1189(w), 1160(w), 1100(s), 1071(w), 1045(m), 1037(w), 1000(m), 971(w), 943(w), 893(m), 880(m), 845(m), 816(s), 785(m), 742(s), 731(vs), 720(s), 705(sh), 695(vs), 661(m), 635(sh), 623(s), 608(s), 592(w), 578(w), 532(vs), 521(vs), 506(s), 495(w), 485(m), 460(w), 445(w), 433(w), 412(s), 379(m). FABMS(+): m/z (of the most intense peak of the peak group): 1370 $(M)^+$, 1342 $(M - CO)^+$, 1314 $(M - 2\ CO)^+$, 1291 $(M - Br)^+$, 1288 $(M - 3\ CO)^+$, 1261 $(M - 4\ CO)^+$, 936 (ReBr(tetraphos))$^+$, 913 (Re(CO)$_2$(tetraphos))$^+$, 885 (ReCO(tetraphos))$^+$, 857 (Re(tetraphos))$^+$.

2.8. *Crystallography*

The X-ray data collections were carried out at a temperature of −50 °C for the complexes $[Et_4N]_2[ReBr_3(CO)_3]$ and [$Re_2Br_2(CO)_6$(tetraphos)], and at 21 °C for [$TcCl(CO)_3(CN\text{-}^tBu)_2$] on a automated single crystal diffractometer CAD4 (Enraf-Nonius). The unit cell dimensions were determined from the angular settings of 25 high angle reflections. The structures of all three compounds were solved by the heavy atom Patterson method. All non-hydrogen atoms were located from succesive Fourier maps and refined with anisotropic thermal parameters. Hydrogen atoms were placed at calculated positions and included in the structure-factor calculations.

In $[Et_4N]_2[ReBr_3(CO)_3]$ a number of split positions had to be considered in the structure calculation, the atoms Br61/Br62, C131/C132, O131/O132, C411/C412, C431/C432, C451/C452 and C471/472 have been calculated with an occupation of 0.6/0.4. In the initial steps of the calculation the C3–O3 bond length was found to be 0.98 Å which is to short to be realistic and may be the result of further disorder problems. In order to obtain more realistic values the bond lengths of the non-disordered CO have been restrained with an esd of 0.03.

For $[Re_2Br_2(CO)_6(\text{tetraphos})]$ disorder could be detected for the atom Br6 which could be located with an occupation factor of 0.2 at the position of the C3–O6 carbonyl ligand. This has been included in the calculations. The positions of the 0.2 occupancies of the atoms C3 and O6 could not be derived from the final Fourier map.

Crystal data and more details of refinement are summarized in Table 1, selected bond lengths and angles for $[NEt_4]_2[ReBr_3(CO)_3]$ in Table 2, for $[TcCl(CO)_3(CN\text{-}{}^tBu)_2]$ in Table 3 and for $[Re_2Br_2(CO)_6(\text{tetraphos})]$ in Table 4.

3. Results and discussion

3.1. Synthesis

In contrast to the high-pressure synthesis of homoleptic metalcarbonyl complexes, low pressure carbonylations of permetallates or mixed oxo-halide complexes are quite rare. Particularly in the case of the Group VII elements, preparations usually begin with the high-pressure synthesis of $M_2(CO)_{10}$ and continue with oxidation to the corresponding halide complexes, $MX(CO)_5$ [12,13]. A low-pressure route to $ReX(CO)_5$ has previously been reported (in situ generation of CO from refluxing formic acid in the presence of HX) [14]. However, the reported yield was low [14] and the reaction conditions are not suitable for radioactive materials or nanomolar syntheses.

We recently reported a new method for the high-yield synthesis of *mer*-$TcCl(CO)_3[P(C_6H_5)_3]_2$ starting

Table 1
Crystallographic data and details of data collection and processing

	$(Et_4N)_2[ReBr_3(CO)_3]$	$Re_2Br_2(CO)_6(\text{tetraphos})$	$TcCl(CN\text{-}{}^tBu)_2(CO)_3$
Crystal data			
Empirical formula	$C_{19}H_{40}N_2Br_3O_3Re$	$C_{52}H_{50}Br_2O_8P_4Re_2$	$C_{13}H_{18}N_2O_3ClTc$
M	770.46	1459.02	384.75
Color, habit	Colorless	Colorless blocks	Yellow platelet
Crystal size (mm)	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2	0.39 × 0.26 × 0.05
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P-1	P-1	$P2_12_12_1$
a(Å)	10.166(2)	11.380(5)	6.1348(4)
b(Å)	16.393(4)	11.436(4)	9.9930(7)
c(Å)	17.243(5)	23.662(10)	29.083(3)
α(°)	69.27(2)	81.43(3)	90
β(°)	86.42(2)	79.51(3)	90
γ(°)	88.61(2)	60.63(4)	90
U(Å^3)	2682(1)	2632(2)	1782.9(3)
Z	4	2	4
D_c(Mg m^{-3})	1.908	1.841	1.43
μ(mm^{-1})	9.019	6.286	9.46
F(000)	1488	1412	776
Data collection			
θ range(°)	3.0 – 26.97	3.03 – 24.96	$1.00 < \theta < 25°$
Index range	$0 < h < 12$, $-20 < k < 20$ $-21 < l < 22$	$-1 < h < 13$, $-12 < k < 13$ $-26 < l < 26$	$-8 < h < 8$, $0 < k < 11$ $0 < 1 < 34$
Reflections collected	11 664	10 720	5269
Independent reflections	11 658	9211	2952
Observed reflections $[F_0 > 2\sigma(F_0)]$	7226	6118	2379 $[F_0 > 3\sigma(F_0)]$
Solution and refinement			
Weighting scheme (w^{-1})	$\sigma^2(F)$	$\sigma^2(F)$	Ref. [23]
Number of parameters refined(restraints)	563(10)	622(0)	181(0)
Final, R,R' (obs. Data)	0.051/0.081 *	0.048, 0.0790	0.0033, 0.034
Goodness of fit	1.161	1.154	

Table 2
Selected bond lengths (Å) and angles (°) for the two independent complex anions $[ReBr_3(CO)_3[^{2-}]$

Bond lengths			
Re(1)–C(1)	1.901(10)	Re(2)–C(11)	1.894(11)
Re(1)–C(2)	1.880(10)	Re(2)–C(12)	1.887(11)
Re(1)–C(3)	1.964(13)	Re(2)–C(131)	1.85(2)
Re(1)–Br(1)	2.6479(14)	Re(2)–C(132)	1.99(5)
Re(1)–Br(2)	2.6619(14)	Re(2)–Br(4)	2.6534(14)
Re(1)–Br(3)	2.6328(14)	Re(2)–Br(5)	2.6569(14)
		Re(2)–Br(61)	2.582(3)
		Re(2)–Br(62)	2.559(6)
Bond angles			
C(2)–Re(1)–C(1)	88.4(4)	C(12)–Re(2)–C(11)	89.5(5)
C(2)–Re(1)–C(3)	90.5(4)	C(12)–Re(2)–C(131)	90.0(11)
C(1)–Re(1)–C(3)	92.7(5)	C(11)–Re(2)–C(131)	89.2(10)
C(1)–Re(1)–Re(1)	91.9(3)	C(11)–Re(2)–Br(4)	177.4(3)
C(1)–Re(1)–Br(2)	90.8(3)	C(11)–Re(2)–Br(5)	88.9(3)
C(1)–Re(1)–Br(3)	179.0(3)	C(11)–Re(2)–Br(61)	92.8(3)
C(2)–Re(1)–Br(1)	87.9(3)	C(12)–Re(2)–Br(4)	92.5(3)
C(2)–Re(1)–Br(2)	177.9(3)	C(12)–Re(2)–Br(5)	176.6(3)
C(2)–Re(1)–Br(3)	92.6(3)	C(12)–Re(2)–Br(61)	89.0(3)
C(3)–Re(1)–Br(1)	175.1(3)	C(131)–Re(2)–Br(4)	89.1(10)
C(3)–Re(1)–Br(2)	91.4(3)	C(131)–Re(2)–Br(5)	92.2(10)
C(3)–Re(1)–Br(3)	87.7(3)	C(131)–Re(2)–Br(61)	178.0(10)
Br(1)–Re(1)–Br(2)	90.25(4)	Br(4)–Re(2)–Br(5)	89.20(4)
Br(2)–Re(1)–Br(3)	88.23(4)	Br(5)–Re(2)–Br(61)	88.00(8)

Table 4
Selected bond lengths (Å) and angles (°) for the complex $[Re_2Br_2(CO)_6(tetraphos)]$

Bond lengths			
Re(1)–C(1)	1.933(13)	Re(1)–Br(1)	2.6381(14)
Re(1)–C(2)	1.911(13)	Re(1)–P(1)	2.434(3)
Re(1)–C(3)	1.962(12)	Re(1)–P(2)	2.460(3)
Re(2)–C(4)	1.960(13)	Re(2)–Br(2A)	2.605(2)
Re(2)–C(5)	1.940(12)	Re(2)–Br(2B)	2.5188(12)
Re(2)–C(6)	1.94(3)	Re(2)–P(3)	2.512(3)
		Re(2)–P(4)	2.475(3)
Bond angles			
C(2)–Re(1)–C(2)	88.0(5)	C(5)–Re(2)–C(6)	86.4(10)
C(2)–Re(1)–C(3)	90.5(4)	C(5)–Re(2)–C(4)	87.6(5)
C(1)–Re(1)–C(3)	91.8(4)	C(6)–Re(2)–C(4)	88.7(9)
C(2)–Re(1)–P(1)	91.4(3)	C(5)–Re(2)–P(4)	87.8(3)
C(1)–Re(1)–P(1)	93.1(3)	C(6)–Re(2)–P(4)	90.3(9)
C(3)–Re(1)–P(1)	174.8(3)	C(4)–Re(2)–P(4)	175.3(4)
C(2)–Re(1)–P(2)	94.5(3)	C(5)–Re(2)–P(3)	173.9(3)
C(1)–Re(1)–P(2)	171.8(3)	C(6)–Re(2)–P(3)	95.6(9)
C(3)–Re(1)–P(2)	96.0(3)	C(4)–Re(2)–P(3)	86.7(4)
P(1)–Re(1)–P(2)	79.02(10)	P(4)–Re(2)–P(3)	97.98(9)
C(2)–Re(1)–Br(1)	177.4(3)	C(5)–Re(2)–Br(2A)	91.9(4)
C(1)–Re(1)–Br(1)	91.5(3)	C(6)–Re(2)–Br(2A)	174.0(9)
C(3)–Re(1)–Br(1)	92.1(3)	C(4)–Re(2)–Br(2A)	85.5(4)
P(1)–Re(1)–Br(1)	86.15(8)	P(4)–Re(2)–Br(2A)	95.32(9)
P(2)–Re(1)–Br(1)	85.68(8)	P(3)–Re(2)–Br(2A)	85.49(8)

from $TBA[TcO_4]$ or $TBA[TcOCl_4]$ [15]. The compound *mer*-$TcCl(CO)_3[P(C_6H_5)_3]_2$ proved to be a useful precursor of a variety of organotechnetium compounds. However, the substitution chemistry that resulted in the "$M(CO)_2(PR_3)$" moiety had to be performed at elevated temperature due to kinetic stabilization of Tc(I) by the phosphine- and the carbonyl ligands.

The reduction of $[MOCl_4]^-$ or $[MO_4]^-$ with $BH_3 \cdot THF$ under an atmosphere of CO in diglyme/[TBA]Cl results in high yields of the dianion *fac*-$[MCl_3(CO)_3]^{2-}$. The reaction mixture undergoes several color changes, from green to yellow and finally to colorless, thus indicating a multistep synthesis. The initial step during the synthesis might be reduction of M(V) to M(III) with concomitant substitution of the terminal oxo ligand. An interesting difference in the reactivity of the two elements is evident by the side-products that are formed during the reduction. In the case of rhenium up to 5% of $[TBA]_2[Re_2Cl_8]$ is formed, while in the case of technetium 30% of $[TBA]_2[TcCl_6]$ can be observed in preference over $[TBA]_2[Tc_2Cl_8]$. However this Tc(IV) side product can be significantly suppressed upon working with dilute reaction solutions. Possibly, the Tc(IV) product is formed from the synproportionation between $[TcOCl_4]^-$ and various Tc(III) intermediates while $[ReOCl_4]^-$, being a much weaker oxidant, is unlikely to oxidize similar Re(III) species.

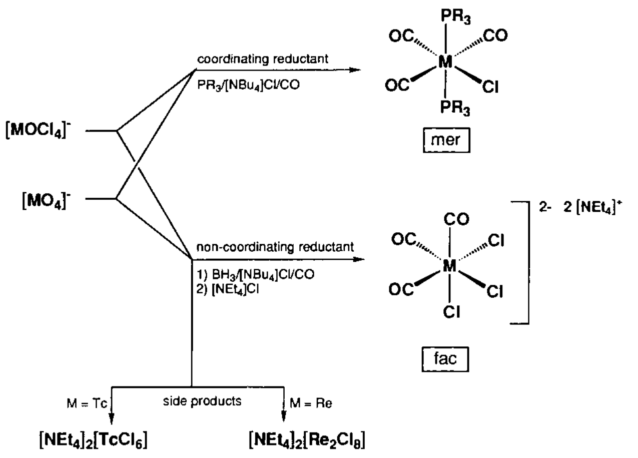
Table 3
Selected bond lengths (Å) and angles (°) for the complex $[TcCl(CN\text{-}{}^tBu)_2(CO)_3]$

Bond lengths			
Tc(1)–C(1)	1.961(6)	C(1)–O(1)	1.129(6)
Tc(1)–C(2)	1.914(7)	C(2)–O(2)	1.121(7)
Tc(1)–C(3)	1.927(6)	C(3)–O(3)	1.141(6)
Tc(1)–C(4)	2.097(5)	C(4)–N(1)	1.133(6)
Tc(1)–C(9)	2.102(6)	C(9)–N(2)	1.153(7)
Tc(1)–Cl(1)	2.496(2)		
Bond angles			
C(1)–Tc(1)–Cl(1)	89.0(2)	C(2)–Tc(1)–C(4)	90.1(3)
C(2)–Tc(1)–Cl(1)	177.9(2)	C(2)–Tc(1)–C(9)	91.4(2)
C(3)–Tc(1)–Cl(1)	91.5(2)	C(3)–Tc(1)–C(4)	87.9(2)
C(4)–Tc(1)–Cl(1)	88.1(2)	C(3)–Tc(1)–C(9)	178.4(2)
C(9)–Tc(1)–Cl(1)	87.6(1)	C(4)–Tc(1)–C(9)	93.5(3)
C(1)–Tc(1)–C(2)	92.8(3)	Tc(1)–C(1)–O(1)	179.6(5)
C(1)–Tc(1)–C(3)	90.5(2)	Tc(1)–C(2)–O(2)	178.6(6)
C(1)–Tc(1)–C(4)	176.7(3)	Tc(1)–C(3)–O(3)	177.5(6)
C(1)–Tc(1)–C(9)	88.1(2)	Tc(1)–C(4)–N(1)	174.2(5)
C(2)–Tc(1)–C(3)	89.6(3)	Tc(1)–C(9)–N(2)	174.2(4)

The reduction of the terminal oxo groups requires a weakly coordinating reducing agent. Otherwise, the latter can compete with the halides resulting in the "*mer*-$M(CO)_3$" fragment containing additional reductant as ligand. In addition, the desired product *fac*-$[MCl_3(CO)_3]^{2-}$ does not occur even under vigorous conditions if only CO is present as the reducing agent. Reaction conditions and products are summarized in Scheme 1.

3.2. Behaviour in coordinating solvents

The halide ligands are readily substituted by various coordinating solvents such as CH_3CN, CH_3OH and H_2O. Particularly in the latter case, the halides are



Scheme 1. Carbonylation products of $[MOCl_4]^-$ and $[MO_4]^-$ arising from different reductants.

completly exchanged to form $[M(H_2O)_3(CO)_3]^+$ as seen in the IR spectra. Thus, a typical "*fac*-$Tc(CO)_3$" pattern for a slightly distorted C_{3v} symmetry is observed for $[Et_4N]_2[TcCl_3(CO)_3]$ in KBr at 2024 (A_1), 1918 and 1892 (E) cm^{-1}. An aqueous solution of $[TcCl_3(CO)_3]^{2-}$ revealed the same pattern but the band positions are strongly shifted to greater wavenumbers (2051 and 1936 cm^{-1}, respectively). The IR spectra remained unchanged when the chlorides were precipitated with silver salts containing weakly coordinating anions such as $[PF_6]^-$ or $[ClO_4]^-$. The IR spectra for both $[TcCl_3(CO)_3]^{2-}$ and the solvated species are shown in Fig. 1 which very much resembles the isostructural Re^1 complex [24]. These spectroscopic studies strongly suggest that in water the halides are no longer coordinated to the metal and the "tris-aqua" species, $[Tc(H_2O)_3(CO)_3]^+$, is likely to be formed.

An aqueous solution of $[Tc(H_2O)_3(CO)_3]^+$ is stable for days even upon exposure to air. Similar stabilities are observed for other solvated species present in CH_3CN, CH_3OH and C_2H_5OH. Dissolution of $[Et_4N]_2[TcCl_3(CO)_3]$ in CH_3CN followed by evaporation quantitatively yields $[Tc(CH_3CN)_3(CO)_3]^+$. This species was reported to be a versatile starting material in various substitution reactions [16,17]. It is now easily available by our method (Schemes 1 and 2).

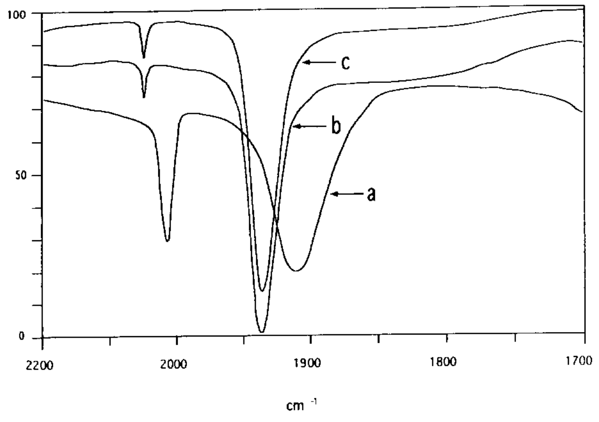


Fig. 1. IR spectra of $[Et_4N]_2[TcCl_3(CO)_3]$ in the CO stretching region: (a) in KBr; (b) in aqueous solution before and (c) after precipitation of Cl^- with $AgNO_3$.

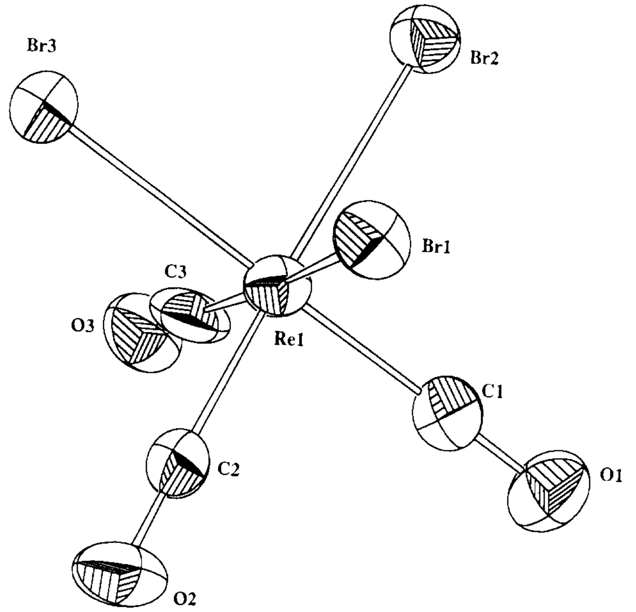
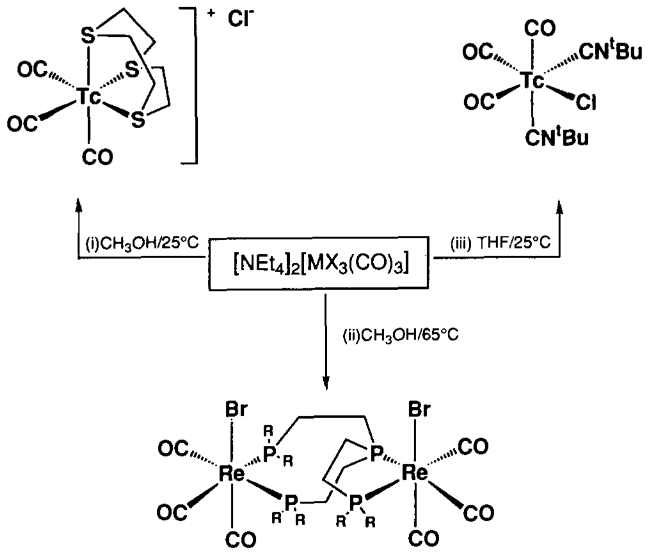


Fig. 2. Thermal ellipsoid plot of the anion $[ReBr_3(CO)_3]^{2-}$. The ellipsoids correspond to 50% probability.

3.3. Crystal structure of $[NEt_4]_2[ReBr_3(CO)_3]$

Our initial attempts to obtain X-ray quality crystals with chloride as a ligand were unsuccessful. However, from a saturated $[NEt_4]Br$/ EtOH solution of $[NEt_4]_2[ReBr_3(CO)_3]$ crystals of sufficient quality were obtained. The ORTEP of the complex anion is depicted in Fig. 2. The compound forms triclinic crystals in the space group *P*-1 (No. 2) with two crystallographically independent molecules per asymmetric unit. Selected bond lengths and angles are given in Table 2. The Re(I) center is coordinated through a facial arrangement of three CO and three bromide ligands in a nearly ideal octahedral geometry. The bond lengths for Re(1)-C(1) and Re(1)-C(2) are averaged at 1.885(10) Å and are equal within one standard deviation. However, the Re(1)-C(3) bond length, i.e. 1.964(13) Å, is significantly longer. Similar structural characteristics are observed in the second complex of the asymmetric unit. Unfortunately, comparison with other monomeric, anionic Re(I) compounds that contain three weakly coordinated anions is not possible, since to our knowledge the title complex is the first such species that has structurally been characterized. Structures of several



Scheme 2. Substitutions pathways of $[Et_4N]_2[TcCl_3(CO)_3]$ with C, P, and S ligands: (i) 9-aneS3, (ii) tetraphos, (iii) CN-^{t}Bu.

cationic complexes of type $[Re(L)_3(CO)_3]^+$ where L = NH_3, CH_3CN and $ON(CH_3)_3$, are known [18–20].

3.4. Subsitution reactions

Quite a number of compounds containing the "*fac*-$M(CO)_3$" moiety have been described in the literature, especially those of rhenium. In such studies the substitution chemistry of $MX(CO)_5$ was exploited, and vigorous reaction conditions often resulted in poor product yields. The choice of ligands is limited by solubility and thermal stability. In contrast, $[MX_3(CO)_3]^{2-}$ contains three easily providable coordination sites which can be filled in by a variety of ligands.

For example, a fast and quantitative reaction occurs with isonitriles at room temperature to yield the neutral complex $TcCl(CN\text{-}^tBu)_2(CO)_3$ (Scheme 2). Precipitation of $[NEt_4]Cl$ is believed to drive the reaction equilibrium to completion. Substitution of the third halide is apparently more difficult. $TcCl(CN\text{-}^tBu)_2(CO)_3$ has been previously reported to result from $TcBr(CO)_5$ [21]. In addition, the analogous rhenium complex is also known, but very vigorous conditions are necessary and the yields are low [22,23].

X-ray quality crystals of $TcCl(CN\text{-}^tBu)_2(CO)_3$ were obtained from Et_2O/hexane by slow diffusion. The ORTEP of $TcCl(CN\text{-}^tBu)_2(CO)_3$ is depicted in Fig. 3 and selected bond lengths and angles are given in Table 3. Substitution of isonitrile ligands for all three halides is possible upon the initial addition of $Ag[PF_6]$ in water (Scheme 2). Subsequent addition of CN-^{t}Bu to the "tris-aquo" complex precipitates $[Tc(CN\text{-}^tBu)_3(CO)_3]PF_6$ directly from the aqueous solution (Scheme 3).

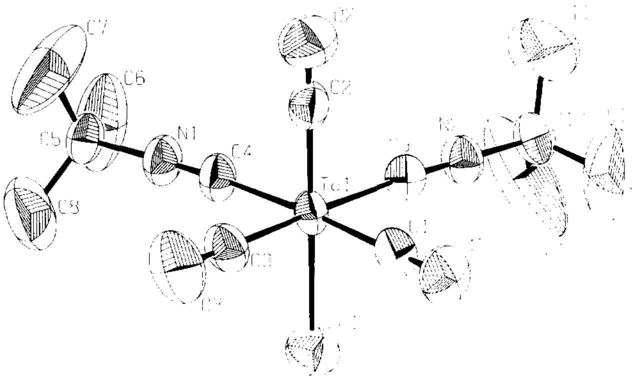
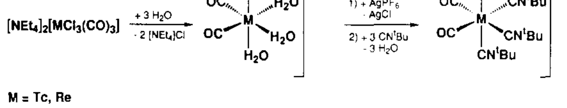


Fig. 3. Thermal ellipsoid plot of the neutral compound $[TcCl(CN\text{-}^tBu)_2(CO)_3]$. The ellipsoids correspond to 50% probability.

The sulfur macrocycle 1,4,7 trithiacyclononane "9-aneS3" behaves like the isonitriles. This tridentate, facially coordinating ligand exchanges all three chlorides within minutes at room temperature to form *fac*-$[(9\text{-aneS3})Tc(CO)_3]Cl$ (Scheme 2). This complex is isolated in 95% yield based on $[TcO_4]^-$ if 9-aneS3 is added directly to the crude diglyme solution after carbonylation. This type of ligand is interesting for protein labelling purposes, since 9-aneS3 or its triaza-congener can be bifunctionalized and $[M(H_2O)_3(CO)_3]^+$ be used to perform post-labelling. If *fac*-$[(9\text{-aneS3})Tc(CO)_3]Cl$ is synthesized first, then this complex can be used for a pre-labelling procedure.

The substitution chemistry of $[MBr_3(CO)_3]^{2-}$ with the potentially tetradentate ligand tetraphos is similar to CN-^{t}Bu, since only two of the possible three bromides are easily substituted. It could be expected from thermodynamic considerations that three of the phosphorus atoms bind to the same Re-center, with the forth one remaining uncoordinated. However, coordination to two rhenium centers with the tetradentate ligand is observed; the product seems kinetically favored. Consequently only two of the phosphorus atoms bind to one rhenium atom while the remaining two bind to a second rhenium center thus forming a binuclear complex.

X-ray quality crystals of $[Re_2Br_2(CO)_6(tetraphos)]$ were obtained by recrystallization from a CH_2Cl_2/ethylacetate solution. An ORTEP is shown in Fig. 4, and selected bond lengths and angles are listed in Table 4. The binuclear complex consists of two "$Re(CO)_3Br$"



Scheme 3. Substitution pathway to $[M(CO)_3(CN\text{-}^tBu)_3]PF_6$ in water: (1) $Ag[PF_6]$, (2) CN-^{t}Bu.

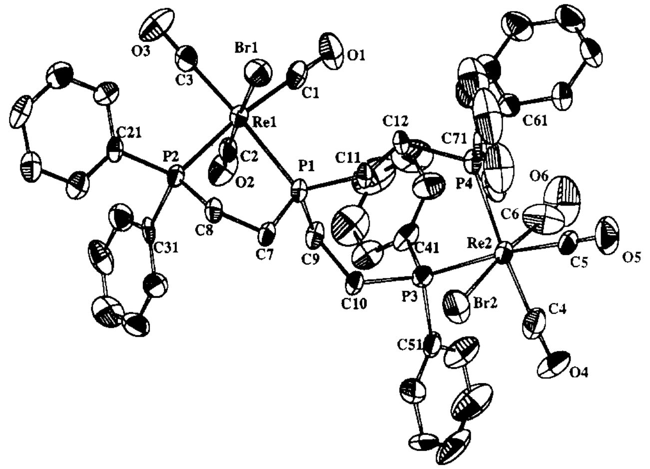


Fig. 4. Thermal ellipsoid plot of the neutral compound $[Re_2Br_2(CO)_6(tetraphos)]$. The ellipsoids correspond to 50% probability.

units which are connected by the tetradentate ligand. The coordination about both rhenium atoms are of nearly ideal octahedral geometry, and the observed bond lengths are typical for other rhenium carbonyl complexes. The crystal contains one molecule of ethyl acetate per formula unit.

4. Conclusion

The technetium and rhenium complexes $[Et_4N]_2[fac\text{-}MX_3(CO)_3]$ are prepared in a convenient, one-step synthesis directly from the readily available oxometallates $[MOCl_4]^-$ and $[MO_4]^-$. This procedure is of particular interest in the case of technetium since it provides a novel route to a variety of Tc(I) carbonyl complexes without the necessity of high pressure reaction conditions. The conventional starting material $Tc_2(CO)_{10}$ the preparation of which depends on high pressure conditions is thus no longer necessary to be applied. In contrast, the halide ligands of $[Et_4N]_2[fac\text{-}MX_3(CO)_3]$ are easily substituted by other ligands. Substitution occurs at ambient temperature in various solvents (solv) including water to give $[fac\text{-}M(solv)_3(CO)_3]X$. In addition, the reaction with more typical coordination ligands such as isonitriles, thioethers, and phosphines leads to a variety of low-valent carbonyl complexes under ambient reaction conditions. Our present interest is to take advantage of both the stability in aqueous media and the facile substitution chemistry of $[Et_4N]_2[fac\text{-}MX_3(CO)_3]$ for the development of a new class of radiodiagnostic and radiotherapeutic pharamaceuticals. Consequently investigations with aromatic water soluble ligands, and the determination of stability constants with amino acids and small peptides are currently in progress.

Acknowledgements

This work was supported by the Alexander von Humboldt Foundation through a grant awarded to R.A. and by the Technische Universität München.

References

[1] W.A. Herrmann, D. Mihalios, K. Öfele, P.Kiprof and F. Behmedjahed, *Chem. Ber.*, *125* (1992) 1795.
[2] (a) E. Deutsch and K. Libson, *Comm. Inorg. Chem.*, *3* (1984) 83; (b) M.J. Clarke and J. Podbielsky, *Coord. Chem. Rev.*, *78* (1987) 253.
[3] W.A. Volkert, G.J. Goeckeler and A.R. Ketring, *J. Nucl. Med.*, *32* (1991) 174.
[4] A. Fritzberg, R. Berninger and S. Hadley, *Pharmaceut. Res.*, *5* (1988) 325.
[5] P.L. Beaumier, P. Venkatesan, J.-L. Vanderheyden, W.D. Burgua, L.L. Kunz, A.R. Fritzberg, P.G. Abrams and A.C. Morgan, *Cancer Res.*, *51* (1991) 676.
[6] M. Gerretsen, G.W.M. Vissen, M. van Walsum, C.J.L.M. Meijer, G.B. Snow and G.A.M.S. van Dongen, *Cancer Res.*, *53* (1993) 3524.
[7] G. Winkhaus, L. Pratt and G. Wilkinson, *J. Chem. Soc. A*, (1975) 1677.
[8] C. Pomp, S. Drücke, H.-J. Küppers, K. Wieghardt and C. Krüger, *Z. Naturforsch., Teil B*, *43* (1988) 299.
[9] W.A. Herrmann, R. Alberto, J.C. Bryan and A.P. Sattelberger, *Chem. Ber.*, *124* (1991) 1107.
[10] J.C. Hileman and W.J. Jolly (eds.), *Preparative Inorganic Reactions*, Vol. 1, Interscience, New York, 1964, p. 77.
[11] W. Preetz and G.Z. Peter, *Z. Naturforsch.*, *35B* (1980) 1355.
[12] J.C. Hileman, D.K. Huggins and H.D. Kaesz, *Inorg. Chem.*, *1* (1962) 933.
[13] H.D. Kaesz, R. Bau, D. Hendrickson and J.M. Smith, *J. Am. Chem. Soc.*, *89* (1967) 2844.
[14] E.W. Abel, R.W.N. Mclean and S.M. Moorhouse, *Inorg. Nucl. Chem. Lett.*, *7* (1971) 587.
[15] R. Alberto, W.A. Herrmann and F. Baumgaertner, *Inorg. Chem.*, *31* (1992) 895.
[16] L. Kaden, B. Lorenz, S. Rummel, K. Schmidt and M. Wahren, *Inorg. Chim. Acta*, *142* (1988) 1.
[17] H.H. Knight Castro, C.E. Hissink, J.H. Teuben and W. Vaalburg, *Recl. Trav. Chim. Pays-Bas*, *111* (1992) 105.
[18] M. Herberhold, F. Wehrmann, D. Neugebauer and G. Huttner, *J. Organomet. Chem.*, *152* (1978) 329.
[19] L.Y.Y. Chan, E.E. Isaacs and W.A.G. Graham, *Can. J. Chem.*, *55* (1977) 111.
[20] S.D. Christie, M.D. Clerk and M.J. Zaworotko, *J. Cryst. Spectrosc.*, *23* (1993) 591.
[21] B.Lorenz, M. Findeisen, B. Olk and K. Schmidt, *Z. Anorg. Allg. Chem.*, *566* (1988) 160.
[22] P.M. Treichel and J.P.Williams, *J. Organomet. Chem.*, *135* (1977) 39.
[23] E. Prince in *Mathematical Technical Techniques in Crystallography*, Springer, Berlin, 1982.
[24] R. Alberto, A. Egli, U. Abram, K. Hegetsweiter, V. Gramlich and P.A. Schubiger *J. Chem. Soc., Dalton Trans.*, (1994) 2815.