Journal of Organometallic Chemistry, 135 (1977) 177—182

PHOSPHINE CARBONYL-TECHNETIUM(I) AND -TECHNETIUM(III) COMPLEXES

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(Received February 1st, 1977)

Summary

Treatment of *trans*-[TcX_4L_2] (X = Cl, Br and L = PPh_3, PMe_2Ph) with carbon monoxide (1 atm) in boiling ethyleneglycol methyl ether, gives *trans*-[$TcX(CO)_3L_2$]. Under these conditions the *mer*-[$TcX_3(PMe_2Ph)_3$] (X = Cl, Br) gives a mixture of the *trans*-[$TcX(CO)_3(PMe_2Ph)_2$] and *cis*-[$TcX(CO)_2(PMe_2Ph)_3$] complexes, but when added free dimethylphenylphosphine is present only the second product is obtained. Carbon monoxide reacts with *mer*-[$TcCl_3(PMe_2Ph)_3$] in refluxing ethanol to give [$TcCl_3(CO)(PMe_2Ph)_3$] a C_{3v} seven-coordinate technetium(III) complex.

The stereochemistry of the complexes was determined from their IR and ^{1}H NMR spectra.

It was recently reported that the most convenient route to mixed phosphine carbonyl complexes of rhenium and technetium starts from tertiary phosphine complexes [1—3]. The only known phosphine carbonyl complexes of technetium were made from [$TcCl_2(P(OEt)_2Ph)_4$]ClO_4 and carbonyl monoxide at 50° C and 1 atm [3]. Under those conditions the *cis*- and the *trans*-isomers of [$Tc(CO)_2\{P(OEt)_2Ph\}_4$]ClO_4, in which technetium is formally 1+, were obtained. We now describe some reactions of the phosphine technetium complexes with CO.

Refluxing an ethanolic solution of the *mer*-[$TcCl_3(PMe_2Ph)_3$] complex under CO (1 atm) gave the C_{3v} seven-coordinate [$TcCl_3(CO)(PMe_2Ph)_3$]. This complex forms air-stable yellow crystals, which are soluble in common polar solvents. The complex is diamagnetic in solution. Its IR spectrum both in solid and in solution shows a strong absorption band in the carbonyl region (ν(CO) 1874 cm^{-1} (solid), 1882 cm^{-1} (solution)), and some bands at 338, 282, 253 and 228 cm^{-1} in the ν(Tc—Cl) region. The ^{1}H NMR spectrum in $CDCl_3$ shows a partially resolved multiplet at δ 1.45 ppm coming from the methyl protons. An X-ray structural determination has confirmed the seven-coordination with C_{3v} symmetry [4]. An ethanolic molecule is present in the unit cell, but recrystallization from CH_2Cl_2/pentane gives a solvent-free powder.

The rhenium complex *mer*-$[ReCl_3(PMe_2Ph)_3$ reacts analogously with CO under similar conditions, to give a seven-coordinate compound [1].

Higher temperatures are needed to produce complexes of technetium(I) starting from complexes of the type $[TcX_3L_3]$ and $[TcX_4L_2]$ (X = Cl, Br and L = PPh_3, PMe_2Ph). When carbon monoxide (1 atm) was passed through a refluxing solution of *mer*-$[TcX_3(PMe_2Ph)_3]$ (X = Cl, Br) in ethyleneglycol methyl ether, the solution became colourless after some hours. When the glycol was removed, a white powder was obtained, from which two compounds, *trans*-$[TcX(CO)_3(PMe_2Ph)_2]$ and *cis*-$[TcX(CO)_2(PMe_2Ph)_3$ (X = Cl, Br) were isolated, the second in only 10% yield. The addition of PMe_2Ph improves the yield of *cis*-$[TcX(CO)_2(PMe_2Ph)_3]$; thus with a 5/1 phosphine/technetium ratio only the complex containing three phosphine ligands is obtained.

The complexes $[TcX_4L_2]$ (X = Cl, Br and L = PPh_3; PMe_2Ph) react with CO in the same glycol during some hours under reflux to give exclusively products formulated as $[TcX(CO)_3L_2]$. These form white crystals, stable as solids and in anhydrous solvents. Chlorinated solvents cause slow decomposition to a unidentified brown product. Elemental analyses are in accordance with the proposed formulation (Table 1). The complexes are diamagnetic in solution, and their IR and ^1H NMR spectra reveal their conformation in solution.

The IR spectra show three absorption bands assignable to the carbonyl ligands vibrations (three $(2A_1 + B_1)$ modes). The highest frequency is weak, there is a very strong band at a lower frequency and a medium band at the lowest frequency (Table 2). This is characteristic of three C=O groups in meridional positions [5]. The far-IR spectra in the region 400—80 cm^{-1} reveal the ν(Tc—X) stretching vibrations at ν(Tc—Cl) 275 cm^{-1} and ν(Tc—Br) 175 cm^{-1}. These low values are consistent with halogen *trans* to a C=O group [5], indicating a *trans*-configuration for the phosphine ligands. The ^1H NMR spectra also agree with

TABLE 1

ANALYTICAL DATA FOR THE PHOSPHINECARBONYLTECHNETIUM COMPLEXES

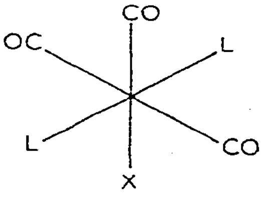
Compound	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))	
			X	Tc
$TcCl_3(CO)(PMe_2Ph)_3$	91	140	16.86 (16.42)	15.12 (15.27)
trans-$TcCl(CO)_3(PPh_3)_2$	71	174 (dec.)	4.87 (4.77)	13.05 (13.31)
trans-$TcBr(CO)_3(PPh_3)_2$	73	172 (dec.)	10.81 (10.15)	11.82 (12.56)
trans-$TcCl(CO)_3(PMe_2Ph)_2$	60	100	7.24 (7.16)	18.46 (19.99)
trans-$TcBr(CO)_3(PMe_2Ph)_2$	65	122	13.56 (14.82)	17.72 (18.34)
cis-$TcCl(CO)_2(PMe_2Ph)_3$	78	142 (dec.)	5.98 (5.86)	15.91 (16.35)
cis-$TcBr(CO)_2(PMe_2Ph)_3$	80	144	12.20 (12.31)	14.81 (15.23)

TABLE 2

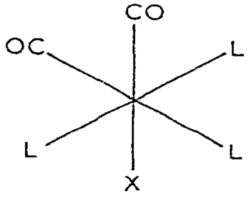
INFRARED DATA FOR THE PHOSPHINECARBONYLTECHNETIUM COMPLEXES IN THE RANGE 4000—80 cm^{-1}

Compound	$\nu(C{=}O)$ (cm^{-1})		$\nu(Tc{-}X)$ (cm^{-1}) nujol
	sol. CH_2Cl_2	nujol	
$TcCl_3(CO)(PMe_2Ph)_3$	1882(s)	1874(s)	
trans-$TcCl(CO)_3(PPh_3)_2$	2059(w) 1968(s) 1916(m)	2060(w) 1963(s) 1946(m)	278
trans-$TcBr(CO)_3(PPh_3)_2$	2070(w) 1979(s) 1930(m)	2060(w) 1973(s) 1913(m)	192
trans-$TcCl(CO)_3(PMe_2Ph)_2$	2040(w) 1961(s) 1908(m)	2055(w) 1965(s) 1874(m)	275
trans-$TcBr(CO)_3(PMe_2Ph)_2$	2069(w) 1975(s) 1920(m)	2062(w) 1982(s) 1905(m)	175
cis-$TcCl(CO)_2(PMe_2Ph)_3$	1950(s) 1851(s)	1930(s) 1831(s)	272
cis-$TcBr(CO)_2(PMe_2Ph)_3$	1959(s) 1866(s)	1952(s) 1851(s)	170

this formulation; the CH_3 triplet (1/2/1) appears at δ 1.91 ppm in $CDCl_3$ at 300 K, and at δ 1.58 ppm in C_6D_6 at the same temperature. The occurrence of this triplet, which arises from virtual coupling with phosphorus nuclei, again indicates a *trans* position of the phosphine ligands [6,7]. We conclude that the only possible configuration is A, in which the symmetry is C_{2v}.



(A)



(B)

The *cis*-[$TcX(CO)_2(PMe_2Ph)_3$] complexes (X = Cl, Br) are white crystals, air stable, soluble in polar solvents, slightly soluble in alcohols, and insoluble in nonpolar solvents. In chlorinated solvents they give yellow solutions which upon evaporation yield crystals of [$TcCl_3(CO)(PMe_2Ph)_3$] (C_{3v}).

These octahedral complexes are diamagnetic, which is consistent with a t_{2g}^6 configuration. The IR spectra for both the solid and solutions, show two bands of equal intensity in the $\nu(C{=}O)$ region (two 2A′ modes) (Table 2), indicating that the CO groups are in *cis* position. The far-IR spectra reveal no significant

TABLE 3

^{1}H NMR DATA FOR THE TECHNETIUM CARBONYL COMPLEXES WITH PMe_2Ph LIGANDS

Compound	(δ(CH_3) in ppm)	Solvent
$TcCl_3(CO)(PMe_2Ph)_3$	1.45(m)	$CDCl_3$
trans-$TcCl(CO)_3(PMe_2Ph)_2$	1.91(t)(*J* 3.5 Hz) 1.58(t)(*J* 3.3 Hz)	$CDCl_3$ C_6D_6
trans-$TcBr(CO)_3(PMe_2Ph)_2$	1.94(t)(*J* 3.5 Hz)	$CDCl_3$
cis-$TcCl(CO)_2(PMe_2Ph)_3$	1.70(m) and 1.17(d)(*J* 7.0 Hz)	$CDCl_3$
cis-$TcBr(CO)_2(PMe_2Ph)_3$	1.73(m) and 1.22(d)(*J* 7.1 Hz)	$CDCl_3$

difference in the Tc—X frequency compared with the $[TcX(CO)_3L_2]$ complexes, and so the halogen atom must be *trans* to a CO group. The ^{1}H NMR spectra for $[TcCl(CO_2(PMe_2Ph)_3]$ in $CDCl_3$ show two absorption bands at δ 1.70 ppm (a multiplet) and at δ 1.17 ppm (a doublet), in a 2/1 area ratio. These results suggest a *meridional* configuration for the phosphine ligand in which two phosphine ligands are equivalent. The multiplet arises because there is no plane of symmetry containing the two *trans* phosphorus atoms [5]. The methyl groups on the same phosphine ligand are not equivalent and the multiplet results from a partial overlapping of two triplets. Therefore the only possible configuration is B (C_s symmetry).

Experimental

Solid samples of NH_4TcO_4 were obtained by concentration of the ammonia solution (Radiochemical Centre Ltd, Amersham, England). Other materials were Reagent Grade chemicals. All solvents were purified and dried by standard methods. All the preparations were carried out under dinitrogen.

Magnetic measurement on dichloromethane solutions were measured by the Evans' method [9] and corrected for diamagnetism of the ligands [10]. ^{1}H NMR spectra were recorded on a Bruker HFX 10 instrument with TMS as internal standard. Infrared spectra were recorded on a Perkin—Elmer 621 instrument (4000—400 cm^{-1}) or a Beckman IR11 spectrophotometer (400—80 cm^{-1}).

Amounts of technetium larger than 1 g were handled in glove boxes under a light vacuum to afford protection against radiation and avoid contamination.

Analyses were carried out as previously described [11].

Trichlorocarbonyltris(dimethylphenylphosphine)technetium(III)

Method (a). Carbon monoxide was passed through a boiling solution of *mer*-trichlorotris(dimethylphenylphosphine)technetium(III) (0.5 g) in ethanol (30 ml) for 7 h. The yellow-orange solution became pale yellow. Upon cooling the solution gave pale-yellow plates. Concentration of the mother liquor gave more product. Recrystallization was from CH_2Cl_2/pentane.

Method (b). A solution of chlorodicarbonyltris(dimethylphenylphosphine)-technetium(I) (0.2 g) in chloroform (20 ml) was stirred at room temperature for 20 h. Concentration under vacuum gave $TcCl_3(CO)(PMe_2Ph)_3$ as a yellow powder.

trans-Chlorotricarbonylbis(triphenylphosphine)technetium(I)

Carbon monoxide was passed through a boiling solution of *trans*-tetrachlorobis(triphenylphosphine)technetium(IV) (0.5 g) in ethyleneglycol methyl ether (30 ml) for 20 h, during which the green colour disappeared. On cooling the solution white crystals were deposited, and concentration of the mother liquor gave further product. The solid was washed with ethanol and then with pentane and dried.

trans-Bromotricarbonylbis(triphenylphosphine)technetium(I)

This was prepared analogously from *trans*-tetrabromobis(triphenylphosphine)-technetium(IV), with refluxing for 3 h. White crystals were obtained from CH_2Cl_2/pentane.

trans-Chlorotricarbonylbis(dimethylphenylphosphine)technetium(I)

Method (a). An ethyleneglycol methyl ether solution (30 ml) of *mer*-trichlorotris(dimethylphenylphosphine)technetium(III) (0.5 g) was refluxed under carbon monoxide. The orange colour changed to green after 30 min, then the solution became clear and colourless. After 8 h heating, the solvent was removed under vacuum. The yellow-white residue was washed with ethanol (3 ml) and dried. The white solid was washed with 5 ml of diethyl ether recrystallized from CH_2Cl_2/pentane, and shown to be *trans*-$[TcCl(CO)_3(PMe_2Ph)_2]$. The ether solution was concentrated to give a powder containing the same product along with *cis*-$[TcCl(CO)_2(PMe_2Ph)_3]$.

Method (b). A solution of *trans*-tetrachlorobis(dimethylphenylphosphine)-technetium(IV) (0.5 g) in ethyleneglycol methyl ether was treated with carbon monoxide. The mixture was refluxed for 15 h, then the colourless solution was evaporated to dryness. The white-yellow residue was washed with ethanol then pentane and dried. White needles of *trans*-$[TcCl(CO)_3(PMe_2Ph)_2]$ were obtained from CH_2Cl_2/pentane.

trans-Bromotricarbonylbis(dimethylphenylphosphine)technetium(I)

This was prepared analogously from *mer*-$[TcBr_3(PMe_2Ph)_3]$ or *trans*-$[TcBr_4(PMe_2Ph)_2]$ with refluxing for 4 or 7 h respectively.

cis-Chlorodicarbonyltris(dimethylphenylphosphine)technetium(I)

Method (a). Carbon monoxide was passed for 40 h through a boiling solution of *mer*-trichlorotris(dimethylphenylphosphine)technetium(III) (1.0 g) and dimethylphenylphosphine (1.0 ml) in ethyleneglycol methyl ether (35 ml). The orange solution became colourless. Evaporation to dryness left a yellow oil, which was treated with ethanol (3 ml) to give a white powder. White needles were obtained from CH_2Cl_2/pentane.

Method (b). *trans*-Chlorotricarbonylbis(dimethylphenylphosphine)technetium-(I) (0.5 g) was treated with dimethylphenylphosphine (0.7 ml) in refluxing THF solution (20 ml) for 10 min. Addition of pentane to the cooled solution gave *cis*-$[TcCl(CO)_2(PMe_2Ph)_3]$ as a white powder.

cis-Bromodicarbonyltris(dimethylphenylphosphine)technetium(I)

This was prepared analogously to the chloro compound from *mer*-$[TcBr_3(PMe_2Ph)_3]$ with refluxing for 8 h.

Acknowledgment

We thank Mr Giovanni Agostini and Miss Piera Destro for technical assistance.

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