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Synthesis and Characterization of New Technetium(I) Tricarbonyl Complexes

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From $Mn(CO)_5Hal$ (Hal = Cl, Br, J) [1, 2] and $Re(CO)_5Hal$ [1, 3] a series of neutral [2] or cationic [1, 3] complexes containing the structure element $M(I)(CO)_3$ (M = Mn, Re) was obtained in good yields by ligand exchange reactions. Similar complexes of technetium(I) were of interest to us for studies of ^{99}Tc NMR and catalytic activation of carbon monoxide. Besides that considerable general interest has arisen in cationic Tc complexes as radiopharmaceuticals for myocardial perfusion imaging.

From $Tc(CO)_5Br$ [4] we obtained, by reaction with acetonitrile and $AgPF_6$ in nearly quantitative yield, the cationic complex $[Tc(CO)_3(CH_3CN)_3]^+PF_6^-$ (**1**). **1** proved to be a promising starting material for other carbonyl complexes of Tc by exchange of the labile nitrile groups for other types of ligands. Here we report the complexes obtained from **1** with four different phenylphosphines $PhPL_2$. Three different types of products were obtained, indicating the broad preparative scope of ligand exchange reactions with complex **1**. The results are summarized in Table I.

The products **2** and **4** were those expected from the stoichiometric relations of the reactants in refluxing CH_2Cl_2. However under quite identical reaction conditions the water soluble sodium salt of monosulfonated PPh_3 m-$NaO_3SC_6H_4PPh_2$ was able to replace all three nitrile ligands yielding **2** in contrast to unsubstituted PPh_3, which left one nitrile group unaffected yielding the bisphosphine complex **3**.

The replacement of CH_3CN for Me_2PPh was rather sluggish in refluxing CH_2Cl_2. Under more drastic conditions (excess of Me_2PPh, refluxing $CHCl_3$), quite unexpectedly, compound **5**, a neutral complex of Tc(I), was obtained. The coordinated chlorine must come from the solvent.

The structural assignment of **1–5** was made by IR spectroscopy. The intensity relations of carbonyl bands $\nu(C-O)$ are different for facial structure with symmetry C_S and meridional arrangement of ligands (symmetry C_{2v}) [2, 5]. The *fac*-compounds have three strong IR bands around 2000 cm^{-1}, while in the *mer*-compounds the band above 2000 cm^{-1} is very weak. As in the case of Mn complexes [1] in our reactions the *fac*-products were predominant. While compound **2** is pure *fac*-isomer, in **1**, **3**, **4** and **5** small amounts of the *mer*-forms cannot be excluded from the IR spectra (see 'Experimental').

Compounds **1–5** were subjected to NMR investigations. Compound **2** was shown to be stable in water solution for at least 20 days and not to contain coordinated CH_3CN. Detailed data on ^{99}Tc NMR spectra of **1** and **3–5** are given in a separate paper [6] together with other Tc(I) complexes.

Experimental

All operations were made under nitrogen. The pure substances withstand short contact with air.

$[Tc(CO)_3(CH_3CN)_3]PF_6$ (1)

450 mg (1.4 mmol) $Tc(CO)_5Br$ are refluxed in 40 ml acetonitrile for 4 h and the suspension obtained from 400 mg NH_4PF_6, 400 mg $AgNO_3$, 3 ml EtOH and 3 ml water added. After standing overnight at room temperature the mixture is filtered, the solution evaporated and the residue extracted with three 30 ml portions of refluxing CH_2Cl_2. After concentration to 15 ml addition of n-hexane yields 600 mg (95%) colourless crystals. Melting point (m.p.) 138–140 °C. *Anal.* Calc. for $C_9H_9N_3O_3F_6PTc$ C, 24.0;

TABLE I. Ligand Exchange Products of **1** with Phosphines in CH_2Cl_2

Phosphine	Molar ratio (1:phosphine)	Product	
m-$NaO_3SC_6H_4PPh_2$	1:3	$[Tc(CO)_3(m\text{-}NaO_3SC_6H_4PPh_2)_3]^+PF_6^-$	**2**
PPh_3	1:3	$[Tc(CO)_3(CH_3CN)(PPh_3)_2]^+PF_6^-$	**3**
$Ph_2PCH_2CH_2PPh_2$	1:1	$[Tc(CO)_3(CH_3CN)(diphos)]^+PF_6^-$	**4**
Me_2PPh (in $CHCl_3$)	1:8	$Tc(CO)_3Cl(Me_2PPh)_2$	**5**

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N, 9.3; Tc, 22.0. Found: C, 22.6; N, 9.5; Tc, 21.9%. IR spectrum (KBr): 834(s), 1930(w), 1948(s), 1960(s), 1979(w), 2060(w), 2075(s), 2303 cm^{-1}.

fac-$[Tc(CO)_3(m\text{-}NaO_3SC_6H_4PPh_2)_3]PF_6$ (2)

Solutions of 100 mg (0.22 mmol) of **1** in 15 ml CH_2Cl_2 and 240 mg sodium salt of *m*-diphenylphosphinobencenesulfonic acid in 35 ml CH_2Cl_2 are combined and refluxed for 4 h. While still hot colourless crystals form. They were recrystallized from water.

Yield: 220 mg (70%). *Anal.* Calc. for $C_{57}H_{42}O_{12}F_6Na_3P_4S_3Tc$: C, 48.2; Tc, 7.0. Found: C, 47.3; Tc, 6.0%. IR spectrum (KBr): 848(s), 1200, 1240, 1935(s), 1976(s), 2053(s) cm^{-1}.

Compounds **3** and **4** were made in the same way by refluxing **1** and the ligand in CH_2Cl_2 and concentrating the solutions. Recrystallization from CH_2Cl_2/n-hexane.

$[Tc(CO)_3CH_3CN(PPh_3)_2]PF_6$ (3)

80 mg (0.18 mmol) **1**, 0.54 mmol PPh_3. Yield: 80 mg (50%); m.p. 166–168 °C. *Anal.* Calc. for $C_{41}H_{33}NO_3F_6P_3Tc$: C, 55.0; Tc, 11.0. Found: C, 55.7; Tc, 10.2%. IR spectrum (KBr): 833(s), 1444, 1489, 1890(w), 1953(w), 1963(s), 1995(s), 2044(w), 2065(s), 2296, 2326 cm^{-1}.

$[Tc(CO)_3(CH_3CN)(diphos)]PF_6$ (4)

60 mg (0.13 mmol) **1**, 0.13 mmol diphos. Yield: 50 mg (50%); m.p. 94–96 °C. *Anal.* Calc. for $C_{31}H_{27}NO_3F_6P_3Tc$: C, 48.5 Tc, 12.9. Found: C, 50.0; Tc, 12.9%. IR spectrum (KBr): 840, 1452, 1502, 1929(w), 1950(s), 1965(s), 1981(w), 2041(w), 2060(s), 2303, 2858, 2927, 2965 cm^{-1}.

$Tc(CO)_3Cl(Me_2PhP)_2$ (5)

113 mg (0.25 mmol) **1**, 276 mg (2 mmol) Me_2PhP were refluxed in 30 ml $CHCl_3$ for 2 h. After concentration and addition of n-hexane white crystals were obtained, which were purified from CH_2Cl_2/n-hexane. Yield: 60 mg (51%); m.p. 121–124 °C. *Anal.* Calc. for $C_{19}H_{22}O_3P_2ClTc$: C, 46.1; Tc, 20.0. Found: C, 47.3; Tc, 19.0%. IR spectrum (KBr); 267, 302, 333, 1432, 1447, 1897(s), 1915(w), 1929(w), 1944(s), 2013(w), 2034(s) cm^{-1}.

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