# Mixed Ligand Complexes of Technetium. II. $[Tc(dppe)_2(R\text{-}NC)_2]^+$ Complexes (dppe = bis(diphenylphosphino)ethane; R = tert. butyl, cyclohexyl)

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Cationic complexes of $^{99m}Tc$ with ditertiary phosphines [1–3], isonitriles [4, 5], phosphites [6, 7] and phosphonites [8] are promising agents for myocardial imaging in diagnostic nuclear medicine ($^{99m}Tc$: $\gamma$-emitter with $E_\gamma = 140$ keV, half-life $t_{1/2} = 6$ h). Chemical studies, however, are made with the long-lived nuclide $^{99}Tc$ (weak $\beta^-$-emitter with $E_{max} = 0.3$ MeV, $t_{1/2} = 2.12 \times 10^5$ years) showing technetium(I) complexes of the general formulae $[TcL_3]^+$ (L = bidentate ligands) and $[TcL_6]^+$ (L = monodentate ligands) to be the most stable products.

Here we present a first study dealing with so-called mixed ligand complexes of technetium containing the ditertiary phosphine bis(diphenylphosphino)ethane (DPPE) as well as isonitrile ligands.

## Experimental

All operations were carried out under dry nitrogen. The starting complex $Tc(N_2)H(dppe)_2$ was synthesized by a literature method [9, 10].

### *Preparation of trans-[Tc(dppe)₂(buᵗ-NC)₂]PF₆*

46 mg (0.05 mmol) of $Tc(N_2)H(dppe)_2$ were suspended in 20 ml MeOH. After addition of 1 ml of $bu^t$-NC the mixture was refluxed until the yellow starting material was dissolved and a colourless clear solution could be obtained (about 2 h). The volume was reduced to 5 ml and after cooling an excess of $KPF_6$ in MeOH was added resulting in precipitation of a colourless solid. After separation the microcrystalline product was recrystallized from $CH_2Cl_2$/MeOH to obtain colourless plates. Yield: 49 mg (81% based on Tc), melting point (m.p.) 285–286 °C. *Anal.* Calc. for $C_{62}H_{66}N_2P_5F_6Tc$: C, 61.7; H, 5.7; N, 2.3; Tc, 8.2. Found: C, 60.6; H, 5.7; N, 2.5; Tc: 7.9%. Optical spectrum (nm (lg $\epsilon$)): 271 (4.11), 277 (4.09). Conductivity (acetonitrile, $10^{-3}$ M): $\Lambda_M = 129.1\ \Omega^{-1}\ cm^2\ mol^{-1}$.

### *Preparation of trans-[Tc(dppe)₂(cyclohex-NC)₂]PF₆*

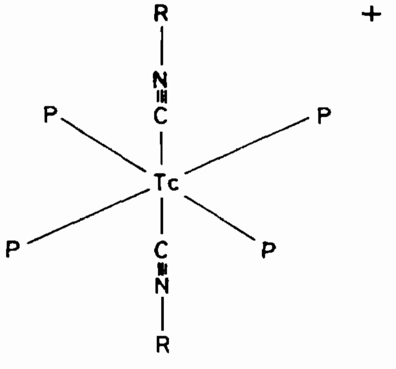
This compound was synthesized following the route stated above giving 20 mg (31%) of a colourless, microcrystalline solid, m.p. 313–314 °C. *Anal.* Calc. for $C_{66}H_{70}N_5F_6Tc$: C, 63.0; H, 5.6; N, 2.2; Tc, 7.9. Found: C, 63.4; H, 5.9; N, 2.0; Tc, 7.7%. Optical spectrum (nm(lg $\epsilon$)): 271 (4.12), 278 (4.11). Conductivity (acetonitrile, $10^{-3}$ M): $\Lambda_M = 118.6\ \Omega^{-1}\ cm^2\ mol^{-1}$.

### *Physical Measurements*

Infrared spectra were recorded in KBr pellets with an UR 20 instrument and the UV–Vis spectra in acetonitrile solutions with a SPECORD M 40 of Carl-Zeiss-Jena. NMR measurements were carried out with an AM 250 instrument (Bruker). Tc contents of the samples were determined by liquid scintillation measurements.

## Results and Discussion

The dinitrogen technetium(I) complex is a suitable starting material for the synthesis of mixed ligand complexes of the metal in its lower oxidation states. Reaction with isocyanide ligands leads to replacement of the dinitrogen as well as the hydride ligands to form cationic technetium(I) compounds of general formula *trans*-$[Tc(R\text{-}NC)_2(dppe)_2]^+$ (I).



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Their $PF_6^-$ salts are colourless solids which are soluble in $CH_2Cl_2$, acetonitrile and acetone, very slightly soluble in methanol and practically insoluble in hydrocarbons. The compounds are air-stable as solids and in solution.

The complexes are diamagnetical. $^1H$ NMR spectra are characterized by small lines. The patterns obtained (Table I) confirm their structure. No evidence was found for hydride hydrogens. The $^{31}P$ NMR spectra show singlets in agreement with the stated *trans*-coordination. Strong infrared absorptions at

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TABLE I. NMR Spectral Results ($CD_2Cl_2$ Solutions) Relative to TMS[a]

| $^1$H NMR | | | |
|---|---|---|---|
| *trans*-[Tc(dppe)$_2$(bu$^t$-NC)$_2$]$^+$ | | *trans*-[Tc(dppe)$_2$(cyclohex-NC)$_2$]$^+$ | |
| $CH_3$ | 0.68s (18H) | cyclohexyl | 0.83–1.55m (22H) |
| $CH_2$ | 2.49tr (8H) | $CH_2$ | 2.43tr (8H) |
| phenyl | 7.14–7.37m (40H) | phenyl | 7.13–7.39m (40H) |

[a]Chemical shift in ppm, multiplicity (intensity).

2049 and 2079 $cm^{-1}$ (for R = tert. butyl) and 2058 and 2115 $cm^{-1}$ (for R = cyclohexyl), respectively, can be assigned to the C≡N stretch. The frequencies found are in the same range as those obtained for the hexakis complexes of Tc(I) with the same ligands [11] and suggest a strong back donation from the metal centre. The results of the electric conductivity measurements are in accordance with those expected for a 1:1 electrolyte.

The displacement of the dinitrogen and hydride ligands in $Tc(N_2)H(dppe)_2$ by isocyanides comes not unexpected, taking into account the behaviour of a similar rhenium complex, $Re(N_2)Cl(dppe)_2$, losing the dinitrogen ligand during a 5 d refluxing period [12]. The technetium compound used seems to be much less inert, so the reaction is completed after some hours. During this time also, the hydride ligand is abstracted quantitatively.

The compounds described present prototype-complexes of a new class of low-valent technetium cations, which possess a potential for myocardial imaging agents. By stepwise variation of either of the ligands a large number of mixed ligand complexes can be obtained the polar and lipophilic properties of which can be controlled within a wide range.

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## References

1 J.-L. Vanderheyden, K. Libson, D. L. Nosco, A. R. Ketring and E. Deutsch, *Int. J. Appl. Radiat. Isot., 34,* 1611 (1984).

2 J.-L. Vanderheyden, A. R. Ketring, K. Libson, M. J. Heeg, L. Roecker, P. Metz, R. Whittle, R. C. Elder and E. Deutsch, *Inorg. Chem., 23,* 3184 (1984).

3 R. Syhre, S. Seifert, F. Schneider, R. Muenze and W. Mohnike, *Nuc. Compact, 17,* 199 (1986).

4 A. G. Jones, M. J. Abrams, A. Davison, J. W. Brodack, A. K. Toothaker, S. J. Adelstein and A. I. Kassis, *Int. J. Nucl. Med. Biol., 11,* 225 (1984).

5 (a) J. F. Kronauge, A. G. Jones, A. Davison, J. Lister-James, S. J. Williams and S. A. Mousa, *J. Nucl. Med., 27* 875 (1986); (b) S. J. Williams, S. A. Mousa, R. A. Morgan, T. R. Carrol and L. J. Maheu, *J. Nucl. Med., 27,* 877 (1986).

6 D. W. Wester, D. H. White, F. W. Miller and R. T. Dean, *Inorg. Chem., 23,* 1502 (1984).

7 D. W. Wester, D. H. White, F. W. Miller, R. T. Dean, J. A. Schreifels and J. E. Hunt, *Inorg. Chim. Acta, 131,* 163 (1987).

8 U. Abram and S. Abram, *Z. Chem., 26,* 181 (1986).

9 L. Kaden, B. Lorenz, K. Schmidt, H. Sprinz and M. Wahren, *Z. Chem., 19,* 305 (1979).

10 Y. T. Struchkov, A. S. Bazanov, L. Kaden, B. Lorenz, M. Wahren and H. Meyer, *Z. Anorg. Allg. Chem., 494,* 91 (1982).

11 M. J. Abrams, A. Davison, A. G. Jones, C. E. Costello and H. Pang, *Inorg. Chem., 22,* 2798 (1983).

12 A. J. Pombeiro, M. F. N. N. Corvalho, P. B. Hitchcock and R. L. Richards, *J. Chem. Soc., Dalton Trans.,* 1629 (1981).