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$HTc(N_2)(dppe)_2$ as starting material for mixed-ligand complexes of technetium(I)

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Abstract

In the complex $HTc(N_2)(dppe)_2$ the nitrogen ligand is most labile and can be exchanged under mild conditions for CO, isonitriles and phosphites (L_1), yielding neutral hydridocomplexes of Tc(I) $HTcL_1(dppe)_2$. $HTc(CO)(dppe)_2$ is also formed from the title compound by CO abstraction from methanol. In the complexes $HTcL_1(dppe)_2$ the hydrido ligand can be exchanged for acetonitrile (L_2), yielding cationic mixed-ligand complexes of Tc(I) $TcL_1L_2(dppe)_2{}^+$, which are isolated as hexafluorophosphates.

Introduction

Research on technetium complexes is being strongly stimulated by the wide use of radiodiagnostics based on complex compounds containing the 6h-isotope ^{99m}Tc. Technetium complexes with different types of ligands in the same molecule, so-called mixed-ligand complexes, offer the possibility of tailoring essential properties of the complexes and so recently much work has been devoted to obtain such compounds [1].

Dinitrogen is a rather weak ligand and may be considered as a good leaving group in preparative metal complex chemistry [2]. It may be replaced by related ligands which bind more strongly to the metal. Pombeiro *et al.* reported the replacement of N_2 in $ReCl(N_2)(dppe)_2$ for isocyanides [3], nitriles [4] and 1-alkynes [5]. The corresponding rhenium complexes were obtained in good yields. In 1979 we prepared a dinitrogen complex of Tc [6] which was shown to have the structure $HTc(N_2)(dppe)_2$ (**1**) with the H^- and N_2 ligand in *trans*-position [7]. Both the H^- and the N_2 ligand exchange easily by reacting **1** with a considerable excess of isocyanides [8], trimethylphosphite [9] or thiols [10] yielding cationic complexes of Tc with two different types of ligands as dppe is retained.

The rhenium analogue of **1**, $HRe(N_2)(dppe)_2$, was shown to exchange the dinitrogen for CO or ethylene [11] retaining the hydrido ligand. The complex **1** is itself a typical mixed-ligand complex of Tc. Possessing three different ligands with clear differences in exchangeability **1** should be able to serve as a starting material for well defined complexes of Tc(I) with three different types of ligands, if the N_2 and the H^- ligand could be exchanged stepwise. The aim of this paper is to prove this assumption.

Experimental

Reactions were carried out under nitrogen using solvents dried by standard procedures before use. $HTc(N_2)(dppe)_2$ was prepared according to ref. 6. IR spectra (in KBr) were recorded on a Zeiss UR-10 spectrometer. The NMR spectra were performed on a Bruker AM-250 spectrometer (250 MHz for ^1H and 56.3 MHz for ^{99}Tc, respectively). The spectra are referred to the solvent peak ($C_6D_6 = 7.16$ ppm) for ^1H and to an external solution of $NaTcO_4$ in D_2O (0 ppm) for ^{99}Tc, respectively. The Tc content of the samples was determined by liquid scintillation measurements.

$HTc(CO)(dppe)_2$

A solution of 150 mg of **1** in benzene (15 ml) was stirred for 24 h at room temperature under pure CO. Benzene was evaporated by a stream of CO down to 5 ml and n-hexane (20 ml) was added to precipitate a white powder. The compound was quite pure after washing with n-hexane and vacuum drying. Yield 55%.

Anal. Found: Tc, 10.9; C, 68.8. Calc. for $C_{53}H_{49}OP_4Tc$: Tc, 10.7; C, 68.1%. ^1H NMR: H^-, -5.53 quin (1H); CH_2, 2.05–2.28 (8H); C_6H_5, 6.91–7.75 (40H).

The same complex is also obtained by boiling 100 mg of **1** in methanol (40 ml) which contains 50 mg Na or 50 μl pyridine. The yellow **1** dissolves gradually and

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white HTc(CO)(dppe)$_2$ precipitates. After 12 h of boiling 85% of **1** had reacted.

HTc(C$_6$H$_{11}$NC)(dppe)$_2$

150 mg (0.16 mmol) of **1** were refluxed in benzene (20 ml) containing 0.48 mmol cyclohexylisocyanide for 1 h. The solution was evaporated to about 2 ml in a stream of nitrogen, filtered, and the solid obtained was washed with ethanol and recrystallized from benzene. Yellow crystals, yield 57%.

Anal. Found: Tc, 9.8; C, 70.7; N, 1.4. Calc. for $C_{59}H_{60}NP_4Tc$: Tc, 9.8; C, 70.4; N, 1.4%. ^{1}H NMR: H^-, −6.73 quin (1H); C_6H_{11}, 1.04–1.51; 3.23 (11H); CH_2 (dppe), 2.12–2.33 (8H); C_6H_5, 6.91–7.79 (40H).

HTc(tert-C$_4$H$_9$NC)(dppe)$_2$

The compound was prepared as described above using 0.48 mmol tert-butylisocyanide. Yellow crystals, yield 36%.

Anal. Found: Tc, 9.2; C, 71.5; N, 1.4. Calc. for $C_{57}H_{58}NP_4Tc$: Tc, 10.1; C, 69.9; N, 1.4%. ^{1}H NMR: H^-, −7.02 quin (1H); CH_3, 0.86 s (9H); CH_2, 2.14–2.33 (8H); C_6H_5, 6.90–7.76 (40H).

HTc[(CH$_3$O)$_3$P](dppe)$_2$

330 mg (0.36 mmol) of **1** were boiled in benzene (50 ml) containing 250 μl (1.98 mmol) of trimethylphosphite for 3.5 h. The solution was evaporated in a nitrogen stream to 5 ml. A yellow solid crystallized out, yield 10%.

^{1}H NMR: H^-, −7.28 quin (1H); CH_2, 2.0–2.63 (8H); CH_3O, 2.63 d (9H); C_6H_5, 6.90–7.86 (40H).

[Tc(CO)(CH$_3$CN)(dppe)$_2$]$^+$PF$_6^-$

30 mg (0.03 mmol) of HTc(CO)(dppe)$_2$ were refluxed in acetonitrile (15 ml) for 8 h. The solution was filtered and an excess of NH_4PF_6 in methanol added dropwise. The mixture was evaporated to dryness in a nitrogen stream and recrystallized from CH_2Cl_2/n-hexane. Greyish crystals, yield 57%.

Anal. Found: Tc, 8.5; C, 58.5; N, 1.2. Calc. for $C_{55}H_{51}NOP_5F_6Tc$: Tc, 8.9; C, 59.5; N, 1.3%. ^{1}H NMR: CH_3, 1.27 (3H); CH_2, 2.37–2.59 (8H); C_6H_5, 5.30–7.38 (40H).

[Tc(tert-C$_4$H$_9$NC)(CH$_3$CN)(dppe)$_2$]$^+$PF$_6^-$

132 mg (0.13 mmol) of HTc(tert-C$_4$H$_9$NC)(dppe)$_2$ were refluxed in acetonitrile (40 ml) for 9 h. A solution of excess NH_4PF_6 in methanol was added and the mixture evaporated to dryness in a stream of nitrogen. The solid was extracted twice with 2.5 ml CH_2Cl_2. The solution was filtered and 15 ml n-hexane were added. A greyish-green solid precipitated and was washed with hexane. Yield 59%.

Anal. Found: Tc, 8.3; C, 60.5; N, 2.4. Calc. for $C_{59}H_{60}N_2P_5F_6Tc$: Tc, 8.5; C, 60.8; N, 2.4%. ^{1}H NMR: CH_3 (tert-C_4H_9), 1.08 (9H); CH_3 (CH_3CN), 1.27 (3H); CH_2, 2.27–2.54 (8H); C_6H_5, 6.65–7.60 (40H).

Results and discussion

It is possible to exchange the dinitrogen ligand in the title complex **1** for other ligands L_1 of the π-acceptor type under conditions retaining the H^- ligand. The structure of the new hydridotechnetium complexes HTcL$_1$(dppe)$_2$ is derived from that of the parent nitrogen complex **1**; H^- and L_1 are in *trans*-position. This is indicated by the splitting pattern of the ^{1}H NMR peaks of the H^- ligands (see Table 1) which are quintets due to coupling with four identical phosphorus atoms (J(P–H) = 22–24 Hz). In the complex HTc[(CH$_3$O)$_3$P](dppe)$_2$ the presence of the additional phosphite phosphorus leads to a more complex pattern, which can be interpreted as a doublet whose components are split into quintets. No signs of structural rearrangements were found.

The strong IR signal of the N_2 ligand in **1** at 2050 cm^{-1} disappeared completely during the formation of all new HTcL$_1$(dppe)$_2$ complexes. The relation of H^-: dppe was never influenced by the exchange of N_2 for L_1 and remained exactly 1:2 as in **1**. This was proved by the relative intensities of the ^{1}H NMR peaks for H^-, CH_2– and C_6H_5– protons, which were always 1:8:40, respectively. The π-acceptor properties of the different ligands L_1 and their influence on the H^- ligand lead to parallel effects upon the relative positions of the absorption band $\tilde{\nu}$(Tc–H) in the IR spectra and the chemical shift $\delta(H^-)$ in the ^{1}H NMR spectra as could be expected in such a related series (see Table 1). All complexes are diamagnetic. The chemical shifts of Tc are not so strictly correlated. For $L_1 = N_2$ the highest magnetic shieldings are obtained for Tc as well as for H^-.

The formation of HTc(CO)(dppe)$_2$ from **1** in methanol in the presence of a base was quite unexpected. Without a base the same product was obtained [1], but the reaction is very sluggish and yields a mixture of products, among them the starting material **1** and compounds without a Tc–H bond. Obviously the first step in this remarkable reaction is the exchange of dinitrogen for methoxide yielding formally an anionic intermediate complex which could be stabilized by the base. Hydrogen elimination via formaldehyde and formyl complexes was proposed by Chaudret *et al.* [12] in a similar formation of a ruthenium carbonyl complex.

The exchange of H^- for L_2 = acetonitrile by boiling the hydrido complexes with the neat ligand resulted in cationic complexes TcL$_1$L$_2$(dppe)$_2^+$ which were iso-

TABLE 1. IR and NMR spectra of $HTcL_1(dppe)_2$ complexes

L_1	IR[a]		^1H NMR δH^- (ppm)	^{99}Tc NMR[b]	
	$\tilde{\nu}$(Tc–H)	$\tilde{\nu}(L_1)$ (cm^{-1})		δ (ppm)	$\Delta\tilde{\nu}_{1/2}$ (Hz)
N_2	1750	2050	−10.1 quin[c]	−1676	5130
$P(OCH_3)_3$	1735	805, 1037 (P–O)	−7.3 2×quin[c]		
$t\text{-}C_4H_9NC$	1665	1985 ($N{\equiv}C$)	−7.0 quin[c]	−1080 quin[d]	400
$C_6H_{11}NC$	1655	1945	−6.7 quin[c]	−1310	7300
CO	1634	1859	−5.5 quin[c]	−1321	1810

[a]In KBr except for $L_1 = N_2$ (nujol). [b]$\delta TcO_4^- = 0$, external standard $NaTcO_4$ in D_2O. [c]J(P–H) = 22–24 Hz. For signals of dppe or L_1 protons, see 'Experimental'. [d]J(Tc–P) = 605 Hz.

TABLE 2. Comparison between IR and NMR data of neutral and cationic technetium complexes

Compound	IR	^{99}Tc NMR	
	$\tilde{\nu}(C{\equiv}O)$ or $(N{\equiv}C)$ (cm^{-1})	δ (ppm)[a]	$\Delta\tilde{\nu}_{1/2}$ (Hz)
$HTc(CO)(dppe)_2$	1859	−1321	1810
$[(CH_3CN)Tc(CO)(dppe)_2]^+PF_6^-$	1882	−1436 quin[b]	330
$HTc(t\text{-}C_4H_9NC)(dppe)_2$	1985	−1080 quin[c]	400
$[(CH_3CN)Tc(t\text{-}C_4H_9NC)(dppe)_2]^+PF_6^-$	2022	−1250	2100
$BrTc(CO)_3dppe$	1929, 1968, 2035	−1816	2160
$[(CH_3CN)Tc(CO)_3dppe]^+PF_6^-$	1950, 1965, 2060	−3517	2000

[a]$\delta TcO_4^- = 0$. [b]J(Tc–P) = 580 Hz. [c]J(Tc–P) = 605 Hz.

lated in good yields as hexafluorophosphates. The *trans*-position of the ligands $L_1 = CO$ and $L_2 = CH_3CN$ in the complex $(CH_3CN)Tc(CO)(dppe)_2{}^+PF_6^-$ is evidenced by the ^{99}Tc NMR spectrum. The Tc peak at −1436 ppm (relative to TcO_4^-) is split into a quintet due to coupling with four equivalent phosphorus atoms (J(Tc–P) = 580 Hz). If L_1 and L_2 were located in *cis*-position, not all P atoms would be equivalent. For the structure of the complex $(CH_3CN)Tc(tert\text{-}C_4H_9NC)(dppe)_2{}^+PF_6^-$ such proof does not yet exist. The ^{99}Tc peak is rather broad, so any splitting pattern is obscured. As can be seen from Table 2 the spectral properties in IR and ^{99}Tc NMR are changed in the expected way in the conversion of neutral to cationic complexes. Nevertheless the effect in the ^{99}Tc NMR is much smaller than for the substitution of chloro or bromo ligands for acetonitrile in the $Tc(CO)_3dppe$ series [13] of which one example is given in Table 2 for comparison. The ligated acetonitrile gives no IR signals in the triple bond region for $\tilde{\nu}(C{\equiv}N)$.

Unfortunately, technetium–dinitrogen complexes other than **1** are unknown so far and therefore the reactions are limited to the $Tc(dppe)_2$ series. It seems very probable, however, that from **1** still other types of diamagnetic Tc(I) complexes with d^6-configuration such as $HTcL(dppe)_2$, $Tc(L)_2(dppe)_2{}^+$ and $TcL_1L_2(dppe)_2{}^+$ could be obtained.

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