

Nitrosyltechnetium complexes with (2-aminomethylphenyl)diphenylphosphine



Janine Ackermann, Adelheid Hagenbach, Ulrich Abram*

Freie Universität Berlin, Institute of Chemistry and Biochemistry, Fabeckstr. 34/36, D-14195 Berlin, Germany

ARTICLE INFO

Article history:

Received 28 February 2014
Received in revised form 17 April 2014
Accepted 25 April 2014
Available online 6 May 2014

Keywords:

Technetium
Nitrosyls
Phosphaneamine
Synthesis
X-ray structure
EPR

ABSTRACT

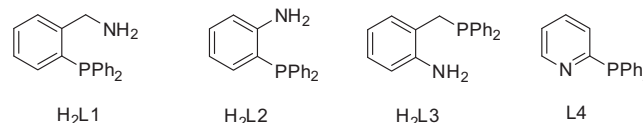
Reactions of $(\text{NBu}_4)[\text{Tc}(\text{NO})\text{Cl}_4(\text{MeOH})]$ (**1**) with (2-aminomethylphenyl)diphenylphosphine, $\text{H}_2\text{L1}$, give different products depending on the conditions applied. An equimolar reaction in MeOH gives the technetium(II) monochelate $[\text{Tc}(\text{NO})\text{Cl}_3(\text{H}_2\text{L1-}\kappa\text{N,P})]$ (**2**) as the sole product, which could be isolated. Reduction of the metal ion and the formation of the Tc(I) complexes $[\text{Tc}(\text{NO})\text{Cl}_2(\text{H}_2\text{L1-}\kappa\text{N,P})(\text{H}_2\text{L1-}\kappa\text{N})]$ (**3**) and $[\text{Tc}(\text{NO})\text{Cl}(\text{H}_2\text{L1-}\kappa\text{N,P})_2\text{Cl}]$ (**4**), besides some $(\text{NBu}_4)[\text{Tc}(\text{NO})\text{Cl}_4(\text{H}_2\text{L1-}\kappa\text{N})]$ (**5**), is observed when an excess of the $\text{H}_2\text{L1}$ is used in the same solvent. Reactions in acetonitrile are less defined and only the Tc(II) compound $(\text{NBu}_4)[\text{Tc}(\text{NO})\text{Cl}_4(\text{H}_2\text{L1O-}\kappa\text{N})]$ (**6**) could be isolated from such reactions in crystalline form.

The products were studied spectroscopically and by X-ray diffraction. The aminophosphine acts as monodentate nitrogen donor ligand or as *N,P* chelator.

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1. Introduction

(2-Aminomethylphenyl)diphenylphosphine, $\text{H}_2\text{L1}$, belongs to a series of aminophosphines, which are versatile ligands. They combine hard and soft donor atoms and stabilize transition metals in different oxidation states. This has attracted considerable attention and several studies concerning their complex formation behavior have been performed [1–21]. Most of them, however, focus to (2-aminophenyl)phosphine, $\text{H}_2\text{L2}$. Also the coordination chemistry of rhenium and technetium has previously been studied in detail and shows a high degree of flexibility of the ligand [15–20]. Reactions starting from MO_4^- ($\text{M} = \text{Re}, \text{Tc}$) or other common oxidorhenium(V) or oxidotechnetium(V) precursors frequently give neutral oxido complexes of the composition $[\text{MO}(\text{HL2})_2\text{X}]$ ($\text{M} = \text{Re}, \text{Tc}$; $\text{X} = \text{halide}, \text{hydroxido}, \text{alkoxido}$ or carboxylic ligands) [16]. But also neutral or cationic homoleptic $[\text{Tc}^{\text{III}}(\text{HL2})_3]$ or $[\text{Tc}^{\text{III}}(\text{H}_2\text{L2})(\text{HL2})_2]$ complexes with single-deprotonated aminophosphines were isolated [19]. Under particular conditions, the aromatic amine deprotonates completely and replaced the oxido ligand under formation of a phenylimido ligand [17,19].



A partially different reaction pattern is observed for the derived ligand $\text{H}_2\text{L3}$, which also readily forms oxidorhenium complexes, but does not deprotonate in all hitherto known examples [22]. Not even the addition of a supporting base results in a reaction of $\text{H}_2\text{L3}$ with $[\text{ReOCl}_4]^-$ results in ligand deprotonation but in chloride abstraction from the starting complex and the formation of the trimeric complex $[\{\text{ReOCl}(\text{H}_2\text{L3})\}\text{O}]_3$ with the unusual $\{(\text{ReO})\text{O}\}_3^{3+}$ core [22]. One of the driving forces for the different reactivity of $\text{H}_2\text{L2}$ and $\text{H}_2\text{L3}$ may be the opportunity of a better electron delocalization in the five-membered chelate rings with $\{\text{HL2}\}^-$ compared with the six-membered rings of the $\text{H}_2\text{L3}$ complexes which contain CH_2 units interrupting a possible π -conjugation. This makes a comparison with the related aminophosphine $\text{H}_2\text{L1}$ interesting, also keeping in mind that this compound contains an aliphatic NH_2 group instead the aromatic amines $\text{H}_2\text{L2}$ and $\text{H}_2\text{L3}$.

Surprising less is known about the coordination behavior of $\text{H}_2\text{L1}$. To the best of our knowledge, there is up to now only one example of a structurally characterized transition metal complex with the unsubstituted ligand $\text{H}_2\text{L1}$, the cationic ruthenium(II) complex $[\text{Ru}(\text{H}_2\text{L1})(\text{py})(\text{cp}^*)]^+$ [23], but there are many more exam-

* Corresponding author. Tel.: +49 30 838 54002; fax: +49 30 838 52676.
E-mail address: ulrich.abram@fu-berlin.de (U. Abram).

ples with the corresponding NMe₂ derivative or tri- or tetradentate ligands having the *P,N* coordination site of H₂L1 as building block [24].

In the present paper, we report about reactions of H₂L1 with the technetium(II) complex (NBu₄)[Tc(NO)Cl₄], a starting material, which has also been used for reactions with another aminophosphine ligand, namely 2-pyridyldiphenylphosphine, L4 [25].

2. Experimental

2.1. Materials

All reagents used in this study were reagent grade and used without further purification. The synthesis of H₂L1 was done following literature procedures [26]. (NBu₄)[Tc(NO)Cl₄(MeOH)] was prepared from tetrabutylammonium pertechnetate, HCl and hydroxylamine hydrochloride [27,28].

2.2. Physical measurements

Infrared spectra were measured from KBr pellets on a Shimadzu FTIR-spectrometer between 400 and 4000 cm⁻¹. NMR spectra were recorded on a JEOL-400MHz nuclear magnetic resonance spectrometer. The EPR spectra were recorded on an ER 200D-SCR spectrometer with a Bruker B-E25 magnet and an ER 041MR microwave generator. Simulated spectra were obtained by computer simulation (Bruker SIMFONIA) based on second-order perturbation theory. Tc values were determined by liquid scintillation counting.

2.3. Radiation precautions

⁹⁹Tc is a weak β⁻ emitter (*E*_{max} = 0.292 MeV) with a half-life of 2.12 × 10⁵ years. All manipulations were done in a laboratory approved for the handling of radioactive materials. Normal glassware provides adequate protection against the weak beta radiation when only milligram amounts of the isotope are used, and no extra shielding is required. Secondary X-rays (bremsstrahlung), however, become important when larger amounts of solid samples of ⁹⁹Tc are handled.

2.4. Syntheses

2.4.1. [Tc(NO)Cl₃(H₂L1-κN,P)] (2)

(NBu₄)[Tc(NO)Cl₄(MeOH)] (1) (55 mg, 0.1 mmol) was dissolved in 5 mL of MeOH and H₂L1 (30 mg, 0.1 mmol) was added in 5 mL MeOH. The reaction mixture was heated on reflux for 2 h. The volume of the obtained orange-red solution was reduced to about 2 mL and the mixture was placed in a refrigerator. The formed orange-brown solid was filtered off and recrystallized from CH₂Cl₂/MeOH. Single crystals for X-ray diffraction were obtained from slow evaporation of this solution. Yield: 40%. *Anal. Calc.* for C₁₉H₁₈Cl₃N₂OPTc (526.6): Tc, 18.8%, Found: Tc, 19.0%. IR (KBr, *v*_{max} in cm⁻¹): 3424 (w), 3291 (w), 3202 (w), 2959 (w), 2922 (w), 1789 (vs) *v*_{NO}, 1655 (m), 1560 (m), 1476 (w), 1433 (m), 1381 (w), 1315 (w), 1263 (w), 1215 (w), 1153 (m), 1123 (m), 1094 (m), 102 (w), 997 (w), 893 (w), 756 (m), 692 (m), 519 (m), 488 (w), 405 (s).

2.4.2. [Tc(NO)Cl₂(H₂L1-κN,P)(H₂L1-κN)] (3), (NBu₄)[Tc(NO)Cl₄(H₂L1-κN)] (4), [Tc(NO)Cl(H₂L1-κN,P)₂]Cl (5)

(NBu₄)[Tc(NO)Cl₄(MeOH)] (1) (55 mg, 0.1 mmol) was dissolved in 5 mL of MeOH and H₂L1 (87 mg, 0.3 mmol) was added in 5 mL MeOH. The reaction mixture was heated on reflux for 2 h. The volume of the obtained orange-red solution was reduced to about 5 mL and the mixture was kept overnight for crystallization at

room temperature. The formed orange-yellow solid of [Tc(NO)Cl₂(H₂L1-κN,P)(H₂L1-κN)] was filtered off and recrystallized from CH₂Cl₂/MeOH. The remaining solution was concentrated to a volume of 2 mL and placed in a refrigerator, which gave green plates of (NBu₄)[Tc(NO)Cl₄(H₂L1-κN)] and a few yellow blocks of the bis-chelate [Tc(NO)Cl(H₂L1-κN,P)₂]Cl.

[Tc(NO)Cl₂(H₂L1-κN,P)(H₂L1-κN)] (3): Yield: 40%. *Anal. Calc.* for C₃₈H₃₆Cl₂N₃OP₂Tc (782.5): Tc, 12.6%, Found: Tc, 12.0%. IR (KBr, *v*_{max} in cm⁻¹): 3410 (m), 3250 (m), 3215 (m), 3055 (m), 1717 (vs) *v*_{NO}, 1585 (m), 1477 (m), 1433 (s), 1396 (m), 1310 (m), 1240 (s), 1184 (m), 1151 (m), 1126 (m), 1094 (m), 1020 (m), 986 (m), 748 (s), 696 (s), 521 (m), 507 (m), 401 (s).

¹H NMR (DMSO): δ = 7.57–7.12 (m, 28H, phenyl), 3.13 (d, *J* = 5.0 Hz, 2H, CH₂), 1.01 (t, *J* = 6.9 Hz, 2H, CH₂) ppm. ³¹P NMR (DMSO): δ = -17.1 ppm.

(NBu₄)[Tc(NO)Cl₄(H₂L1-κN)] (4): Yield: 20%. *Anal. Calc.* for C₃₅H₇₂Cl₄N₃O₂PTc (838.7): Tc, 12.1%, Found: Tc, 12.6%. IR (KBr, *v*_{max} in cm⁻¹): 3302 (w), 2961 (m), 2931 (m), 2874 (m), 1784 (vs) *v*_{NO}, 1479 (w), 1381 (w), 1188 (w), 1149 (m), 1120 (m), 1071 (w), 1030 (m), 999 (m), 881 (m), 772 (w), 746 (w), 692 (m), 401 (m).

2.4.3. (NBu₄)[Tc(NO)Cl₄(H₂L1O-κN)] (6)

(NBu₄)[Tc(NO)Cl₄(MeOH)] (55 mg, 0.1 mmol) was dissolved in 5 mL of acetonitrile and H₂L1 (30 mg, 0.1 mmol) was added in 5 mL acetonitrile. The reaction mixture was heated on reflux for 2 h. The volume of the obtained orange-red solution was reduced to about 5 mL and the mixture was kept at 4 °C for 12 h. During this time, the color of the solution changed to dark brown and large, green crystals of (NBu₄)[Tc(NO)Cl₄(H₂L1O-κN)] precipitated, which were filtered off. Further concentration of the solution did not result in the isolation of defined products. Yield: 20%. *Anal. Calc.* for C₃₅H₇₂Cl₄N₃OPTc (822.7): Tc, 12.1%, Found: Tc, 12.6%. IR (KBr, *v*_{max} in cm⁻¹): 3482 (m), 2963 (s), 2937 (m), 2875 (m), 1789 (vs) *v*_{NO}, 1472 (m), 1381 (m), 1364 (w), 1263 (w), 1161 (w), 1107 (w), 1070 (w), 1047 (w), 1016 (m), 926 (w), 880 (m), 802 (w), 741 (m), 629 (s), 401 (m).

2.5. X-ray crystallography

The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (λ = 0.71073 Å). Standard procedures were applied for data reduction. Structure solution and refinement were performed with SHELXS and SHELXL [29]. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL.

More details on data collections and structure calculations are contained in Table 1. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

Reactions of H₂L1 with (NBu₄)[Tc(NO)Cl₄(MeOH)] (1) form different complexes depending on the solvents and reaction conditions applied. The products involve technetium(I) and technetium(II) complexes, which contain the phosphineamine in various coordination modes and positions. Scheme 1 summarizes the corresponding reactions in methanol.

When (NBu₄)[Tc(NO)Cl₄(MeOH)] (1) is reacted with H₂L1 in this solvent in a 1:1 ratio, the Tc(II) compound [Tc(NO)Cl₃(H₂L1-κN,P)] (2) is isolated as the sole product in moderate yields. The complex is almost insoluble in common organic solvents such as alcohols, CH₂Cl₂ or CHCl₃, but dissolves in DMF. It represents the expected ligand-exchange product containing one phosphineamine. The IR spectrum of the compound shows the *v*_{NO} vibration as an intense

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