Synthesis, Structure and Complexes of a New Bicyclic N,P-Ligand Derived from Phosphatriazaadamantane

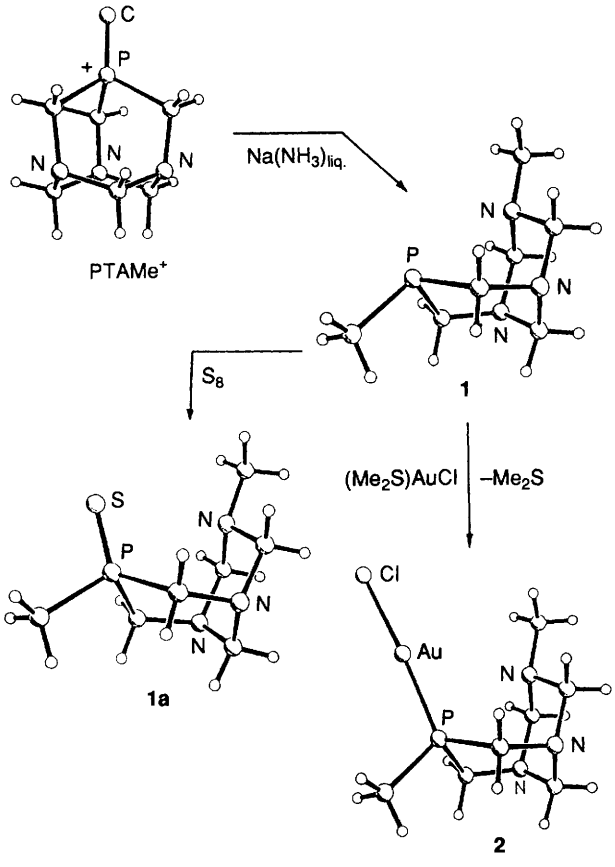
Bernd Assmann, Klaus Angermaier and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Reductive cleavage of the methylphosphoniatriazaadamantane cation by sodium in liquid ammonia affords the new bicyclic ligand (MeP)$(CH_2)_5N_2$(NMe) whose structure has been determined from crystals of its 1 : 1 complex with AuCl.

Phosphatriazaadamantane (PTA) is readily available *via* condensation of $P(CH_2OH)_3$, ammonia, and formaldehyde.[1] This compound is of considerable interest owing to its properties as a ball-shaped, polar tertiary phosphine ligand with a small cone angle, which *e.g.* can be protonated at the nitrogen functions to give water-soluble complexes.[2–4] PTA cannot be methylated regioselectively at the phosphorus atom using methyl iodide, but the desired methyl phosphonium salt ($PTAMe^+I^-$) is available through cage formation from $MeP(CH_2OH)_3^+I^-$, CH_2O, and NH_4^+ $MeCO_2^-$.[5]

In an attempt to convert the cation of this salt into the ylide ($PTA{=}CH_2$) by treating with sodium in liquid ammonia, cage cleavage was observed which leads to a bicyclic tertiary phosphine **1** with the phosphorus and one of the nitrogen atoms bearing methyl substituents, and the remainder two nitrogen atoms in a configuration similar to that already present in the urotropine-type starting material. Compound **1** is obtained in 26% yield as air-stable colourless crystals, sublimable in a vacuum, mp 82 °C, and soluble in most common organic solvents. The ^1H and ^{13}C NMR spectra are consistent with the proposed formula of C_s symmetry. The $\{^1H\}^{31}P$ NMR singlet signal appears at δ −91.8 (in C_6D_6). The mass spectra (CI) showed the parent ion $[M]^+$ at m/z = 173.3 (100%), and m/z = 158.3 (45%) for $[M - Me]^+$. The compound is readily converted into a colourless crystalline phosphine sulfide **1a** (mp 80 °C) upon reaction with elemental sulfur in benzene, in quantitative yield. The ^{31}P resonance is shifted to δ −8.6 (in C_6D_6), and the ^1H and ^{13}C NMR data shows that the mirror symmetry of **1** is retained in **1a**.



Scheme 1 Conversion of $PTAMe^+$ into ligand **1**, followed by generation of the sulfide **1a** and the AuCl complex **2**. The structure of **2** has been determined by X-ray diffraction, the drawings of the remainder molecules are based on this model and on the structure of (PTA)AuCl.[6]

Since both **1** and **1a** tend to form twinned crystals only, a 1:1 AuCl complex **2** with **1** as a ligand was prepared with (Me_2S)AuCl as the AuCl source in trichloromethane. The complex [yield 80%, mp 150 °C with decomposition, δ_P −39.1 in $CDCl_3$] could be obtained as single crystals, and its structure determined by X-ray diffraction.†

The structure of one of the individual complex molecules is shown in Fig. 1. Though not imposed by crystallography, the molecule approaches very closely mirror symmetry. The AuCl unit is attached to the basket-shaped ligand through the phosphorus atom in the *endo* position. The gold atom adopts the expected quasi-linear coordination geometry [P–Au–Cl 173.2(3)°]. The methyl group at the phosphorus is thus in the *exo* position, and this is also true for the methylated nitrogen atom N(2), which is strongly pyramidal and is directing its donor site towards the opening of the ligand basket. The skeleton of the cage is in a strain-free double-chair conformation with the non-methylated nitrogen atoms N(1) and N(3) in bridgehead positions.

The structure of molecule **1** suggests that it should be an excellent bidentate P,N donor ligand for a large variety of metal centres.

This work has been supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie, by the Pinguin Foundation, and through the donation of chemicals by Degussa AG and Heraeus GmbH.

Received, 30th December 1993; Com. 3/07602D

Footnote

† *Crystal data* for compound **2**·$CHCl_3$ (from $CHCl_3$–hexane), $C_7H_{16}AuClN_3P{\cdot}CHCl_3$, M 524.98, monoclinic, space group $P2_1/c$, a = 13.349(3), b = 10.763(2), c = 11.968(2) Å, β = 113.28°, Z = 4, D_c = 2.208 g cm^{-3}; T −80 °C; $F(000)$ = 992e, μ(Mo–Kα) = 100.7 cm^{-1}, λ(Mo–Kα) = 0.71069 cm^{-1}; h, k, l 15/13/±17, 3800 measured reflections, 3353 independent, and 2963 observed [$F_o \geq 4\sigma(F_o)$]; 154 refined parameters (weighting parameter 0.000212), $R(R_w)$ 0.0317(0.0322), $\Delta\rho_{fin}$ (max./min.) 2.39/−1.86. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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