Inorganica Chimica Acta, 41 (1980) 167–170

N- or P-Coordination in Di- and Triazaphosphole Gold Complexes

KAILASH C. DASH, HUBERT SCHMIDBAUR
Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, 8046 Garching, F.R.G.
and ALFRED SCHMIDPETER
Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, 8000 Munich 2, F.R.G.

Received January 30, 1980

AuCl and $(CH_3)_2AuCl$ complexes of the following series of azaphospholes have been prepared and characterized by analytical and spectroscopic data: 2,5-dimethyl-1,2,3-diazaphosphole (1), 5-methyl-2-phenyl-1,2,3-diazaphosphole (2), 2-methyl-5-phenyl-1,2,4,3-triazaphosphole (3), and 1,5-dimethyl-1,2,4,3-triazaphosphole (4). The $(CH_3)_2AuCl$ complexes are assigned a planar cis*-structure with P-coordination for 2 and 3, but N-coordination for 1 and 4. Imidazole forms a 1:1 complex with $(CH_3)_2AuCl$ (9), but a 2:1 complex with AuCl (10). Low solubilities of the 1:1 complexes of AuCl with the azaphospholes preclude detailed structure analyses in solution. The complexes are of interest for pharmacological studies.*

Introduction

Gold complexes of nitrogen or phosphorus donors play an important role in modern chrysotherapy [3, 4]. A large variety of ligands have been introduced at gold(I) and at gold(III) centers in the hope of achieving a gold drug for arthritis or related diseases, which permitted oral administration [5–7]. In the course of pertinent studies [8] we have now initiated investigations on gold compounds of a novel class of ligands containing both nitrogen and phosphorus.

[a]Series: Gold Chemistry, Part XXXVII. For part XXXVI, see [1].

[b]Vier- und fünfgliedrige Phosphorheterocyclen, Part XLV. For part XLIV see [2].

These ambident ligands (Formulae 1–4) can be attached to gold either through the nitrogen sites, as in analogous pyridine, pyrrole, imidazole, triazole and tetrazole complexes [9–12] or through the phosphorus sites as in a related phosphabenzene complex [13]. The coordination may be reversible and fluxional behaviour appears to be possible. For the preparation of the model compounds, ClAu(CO) and $[(CH_3)_2AuCl]_2$ have been chosen as starting materials. Both compounds are readily available, show excellent solubilities in inert solvents and yield no or 'innocent' by-products (CO) in the syntheses. Most of the previous studies have been carried out with these components [9, 13, 14] and hence a direct comparison of the reaction products is feasible.

Results and Discussion

Chlorodimethylgold(III) Complexes

Solutions of the azaphospholes 1–4, (2,5-dimethyl- and 5-methyl-2-phenyl-1,2,3σ^2-diazaphosphole 1 and 2, respectively, and 2-methyl-5-phenyl- and 1,5-dimethyl-1,2,4,3σ^2-triazaphosphole 3 and 4 respectively), in methylene chloride react spontaneously with dimethylgold chloride at room temperature. Discrete 1:1-adducts are formed, which can be isolated as white powders. They decompose readily in solution.

According to their ^{1}H-NMR spectra, the complexes contain tetracoordinate square-planar gold with the two methyl groups exclusively *cis* to each other.

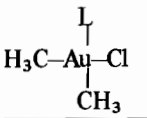
		L = phosphines [15]	L = pyridines [9]
	δ ^{1}H, CH_3 *cis* to L	0.2–0.6	1.0–1.2
	CH_3 *trans* to L	0.6–1.1	1.3–1.5

TABLE I. ^{1}H- and ^{31}P-NMR Chemical Shifts (and Coupling Constants J [Hz]) of the Di- and Triazaphosphole Dimethylgold Chloride Complexes.[a]

		5	6	7	8
δ ^{1}H	$AuCH_3$ *cis*[b]	0.99	1.06 (8)	1.48 (7)	1.19
	trans[b]	1.43	1.24 (9)	1.56 (8)	1.49
	CCH_3	2.33 (1)	2.39[c]		3.03[c]
	NCH_3	4.28 (8.5)		3.66 (6)	4.26
	4-CH	7.58 (22)			
δ ^{31}P		228.5	[d]	223.3	[e]

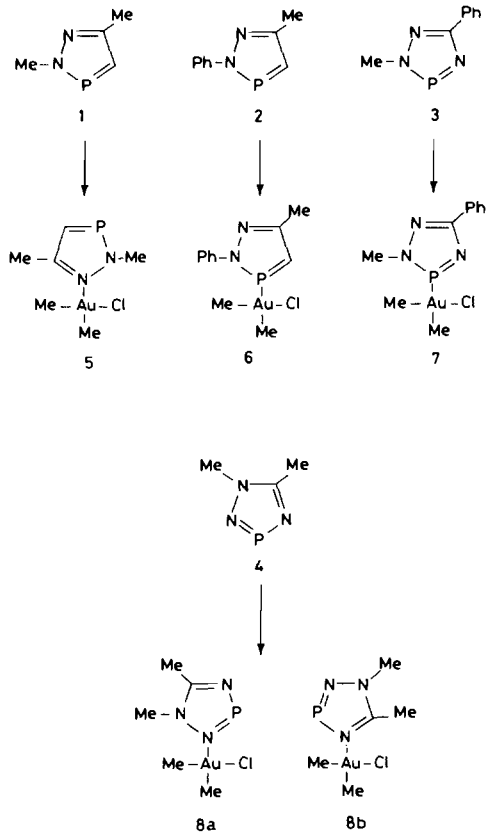
[a]In $CDCl_3$ solution. [b]In respect to the azaphosphole ligand. [c]Broadened by unresolved PH-coupling. [d]No δ ^{31}P determined because of decomposition or [e]low solubility.

Such *cis*-$LAu(CH_3)_2Cl$ complexes give rise to two CH_3 signals of equal intensity, the resonance at lower field being assigned to the methyl group *trans* to the donor ligand L [15]. Both chemical shifts are almost equally sensitive to the nature of L. With pyridines the signals tend to appear at lower field than with phosphines.

The two $AuCH_3$-signals observed for the diaza- and triazaphosphole complexes (Table I) are in the region for complexes with pyridinic ligands and suggest N-coordination of the azaphospholes. With the ligands L = 2 and 3 both signals are split into doublets, however, by typical three-bond ^{1}H–^{31}P-coupling as proven by decoupling experiments; the coupling constant is slightly smaller than in the complexes with L = Me_3P and Ph_3P [15]. With L = 1 and 4 such a coupling is definitely missing and even at low temperature no splitting is observed. This result proves the absence of a ligand fluctuation phenomenon.

The coordination of the ligands appears to be guided by the inductive effect of the substituents at the azaphospholes rather than by the specific donor properties of the donor atoms N or P. The donor character of the phosphorus in azaphospholes is therefore very similar to that of a pyridine nitrogen and slight changes in the substituents of the ligand can lead to 'switches' with regard to the coordination site. As expected for P-coordination, the ^{31}P-NMR signal of the ligand 3 is shifted to higher fields on coordination to $(CH_3)_2AuCl$ in 7, whereas δP for 1 remains virtually unchanged in 5. Similar observations are made in the ^{1}H- and ^{13}C-NMR spectra of N-protonated or N-methylated species derived from azaphospholes, where again only very small changes are encountered. The ^{31}P-shift of P-coordinated $Cr(CO)_5$ complexes of azaphospholes is to lower field [16] however, but this difference is difficult to evaluate.

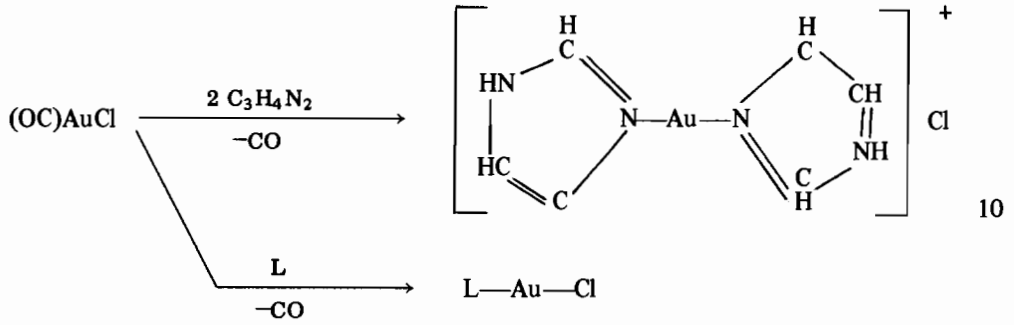
There are two possibilities for N coordination in 4 (8a, b). Our experiments do not allow to distinguish between them unequivocally, though the relative chemical shifts favour isomer 8b.



Chlorogold(I) and Trichlorogold(III) Complexes

Carbonyl(chloro)gold(I) reacts with imidazole, and with the four ligands 1–4, in CH_2Cl_2 solution to form stable 1:2 (10 with imidazole) or 1:1 complexes (11–14 with 1–4). The compounds can be isolated from the reaction mixture on evaporation of the solvent or on addition of diethylether.

10 is a 1:1 electrolyte in methanol (Λ_M = 88.32 Ω^{-1} cm^2), whereas the azaphosphole complexes 11–14 are non-conducting in acetone solution [17]. All complexes are very sparingly soluble in standard nonpolar or polar solvents and an NMR analysis was not possible. The I.R. spectra of 11–14 show ν(AuCl)



10

11–14

(L = azaphospholes 1–4)

absorptions in the expected region of 330–350 cm^{-1} [18, 19].

Anhydrous $AuCl_3$ was found to yield a 1:1 complex 14 with imidazole, which is first of an orange colour at low temperature, but turns to light-yellow on warming to room temperature.

A conductivity Λ_M = 44.24 Ω^{-1} cm^2 in methanol indicates significant dissociation. The I.R. absorptions at 368 and 362 cm^{-1} are consistent with ν(Au-Cl) for an Au(III) compound [20]. A similar $AuCl_3$ complex is formed with the azaphosphole 1. It shows Λ_M = 52.30 and Λ_M = 36.71 Ω^{-1} cm^2 for acetone and methanol solutions, respectively. ν(AuCl) appears at 365 cm^{-1}. 2 and 3 do not form analogous complexes under similar conditions.

Attempts to methylate 11 with CH_3Li failed. Dark decomposition products were obtained even at low temperature. $CH_3AuP(CH_3)_3$ does not react with 1 and unchanged starting materials are recovered.

Experimental

Anhydrous $AuCl_3$ and the carbonyl, Au(CO)Cl, were prepared by standard methods from hydrated $HAuCl_4$ [21]. Me_2AuCl was prepared as described earlier [9].

Chlorodimethyl(2,5-dimethyl-1,2,3σ^2-diazaphosphole)gold(III), 5

At −20 °C solutions of 0.30 g (0.57 mmol) $(Me_2AuCl)_2$ in 3 ml CH_2Cl_2 and 0.13 g (1.14 mmol) 1 were combined and stirred for 2 h. After concentrating and adding ether the product separated as a white powder, m.p. 55 °C; 0.29 g (68%) yield. ^{13}C-NMR (at −60 °C), δ: C-4, 137.8 (d, J_{PC} = 40.0 Hz); C-5, 155.9 (d, J_{PCC} 9.8 Hz); 5-CH_3, 16.2 (d, J_{PCCC} = 2.0 Hz); N-CH_3, 41.9 (d, J_{PNC} = 16.6 Hz); Au–CH_3, 7.0 (s), 5.1 (s). *Anal.*: Calcd. for $C_6H_{13}AuClN_2P$: C, 19.12; H, 3.45; N 7.43%; mol. wt., 376.5. Found: C, 20.12; H, 4.1; N, 7.05%.

Chlorodimethyl(5-methyl-2-phenyl-1,2,3σ^2-diazaphosphole)gold(III), 6

As above from 0.29 g (0.55 mmol) of $(Me_2AuCl)_2$ and 0.19 g (1.08 mmol) of 2; stirring for 6 h was necessary. m.p. 84 °C (decomp.). *Anal.*: Calcd. for $C_{11}H_{15}AuClN_2P$: C, 30.1; H, 3.42; N, 6.38%; mol. wt., 438.5. Found: C, 30.8; H, 4.5; N, 6.13%.

Chlorodimethyl(2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole)gold(III), 7

Prepared as above from 0.24 g (0.45 mmol) of $(Me_2AuCl)_2$ and 0.16 g (0.90 mmol) of 3; m.p. 97 °C (decomp.); 0.30 g (75%) yield. *Anal.*: Calcd. for $C_{10}H_{14}AuClN_3P$: C, 27.3; H, 3.18; N, 9.55%; mol. wt., 439.5. Found: C, 27.2; H, 4.18; N, 9.1%.

Chlorodimethyl(1,5-dimethyl-1,2,4,3σ^2-triazaphosphole)gold(III) 8

Was formed as a white precipitate immediately when the ether solution of 0.27 g (0.52 mmol) of $(Me_2AuCl)_2$ and 0.12 g (1.04 mmol) of 4 were combined; m.p. 93–95 °C; 0.28 g (74%) yield. *Anal.*: Calcd. for $C_5H_{12}AuClN_3P$: C, 15.89; H, 3.17; N, 11.12%. mol. wt., 377.5. Found: C, 16.12; H, 3.58; N, 11.10%.

Imidazole-dimethylgold chloride, 9

Solutions of stoichiometric amounts of $(Me_2AuCl)_2$ and imidazole in CH_2Cl_2 were combined and stirred at −20 °C. After concentrating the solution, addition of ether and standing for 2 weeks at −78 °C a small crop of colourless crystals was obtained; m.p. 79 °C. δ ^{1}H-NMR: a broad signal at 1.16 which at −60 °C splits into two with 3.8 Hz separation. *Anal.*: Calcd. for $C_5H_{10}AuClN_2$: C, 18.15; H, 3.0; N, 8.47%. mol. wt., 330.5. Found: C, 18.9; H, 3.2; N, 8.3%.

Bis-imidazole-gold(I) chloride, 10

To a suspension of 0.15 g of (OC)AuCl (0.57 mmol) in 10 ml CH_2Cl_2 was added slowly a solution of 0.08 g imidazole in 5 ml CH_2Cl_2 at −78 °C with constant stirring. A white precipitate separated,

which was stirred further for 2 h and then filtered washed with CH_2Cl_2 and dried *in vacuo*. m.p. 130 °C (dec.). *Anal.*: Calc. for $C_6H_8N_4Au^+Cl^-$: C, 19.53; H, 2.17; N, 15.19%; mol. wt., 368.5. Found: C, 19.10; H, 2.44; N, 15.01%.

Chloro(2,5-dimethyl-1,2,3σ²-diazaphosphole)gold(I), 11

When a solution of 0.12 g (1.05 mmol) of the ligand in CH_2Cl_2 is added to a suspension of 0.28 g of (OC)AuCl (1.07 mmol) in 20 ml CH_2Cl_2, the reaction mixture becomes clear. After 2 h it is warmed to 0 °C and concentrated *in vacuo*. Addition of 10 ml diethylether precipitates a colorless product. M.p. 77 °C (dec.); Λ_M = 3.61 Ω^{-1} cm² (in acetone at 21 °C, c = 10^{-3} *M*). I.R.: ν(AuCl) = 348, 351 cm^{-1}. *Anal.*: Calcd. for $C_4H_7H_2AuClP$: C, 13.85; H, 2.02; N, 8.08%. mol. wt., 346.5. Found: C, 13.25; H, 2.30; N, 7.42%.

Chloro(5-methyl, 2-phenyl-1,2,3σ²-diazaphosphole)-gold(I), 12

Was prepared similarly from 0.30 g of (OC)AuCl (1.15 mmol) and 0.20 g (1.13 mmol) of the ligand, m.p. 90 °C (dec.), Λ_M = 5.89 Ω^{-1} cm² (as above). I.R.: ν(AuCl): 339, 349 cm^{-1}. *Anal.*: Calcd. for $C_9H_9N_2AuClP$: C, 26.43; H, 2.20; N, 6.85; P, 7.58%. mol. wt., 408.5. Found: C, 26.35; H, 2.20; N, 6.00; P, 7.14%.

Chloro(2-methyl, 5-phenyl-1,2,4,3σ²-triazaphosphole)gold(I), 13

Was prepared as described for 10 from 0.20 g of (OC)AuCl and 0.14 g of the ligand (0.76 and 0.79 mmol, resp.). m.p. 149 °C (dec.), Λ_M = 6.16 Ω^{-1} cm² (as above). I.R.: ν(AuCl) = 340, 348 cm^{-1}. *Anal.*: Calcd. for $C_8H_8N_3AuClP$: C, 23.44; H, 1.95; N, 10.25%. mol. wt., 409.5. Found: C, 23.16; H, 2.29; N, 10.37%.

12 can also be synthesized from AuCl and the ligand in benzene/CH_2Cl_2.

Chloro(1,5-dimethyl-1,2,4,3σ²-triazaphosphole)gold-(I), 14

Was obtained as described for 10. m.p. 148 °C (dec). I.R.: ν(AuCl) = 324, 339 cm^{-1}. *Anal.*: Calcd. for $C_3H_6N_3AuClP$: C, 10.35; H, 1.72; N, 12.08; P, 8.92%. mol. wt., 347.5. Found: C, 9.90; H, 1.70; N, 12.27; P, 8.81%.

(Imidazole)trichlorogold(III), 15

Solutions of $AuCl_3$ and imidazole in CH_2Cl_2 (0.66 and 0.88 mmol, resp.) were combined at −78 °C with stirring. An orange compound formed which turned yellow on warming the reaction mixture to room temperature after 2 h, m.p. 135 °C (dec.). I.R.: 362, 368 cm^{-1}. *Anal.*: Calcd. for $C_3H_4N_2AuCl_3$: C, 9.69; H, 1.07; N, 7.53%. mol. wt., 371.5. Found: C, 10.20; H, 1.41; N, 7.60%.

(2,5-Dimethyl-1,2,3σ²-diazaphosphole)trichlorogold-(III), 16

Was prepared as described for 14. m.p. 77 °C. I.R.: ν(AuCl) = 365 cm^{-1}. *Anal.*: Calcd. for $C_4H_7N_2AuCl_3P$: C, 11.49; H, 1.67; N, 6.70%. mol. wt., 417.5. Found: C, 11.66; H, 2.44; N, 6.64%.

Acknolwedgement

Financial support from Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged. Degussa A.G. is thanked for a generous gift of chemicals. K. C. Dash is grateful to the A. v. Humboldt Foundation for a fellowship and Utkal University, Bhubaneswar, 751004 India, for leave of absence.

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