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Note

Phosphinoamino complexes of copper(I) and silver(I): a combined NMR and IR spectroscopy, and electrospray ionization and fast atom bombardment mass spectrometry analysis

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Abstract

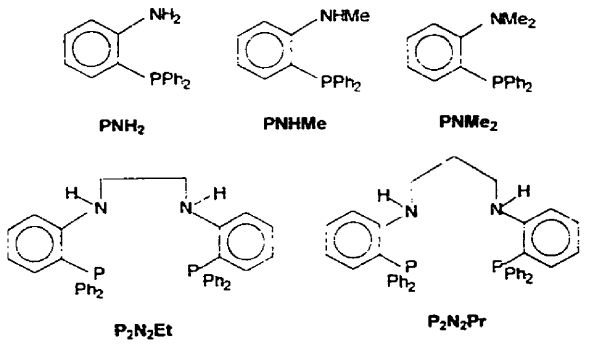
Bidentate 'PN' and tetradentate 'P_2N_2' ligands form stable silver(I) complexes, which were characterized by NMR and IR spectroscopy. Conductivity measurements indicate an ionic nature of the compounds in solution. A thorough mass spectrometric study (electrospray ionization and fast atom bombardment) of these complexes and the corresponding Cu(I) analogues supports the NMR and IR structural information. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phosphinoamine complexes; Copper complexes; Silver complexes

1. Introduction

We have recently reported on the synthesis and characterization of Cu(I) complexes stabilized by the following 'PN' and 'P_2N_2' ligands [1]: 2-(diphenylphosphino)aniline, PNH_2 [2], *N*-methyl-2-(diphenylphosphino)aniline, PNHMe [3], *N,N'*-dimethyl-2-(diphenylphosphino)aniline, $PNMe_2$ [4], *N,N'*-bis[2-(diphenylphosphino)phenyl]-ethane-1,2-diamine, P_2N_2Et [1a] and *N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine, P_2N_2Pr [5] (Scheme 1).

We report here on the synthesis of analogous Ag(I) complexes containing the same ligands, and on a thorough mass spectrometric analysis (electrospray ionization (ESI) and fast atom bombardment (FAB)) of these complexes and of the corresponding Cu(I) analogues (Scheme 2).



Scheme 1.

2. Experimental

2.1. Materials and instrumentation

$AgNO_3$ (Aldrich) and all the solvents were used as received.

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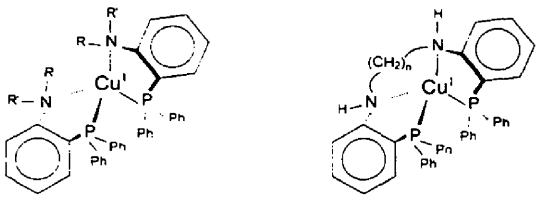


R = H, R' = H (1)
R = H, R' = Me (2)
R = Me, R' = Me (3)

n = 2 (4)
n = 3 (5)

Scheme 2.

Ligands and complexes $[Cu(PNH_2)_2]Cl$ (**1**), $[Cu(PNHMe)_2]Cl$ (**2**), $[Cu(PNMe_2)_2]Cl$ (**3**), $[Cu(P_2N_2Et)]Cl$ (**4**), and $[Cu(P_2N_2Pr)]Cl$ (**5**), were prepared according to Refs. [1a,3,6–8] and Ref. [1], respectively.

Elemental analyses (C, H, N) were performed on a Fisons EA 1108 elemental analyser. IR spectra were recorded on a Mattson 3030 Fourier-transform spectrometer (4000–400 cm^{-1}) using KBr pellets. ^1H and ^{31}P NMR spectra were collected on a Bruker AC-200 instrument, using $SiMe_4$ as internal reference (^1H) and 85% aqueous H_3PO_4 as external reference (^{31}P). Conductivity measurements were carried out in MeCN solutions of $\sim 10^{-3}$ M at 25°C using an Amel model 131 conductimeter. FAB mass spectra were obtained by a VG (Manchester, UK) ZAB2F instrument; 3-nitrobenzoylalcohol solutions of the samples were bombarded by an 8 keV Xe atom beam. ESI mass spectra were obtained using a TSQ 700 Finnigan MAT instrument employing water–acetonitrile solutions of the metal complexes.

2.2. Procedure for the synthesis of Ag(I) complexes

A solution of the phosphinoamine (amounts in mmol are reported in Table 1) in CH_2Cl_2 (10 ml) was added to a suspension of $AgNO_3$ (see Table 1) in CH_2Cl_2 (10 ml). The pale orange solution was stirred for a few hours and the solvent was then removed under reduced pressure. Treatment of the residue with MeOH (10 ml) caused the formation of a white precipitate, which was filtered off, washed with cold MeOH and dried under vacuum.

3. Results and discussion

Silver complexes $[Ag(PNH_2)_2]NO_3$ (**6**), $[Ag(PNHMe)_2]NO_3$ (**7**), $[Ag(PNMe_2)_2]NO_3$ (**8**), $[Ag(P_2N_2Et)]NO_3$ (**9**) and $[Ag(P_2N_2Pr)]NO_3$ (**10**), obtained upon action

Table 1
Selected synthetic and analytical data for Ag(I) complexes

Compound	Phosphinoamine (mmol)	$AgNO_3$ (mmol)	Yield (%)	Elemental analysis: calc. (found) (%)		
				C	H	N
6	PNH_2 1.81	0.91	57	59.7 (57.1)	4.4 (4.2)	5.8 (5.8)
7	PNHMe 0.52	0.26	91	60.6 (61.1)	4.8 (4.9)	5.6 (5.5)
8	$PNMe_2$ 0.49	0.25	56	61.5 (60.8)	5.1 (5.1)	5.4 (5.2)
9	P_2N_2Et 0.9	0.9	70	60.8 (61.5)	4.5 (4.4)	5.6 (5.3)
10	P_2N_2Pr 1.17	1.18	79	61.3 (60.5)	4.7 (4.5)	5.5 (5.3)

Table 2
Selected spectral and conductivity data for Ag(I) complexes

Compound	IR (cm^{-1})		^{31}P NMR (ppm)	^1H NMR (ppm)			S_M (Ω^{-1} cm^2 mol^{-1})
	ν(NH)	$\nu(NO_3^-)$		H_{ar} [a]	H_{al} [b]	N–H	
PNH_2	3431		−22.4(s)	6.5–7.5		4.1(bs)	
PNHMe	3347		−24.4(s)	6.6–7.4	2.8(s)	4.2(bs)	
$PNMe_2$			−16.2(s)	6.7–7.3	2.6(s)		
P_2N_2Et	3370		−22.2(s)	6.0–7.0	3.2(s)	4.8(bs)	
P_2N_2Pr	3360		−23.0(s)	6.0–7.0	2.8(t) 1.5(m)	4.0(bs)	
6	3443 3338	1384	*T* dependent	6.5–7.4		4.2(s)	113
7	3395	1430	*T* dependent	6.6–7.4	3.4(q) 2.6(s)	4.4(s)	160
8		1390	*T* dependent	6.9–7.4	2.3(s)		155
9	3383	1385	−8(2d)	6.6–7.5	3.4(m)	4.8(s)	148
10	3386	1384	−6(2d)	6.5–7.4	3.2(m) 1.7(m)	4.4(s)	143

[a] H_{ar} aromatic protons.
[b] H_{al} aliphatic protons.

of the ligands on $AgNO_3$ in dichloromethane, are air and thermally stable both in the solid and solution state.

The spectroscopic and conductivity data, reported in Table 2, and analytical results indicate that the metal coordinates two N and two P donors.

The conductivity data reveal that the complexes are univalent electrolytes in MeCN [9] (Table 2). In the solid state they are proposed to be cationic species with the nitrate group as counter-ion, since the $\nu(NO_3)$ vibration is similar to that of the free ion (bands close to 1390 cm^{-1} with no splitting and no absorptions around 1051 cm^{-1} due to the symmetrical stretching, which is IR inactive in free NO_3^- [10]).

Complexes **6–10** are characterized conveniently by ^{31}P NMR in chloroform-*d* solutions. ^{31}P NMR spectra of compounds **9** and **10** are temperature independent and exhibit a doublet of doublets at room temperature due to the coupling of the magnetically equivalent phosphorus nuclei with ^{107}Ag ($I = 1/2$) and ^{109}Ag ($I = 1/2$) nuclei. According to the magnitude of the coupling constant, which is in agreement with an Ag:P stoichiometry of 1:2 [11], and the observed downfield shift of the amine hydrogen in the proton spectra, compared with the signal of free P_2N_2Et and P_2N_2Pr, a tetrahedral environment around the silver cation is proposed. In contrast,

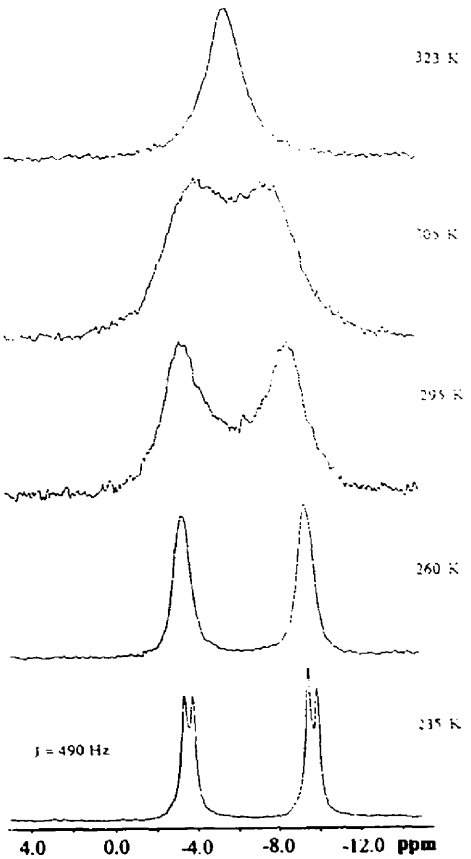
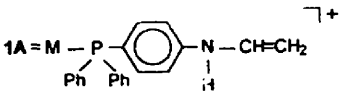


Fig. 1. ^{31}P NMR spectra of $[Ag(PNHMe)_2]NO_3$ **7**.

Table 3
ESI mass spectra of compounds **1–10**; the reported mass values (relative abundance in brackets) correspond to ionic species containing the isotopes ^{63}Cu, ^{107}Ag, ^{31}P, ^{12}C, ^{14}N, and ^{1}H

Compound	Ionic species			
	$[M]^+$	$[M-L]^+$	$[M-L+CH_3CN]^+$	**1A**
1	617 (100)	340 (6)	381 (28)	
2	645 (100)	354 (2)	395 (6)	
3	673 (100)		409 (6)	630 (18)
4	643 (100)			
5	657 (100)			
6	661 (100)			
7	689 (100)	398 (2)	439 (4)	
8	717 (100)		453 (2)	
9	687 (100)			
10	701 (100)			



the ^{31}P NMR spectra, taken at room temperature, of complexes **6–8**, which contain bidentate phosphinoamines, display a more or less broadened singlet as a consequence of a chemical exchange process on the NMR timescale: the expected doublet of doublets is gradually disclosed on lowering the temperature to 235 K (Fig. 1).

Hence, at lower temperatures a tetrahedral arrangement determined by the coordination of the two P and N donors can reasonably be proposed.

Complexes **1–10** were also analysed by mass spectrometry in the solution state: in view of the ionic nature and low volatility of these compounds, FAB [12] and ESI [13] methods were used.

In the present case, FAB only causes sputtering of intact ions enriched energetically by collisional phenomena, while in ESI the interaction of spray-generated droplets of the analyte solution with strong electrical fields leads to the 'simple' desolvation of the analyte.

In all ESI spectra of **1–10** (Table 3) the parent ion peak $[M]^+$, originating through loss of BF_4^- and NO_3^- from compounds **1–5** and **6–10** respectively, is the base peak of the spectra and, since decomposition products are practically absent, this method allows the identification of the molecular weight of the cationic part of compounds **1–10**. Only in the case of **1**, **2** and **7** are ions corresponding to the primary loss of a ligand unit L present in low abundance. For the same compounds and for **3** and **8**, the ions corresponding to the addition of an MeCN molecule on the $[M-L]^+$ ions are also detected. Only in the case of compound **3** is an ion at *m/z* 630 detected, corresponding to a product arising from the cleavage of the ligand moiety (structure **1A** in Table 3).

FAB spectra of compounds **1–10** are more complex (Table 4).

Table 4
FAB mass spectra of compounds **1**–**10**; the reported mass values (relative abundance in brackets) correspond to ionic species containing the isotopes ^{63}Cu, ^{107}Ag, ^{31}P, ^{12}C, ^{14}N, and ^{1}H

Compound	Ionic species					
	$[M]^+$	$[M-L]^+$	$[Me]^+$	$[L]$	$[L-H]^+$	**1A** [a]
1	617 (34)	340 (81)	63 (100)	277 (11)	290 (22)	
2	645 (54)	354 (100)	[b]		304 (54)	
3	673 (39)	368 (53.5)	[c]			
4	643 (45)		[c]			353 (16)
5	657 (40)		[c]			353 (14)
6	661 (27)	384 (100)	[b]	277 (33)		
7	689 (30)	398 (85)	107 (37.5)		290 (50)	
8	717 (4)	412 (13)	[b]		304 (100)	
9	687 (9)					397 (2)
10	701 (100)		[b]			397 (18)

[a] For **1A** see Table 3.
[b] Peak out of the spectrum.
[c] Peak not distinguishable.

$[M]^+$ ions are detected in all cases but with relative abundance ranging from 4 to 100%. The observed fragmentation processes are related mainly to the cleavage of the metal–ligand bond with the formation, in some cases, of $[M-L]^+$, $[L]^+$ and $[Me]^+$ (metal species) cations. For some compounds, $[L-H]^+$ species, stemming from the $[M]^+$ ions through cleavage of the metal–ligand bond with H rearrangement, are also detected and they are responsible for the base peak of the spectrum of **8**.

4. Conclusions

'PN' and 'P_2N_2' phosphinoamines exhibit good coordination properties towards both Cu(I) and Ag(I).

The combination of NMR and ESI-MS and FAB-MS techniques allows a thorough structural characterization of these ionic phosphinoamino complexes in the solution state, where tetracoordination is preferred; however, more complex structures cannot be ruled out for some of the Ag(I) species.

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