

PII: S0277-5387(96)00435-4

# Coordination of *d*<sup>10</sup>-metal cations by thiacycloalkynes

Francesca M. Kerton, G. Farouq Mohmand, Julian D. Webb and Michael J. Went\*

Department of Chemistry, University of Kent, Canterbury, Kent CT2 7NH, U.K.

(Received 2 August 1996; accepted 21 August 1996)

**Abstract**—A range of complexes has been prepared by reaction of thiacycloalkynes with Ag<sup>1</sup>, Cu<sup>1</sup> and Hg<sup>11</sup> cations and cationic MPR<sub>3</sub> (M = Ag, Cu, Hg) fragments. <sup>1</sup>H NMR studies reveal that coordination of 1,4,7-trithiacycloundec-9-yne (L<sup>1</sup>) to Ag<sup>1</sup> results in a change of ligand conformation from exodentate in the free ligand to endodentate in the coordinated ligand implying involvement of the thioether functionalities in coordination. Participation of the alkyne linkage in coordination is less certain and a polymeric structure is suggested in the solid state. Reaction of AgSbF<sub>6</sub> with L<sup>1</sup> and PPh<sub>3</sub> or PMe<sub>2</sub>Ph afforded complexes in which the silver is coordinated by a phosphine and an endodentate  $\eta^3$ -L<sup>1</sup>. Similar studies with Cu<sup>1</sup> and Hg<sup>II</sup> showed a reduced tendency for thioether coordination reflected in a reduced denticity of L<sup>1</sup>. Studies with a range of dithiacycloalkynes and a tetrathiacyclodiyne show that Ag<sup>+</sup> and Cu<sup>+</sup> can be successfully coordinated by ligands containing a combination of two thioether donors and one alkyne. (C) 1997 Elsevier Science Ltd. All rights reserved.

Keywords: silver; copper; mercury; thioether; alkyne; phosphine.

The ability of polythioether macrocycles to coordinate metal ions and metal-ligand fragments has been extensively studied in recent years [1,2]. Interest has focused on 1,4,7-trithiacyclononane (9S3), which forms a remarkable range of stable complexes due to its endodentate conformation, but several other thiacrown ethers which are not preorganized for facial coordination, such as 2,5,8-trithia[9]-o-benzenophane (TTOB), display good ligating properties and useful selectivity [3]. We have reported the synthesis of 1,4,7trithiacycloundec-9-yne  $(L^1)$  via decomplexation from a hexacarbonyldicobalt fragment [4] or via a high dilution method [5]. Several other ligands  $L^2-L^7$  have also been prepared by the high dilution method [5,6]. Selective coordination of the alkyne functionality in such systems has been illustrated by their reactions with  $[Co_2(CO)_8]$  to form monoalkynehexacarbonyldicobalt complexes [5,6] and with  $[Mo(CO)_2]$  $(S_2CNMe_2)_2$ to afford bisalkynebis(dithiocarbamate)molybdenum complexes [5]. In this paper we report the complexation of the soft metal centres  $Cu^{I}$ , Ag<sup>I</sup> and Hg<sup>II</sup> by thiacycloalkynes L<sup>1</sup>–L<sup>7</sup>.

## **EXPERIMENTAL**

All reactions were carried out under nitrogen using standard Schlenk tube and vacuum line techniques. and all solvents were freshly distilled under nitrogen and over appropriate drying agents. Light petroleum (boiling point 40-60°C) and acetonitrile were distilled over calcium hydride and tetrahydrofuran and diethyl ether were distilled over potassium. The ligands were prepared by literature methods [5]. Fast atom bombardment (FAB) mass spectra were recorded from a NOBA matrix by the EPSRC mass spectrometry service at the University of Swansea with a VG ZAB-E instrument. Raman spectra were recorded with an SA multichannel Raman spectrometer model HF640 with a CCD detector. NMR spectra were recorded with a JEOL GX 270 instrument. Molecular-mechanics calculations were carried out using HYPERCHEM (Release 3) [7]. Structures were minimized with conjugate gradients (Polak-Ribiere algorithm) using the MM+ force field until the gradients were less than 0.01 kcal mol<sup>-1</sup> Å<sup>-1</sup>. Elemental analyses were performed by Mr A. J. Fassam at the University of Kent. Analytical and physical data for the new compounds is given in Table 1.

<sup>\*</sup> Author to whom correspondence should be addressed.

Table 1. Analytical and physical data

Compound	Appearance	Yield (%)	"v(C≡C) (cm <sup>-1</sup> )	<sup>b</sup> Analysis (%)		
				С	Н	<sup>c</sup> m/z
1[AgL <sup>1</sup> ][BF <sub>4</sub> ]	White solid	99		24.0 (24.1)	3.0 (3.0)	313 $(M - BF_4)$
$2[AgL^1][SbF_6]$	White solid	67	2231	18.4 (17.5)	2.2 (2.2)	517 $(M + L^1 - SbF_6)$ , 313 $(M - SbF_6)$
$3[AgL^1][O_3SCF_3]$	White solid	92	2238	24.3 (23.4)	2.7 (2.6)	
$4[AgL^{1}(PPh_{3})][SbF_{6}]$	White solid	85	2252, 2222	40.5 (38.5)	3.3 (3.4)	575 ( $M - SbF_{6}$ )
$5[AgL^{1}(PMe_{2}Ph)][SbF_{6}]$	White solid	67	2225	28.0 (28.0)	3.3 (3.4)	$451 (M - SbF_6)$
6[CuL <sup>1</sup> ][PF <sub>6</sub> ]	White solid	100	_	22.8 (23.2)	2.9 (2.9)	$266 (M - H - PF_6)$
$7[CuL^{1}(PPh_{3})][PF_{6}]$	White solid	55	2228, 2223	47.6 (46.3)	4.1 (4.0)	529 $(M - PF_6)$
$8[CuL^{1}(PMe_{2}Ph)][PF_{6}]$	White solid	17	2225	35.2 (34.9)	4.2 (4.2)	$405 (M - PF_6)$
$9[HgL_2^1]Cl_2$	Off-white solid	87	2226	29.5 (28.3)	3.9 (3.6)	
10[HgL <sup>1</sup> (PPh <sub>3</sub> )]Cl <sub>2</sub>	White solid	69		41.4 (42.3)	5.1 (3.7)	761 (M + Na – 2Cl)
$11[Ag_2L^2][BF_4]_2$	White solid	100		22.2 (21.3)	2.4 (2.4)	$504 (M - 2BF_4)$
$12[Cu_2L^2][PF_6]_2$	White solid	100		20.2 (20.4)	2.3 (2.3)	$415 (M - 2PF_6)$
13[AgL <sup>3</sup> ][BF <sub>4</sub> ]	White solid	100	_	23.9 (23.8)	2.6 (2.9)	$265 (M - BF_4)$
14[CuL <sup>3</sup> ][PF <sub>6</sub> ]	White solid	100		22.4 (22.9)	2.9 (2.8)	
$15[AgL^4][BF_4]$	White solid	100		25.9 (26.2)	3.1 (3.3)	
16[CuL⁴][PF <sub>6</sub> ]	White solid	100		24.7 (25.2)	3.3 (3.2)	—
17[AgL <sup>5</sup> ][BF <sub>4</sub> ]	White solid	93		27.8 (28.4)	3.3 (3.7)	
18[CuL <sup>5</sup> ][PF <sub>6</sub> ]	White solid	60				249 (M $-$ PF <sub>6</sub> )
19[AgL <sup>6</sup> ][BF <sub>4</sub> ]	White solid	100				283 ( $M - BF_4$ )
<b>20</b> [CuL <sup>6</sup> ][PF <sub>6</sub> ]	White solid	93		21.2 (22.0)	2.8 (2.6)	_
$21[AgL^7][BF_4]$	White solid	100		25.2 (25.1)	3.3 (3.2)	297 ( $M - BF_4$ )
22[CuL <sup>7</sup> ][PF <sub>6</sub> ]	White solid	100		23.8 (24.2)	3.2 (3.1)	251 ( $M - PF_6$ )

<sup>a</sup> Raman spectroscopy.

<sup>b</sup>Calculated values are given in parentheses.

<sup>c</sup> Fast atom bombardment (FAB) mass spectroscopy.

#### Preparation of $[AgL^{1}][BF_{4}](1)$

To a solution of AgBF<sub>4</sub> (0.162 g, 0.83 mmol) in THF (50 cm<sup>3</sup>) was added 1 equiv of L<sup>1</sup> (0.17 g, 0.83 mmol), which caused the immediate formation of a white precipitate. After stirring for 3 h, Et<sub>2</sub>O (50 cm<sup>3</sup>) was added and the mixture left overnight at  $-25^{\circ}$ C before the product was isolated by filtration and dried *in vacuo* to afford [AgL<sup>1</sup>][BF<sub>4</sub>] (0.33 g, 99%). Compounds 2, 3, 11, 13, 15, 17, 19 and 21 were prepared by similar procedures.

# Preparation of $[AgL^{1}(PPh_{3})][SbF_{6}]$ (4)

To a stirred solution of  $L^1$  (0.10 g, 0.49 mmol) and PPh<sub>3</sub> (0.13 g, 0.49 mmol) in THF (20 cm<sup>3</sup>) was gradually added AgSbF<sub>6</sub> (0.17 g, 0.49 mmol). After 3 h the solution was filtered and the product precipitated by addition of light petroleum (60 cm<sup>3</sup>). The white precipitate was isolated by filtration and dried *in vacuo* to afford [AgL<sup>1</sup>(PPh<sub>3</sub>)][SbF<sub>6</sub>] (0.34 g, 85%).

## Preparation of $[AgL^{1}(PMe_{2}Ph)][SbF_{6}]$ (5)

AgSbF<sub>6</sub> (0.34 g, 0.98 mmol) was gradually added to a stirred solution of  $L^1$  (0.20 g, 0.98 mmol) in THF (30 cm<sup>3</sup>) followed by addition of PMe<sub>2</sub>Ph (0.14 cm<sup>3</sup>, 0.98 mmol). After 3 h the solution was filtered and the product precipitated by addition of light petroleum (60 cm<sup>3</sup>). The white precipitate was isolated by filtration and dried *in vacuo* to afford [AgL<sup>1</sup>(P-Me<sub>2</sub>Ph)][SbF<sub>6</sub>] (0.45 g, 67%).

## Preparation of $[CuL^1][PF_6]$ (6)

To a suspension of  $[Cu(NCMe)_4][PF_6]$  (0.20 g, 0.54 mmol) in THF (50 cm<sup>3</sup>) was added 1 equiv of L<sup>1</sup> (0.11 g, 0.54 mmol), which caused the immediate formation of a white precipitate. After stirring for 5 h, Et<sub>2</sub>O (50 cm<sup>3</sup>) was added and the mixture left overnight at  $-25^{\circ}$ C before the product was isolated by filtration and dried *in vacuo* to afford  $[CuL^1][PF_6]$  (0.22 g, 100%). Compounds **12**, **14**, **16**, **18**, **20** and **22** were prepared by similar procedures.

# Preparation of $[CuL^{1}(PPh_{3})][PF_{6}]$ (7)

To a stirred solution of  $L^1$  (0.10 g, 0.49 mmol) and PPh<sub>3</sub> (0.12 g, 0.49 mmol) in MeCN (15 cm<sup>3</sup>) was added [Cu(NCMe)<sub>4</sub>][PF<sub>6</sub>] (0.18 g, 0.49 mmol). Stirring was continued overnight and then the solvent removed *in vacuo*. The residue was dissolved in hot THF (15 cm<sup>3</sup>)

and filtered before precipitation of the product by addition of light petroleum (50 cm<sup>3</sup>). The white precipitate was isolated by filtration and dried *in vacuo* to afford [CuL<sup>1</sup>(PPh<sub>3</sub>)][PF<sub>6</sub>] (0.18 g, 55%). Compound **8** was prepared in a similar manner except PMe<sub>2</sub>Ph was added to a solution of L<sup>1</sup> and [Cu(NCMe)<sub>4</sub>][PF<sub>6</sub>].

## Preparation of $[Hg(L^1)_2]Cl_2$ (9)

HgCl<sub>2</sub> (0.13 g, 0.49 mmol) was added to a stirred solution of L<sup>1</sup> (0.20 g, 0.98 mmol) in THF (20 cm<sup>3</sup>). After 3 h the solvent was removed *in vacuo* and the residue precipitated from THF (15 cm<sup>3</sup>) by addition of light petroleum (60 cm<sup>3</sup>) to afford  $[Hg(L^1)_2]Cl_2$  (0.58 g, 87%).

## Preparation of $[HgL^{1}(PPh_{3})]Cl_{2}$ (10)

A solution of  $L^1$  (0.10 g, 0.49 mmol) and PPh<sub>3</sub> (0.13 g, 0.49 mmol) in 1 : 1 MeCN : Et<sub>2</sub>O (20 cm<sup>3</sup>) was mixed with a solution of HgCl<sub>2</sub> (0.13 g, 0.49 mmol) in 1 : 1 MeCN : Et<sub>2</sub>O (10 cm<sup>3</sup>). A precipitate formed immedi-

ately which after 2 h was collected by filtration, washed with light petroleum (60 cm<sup>3</sup>) and dried *in* vacuo to afford  $[HgL^{1}(PPh_{3})]Cl_{2}$  (0.25 g, 69%).

#### **RESULTS AND DISCUSSION**

Treatment of a THF solution of  $AgBF_4$  with L<sup>1</sup> affords [AgL<sup>1</sup>][BF<sub>4</sub>] (1) in quantitative yield. Its formulation was confirmed by elemental analysis and by FAB mass spectrometry with observation of an isotope envelope at m/z 313 corresponding to  $[AgL^1]^+$ (Table 1). The formation of a 1:1 product contrasts with the 1:2 products formed between Ag<sup>+</sup> and TTOB<sup>3</sup> and 9S3, although a 1:1 trimer  $[Ag_3(9S3)_3]^{3+}$ has also been characterized [8]. The <sup>1</sup>H NMR spectrum of 1 contains a singlet at 3.42 ppm assigned to the four acetylenic methylene protons and a single AA'BB' pattern due to the CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub> fragment. Simulation and iterative fitting of the spectrum using LAOCOON PC [9] resulted in values for the vicinal coupling of J = 8.34(4) and J' = 3.27(4), which indicates an equilibrium containing pre-



Γ6

dominantly gauche S-C-C-S fragments [10]. This can be compared with the NMR spectrum of  $L^1$  in the same solvent (CD<sub>3</sub>CN), which has values of J = 11.14(2) and J' = 5.13(2), indicating an equilibrium of containing predominantly anti S-C-C-S fragments in accord with the solid-state structure of  $L^1$  as determined by X-ray crystallography [4]. It appears that  $L^{\dagger}$  adopts an endodentate conformation to coordinate to Ag<sup>+</sup>, but 1 is highly fluxional with both sides of the ring being made equivalent on the NMR timescale. Molecular-mechanics calculations suggest that an endodentate conformation of  $L^1$  is accessible with an energy of 8.97 kcal mol<sup>-1</sup> compared with the exodentate conformation observed in the free ligand which has an energy of 8.29 kcal mol<sup>-1</sup>. The <sup>13</sup>C NMR spectrum of 1 is very simple and contains four resonances corresponding to the four different carbon environments in the complex. The acetylenic carbon resonance at 84.5 ppm is shifted to the lower field by 4.8 ppm compared with  $L^1$ , while the other resonances are shifted by ca 3-4 ppm. Relatively few alkyne complexes of silver have been reported [11-15]. The interaction is typically weak and causes only small chemical shift changes to the alkyne carbons so a shift of 4.8 ppm could indicate an interaction between the triple bond and silver in solution. Unfortunately we were unable to grow crystals suitable for X-ray crystallography to determine the solid-state structure of 1. Coordination of the alkyne would be expected to reduce the tripe bond strength and hence its stretching frequency. For example, coordination of silver(I) triflate to 1,6-cyclodecadiyne results in a change of  $v(C \equiv C)$  from 2282, 2224 cm<sup>-1</sup> to 2230, 2160 cm<sup>-1</sup> [14]. The triple bond of  $L^1$  gives a strong absorption in the Raman spectrum at 2227 cm<sup>-1</sup>, but unfortunately the corresponding resonance for 1 could not be observed in either the IR spectrum, presumably because it is very weak, or in the Raman spectrum, due to fluorescence. However, the spectra did indicate that the counter-ion  $BF_4^-$  was not coordinated. In order to gain further information complexes  $[AgL^{1}][SbF_{6}]$  (2) and  $[AgL^{1}][O_{3}SCF_{3}]$  (3) were prepared containing different counter-ions. Both complexes gave NMR spectra similar to 1 and also produced poor Raman spectra, but resonances could be observed at 2231 and 2238 cm<sup>-1</sup>, suggesting negligible interaction of the alkyne with the metal. The FAB mass spectrum of 2 contains an isotope envelope at m/z 517 corresponding to  $[Ag(L^1)_2]^+$  suggesting a polymeric structure in the solid state. Figure 1 illustrates a possible polymeric solid-state structure for compounds 1–3 involving  $\mu$ - $\eta^3$ - $\eta^1$ -L<sup>1</sup> ligands. A similar bonding mode is exhibited by 9S3 in  $[Ag_3(9S3)_3]^{3+}$  [8].

Reaction of AgSbF<sub>6</sub> with L<sup>1</sup> and PPh<sub>3</sub> affords the complex [AgL<sup>1</sup>(PPh<sub>3</sub>)][SbF<sub>6</sub>] (4). The mass spectrum shows an isotope envelope at m/z 575 corresponding to [AgL<sup>1</sup>PPh<sub>3</sub>]<sup>+</sup>. The vicinal coupling constants (Table 2) reveal that the ring is adopting an endodentate confirmation similar to that observed in



Fig. 1. Proposed structure for compounds 1-3.

 $[Co_2(CO)_6L^1AgPPh_3]$  [16]. Strong absorptions are observed in the Raman spectrum at 2252 and 2222 cm<sup>-1</sup>, possibly indicating two different environments for the alkyne linkage in the solid state but neither indicating a significant weakening of the bond as might be expected if metal coordination had occurred. Similar results were obtained with PMe<sub>2</sub>Ph in the formation of  $[AgL^1(PMe_2Ph)][SbF_6]$  (5). Both 4 and 5 display only a single resonance at room temperature in the <sup>31</sup>P NMR spectra at 14.1 and -21.5 ppm, respectively. The spectrum of 5 was also recorded at 212 K and appears as a four line pattern due to coupling to <sup>107</sup>Ag and <sup>109</sup>Ag [J(AgP) = 600 and 690 Hz], indicating that phosphine exchange is rapid at room temperature.

Reaction of  $L^1$  with  $[Cu(NCMe)_4][PF_6]$  affords  $[CuL^1][PF_6]$  (6). Elemental analysis supports the formulation and confirms that no acetonitrile ligands remain coordinated to the copper centre. In acetonitrile the vicinal coupling constants indicate an equilibrium containing equal amounts of *anti* and *gauche* S--C--C--S segments, suggesting that  $L^1$  is acting as

Table 2. <sup>1</sup>H and <sup>13</sup>C NMR data<sup>*a*</sup>

" Chemical shifts ( $\delta$ ) in ppm, coupling constants in Hz, e.s.d.s in parenthesis. Measured in CD<sub>3</sub>CN.

a didentate  $(\eta^2)$  ligand with possibly rapidly exchanging acetonitrile as a co-ligand.

Reaction of L<sup>1</sup> and PPh<sub>3</sub> or PMe<sub>2</sub>Ph with [Cu(NCMe)<sub>4</sub>][PF<sub>6</sub>] affords compounds [CuL<sup>1</sup> (PPh<sub>3</sub>)][PF<sub>6</sub>] (7) and [CuL<sup>1</sup>(PMe<sub>2</sub>Ph)][PF<sub>6</sub>] (8). The vicinal coupling constants (Table 2) indicate that in both compounds the ligand has maintained its exodentate conformation. Raman spectroscopy (Table 1) shows changes of less than 4 cm<sup>-1</sup> in  $\nu$ (C=C) consistent with no interaction between the alkyne and the metal centre. A possible structure of 7 and 8 would be linear with L<sup>1</sup> coordinated in a unidentate ( $\eta^1$ ) fashion *via* the central sulfur atom.

Reaction of L<sup>1</sup> with HgCl<sub>2</sub> affords compound [Hg  $L_2^1$ ]Cl<sub>2</sub> (9). Again the vicinal coupling constants indicate an exodentate conformation and the Raman spectrum suggests that the alkyne is not involved in coordination, so a linear two-coordinate structure is suggested. Reaction of L<sup>1</sup> and PPh<sub>3</sub> with HgCl<sub>2</sub> affords 10, which was too insoluble for NMR measurements and is formulated as [HgL<sup>1</sup>(PPh<sub>3</sub>)]Cl<sub>2</sub> on the basis of FAB mass spectroscopy (Table 1).

The reactions of several other thiacycloalkynes ( $L^{2-}$   $L^{7}$ ) were investigated in less detail and the results tabulated in Tables 1 and 2. The results indicate that Ag<sup>+</sup> and Cu<sup>+</sup> can be successfully coordinated by ligands containing a combination of two thioether donors and one alkyne. Ligand L<sup>2</sup> with four thioethers and two alkynes can coordinate two metal ions simultaneously.

Acknowledgements—We thank Dr J. A. Creighton for recording the Raman spectra and H. A. Bower for experimental assistance. The EPSRC provided a studentship (GFM) and access to the mass spectrometry service.

# REFERENCES

- Blake, A. J. and Schröder, M., Adv. Inorg. Chem. 1990, 35, 1.
- 2. Cooper, S. R. and Rawle, S. C., *Struct. Bonding* (*Berlin*), 1990, **72**, 1.
- de Groot, B., Jenkins, H. A. and Loeb, S. J., *Inorg. Chem.* 1992, 31, 203.
- 4. Mohmand, G. F., Thiele, K. and Went, M. J., J. Organomet. Chem. 1994, **471**, 241.
- Kerton, F. M., Mohmand, G. F., Tersteegen, A., Thiel, M. and Went, M. J., *J. Organomet. Chem.* 1996, **519**, 17.
- 6. Meier, H. and Dai, Y., *Tetrahedron Lett.* 1993, 33, 5277.
- Pazun, J. L., J. Chem. Inf. Comput. Sci. 1993, 33, 931.
- 8. Küppers, H.-J., Wieghardt, K., Tsay, Y.-H., Krüger, C., Nuber, B. and Weiss, J., Angew. Chem. Int. Ed. Engl. 1987, 26, 575.
- 9. Clark, M. and Thrasher, J. S., J. Chem. Educ. 1990, 67, 235.
- Lockhart, J. C. and Tomkinson, N. P., J. Chem. Soc., Perkin Trans. 1992, 2, 533.
- 11. Lang, H., Köhler, K. and Blau, S., Coord. Chem. Rev. 1995, 143, 113.
- Chi, K.-M., Lin, C.-T., Peng, S.-M. and Lee, G.-H., Organometallics 1996, 15, 2660.
- Lewandos, G. S., Gregston, D. K. and Nelson, F. R., J. Organomet. Chem. 1976, 118, 363.
- Gleiter, R., Karcher, M., Kratz, D., Ziegler, M. L. and Nuber, B., *Chem. Ber.* 1990, **123**, 1461.
- Ferrara, J. D., Djebli, A., Tessier-Youngs, C. and Youngs, W. J., J. Am. Chem. Soc. 1988, 110, 647.
- Demirhan, F., Gelling, A., Irisli, S., Jeffery, J. C., Salek, S. N., Sentürk, O. S. and Went, M. J., J. Chem. Soc. Dalton Trans. 1993, 2765.