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Original Scientific Paper

Phenylcyanamidocopper(I) and Silver(I) Complexes: Synthetic and Structural Studies*

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Phenylcyanamidocopper(I) and silver(I) complexes of the type, [{M(PPh_3)$_2$L}$_2$] (M = Cu, L = 4-NO_2pcyd or 4-Me_2Npcyd; M = Ag, L = 4-Me_2Npcyd), [Cu(PPh_3)$_3$L] (L = pcyd or 4-NO_2-pcyd), [Ag(PPh_3)$_3$L] (L = pcyd, 2-Clpcyd, 4-Clpcyd, 4-Brpcyd, 4-MeOpcyd, 4-NO_2pcyd or 4-Me_2Npcyd), [Ag(Me_2phen)(2-Clpcyd)] (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) and [Ag(dppm)(4-Brpcyd)] (dppm = bis(diphenyl-phosphino)methane) have been synthesised and characterised and the crystal structures of four of the complexes determined. For both [{Cu(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] · CH_2Cl_2 and [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$], the cyanamide ligands bridge the metal atoms in a μ-1,3-fashion through the cyano and amido nitrogens. Each metal atom has a distorted tetrahedral geometry, being bound to two triphenylphosphine phosphorus atoms and two nitrogen atoms from 4-Me_2Npcyd ligands to give a 'P_2N_2' coordination sphere. In the case of the Cu complex the dimer is centrosymmetric but for the Ag complex the metal atoms are not equivalent. The complexes, [Ag(PPh_3)$_3$(4-Brpcyd)] and [Ag(PPh_3)$_3$(4-Me-Opcyd)], are discrete monomers, in which each of the Ag atoms adopts a distorted tetrahedral geometry, being bound to three triphenylphosphine phosphorus atoms and one phenylcyanamide ligand binding in a terminal fashion through the cyano nitrogen.

Key words: phenylcyanamide, copper(I), silver(I), X-ray structures.

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

Our interest in the coordinating properties of phenylcyanamides arose from the observation that copper(II) promotes the desulfurization of *N*-phenylthioureas to give complexes such as [{Cu(bipy)(pcyd)$_2$}$_2$] (bipy = 2,2'-bipyridine, pcyd = phenylcyanamide).[1] Interest in phenylcyanamide complexes also centres on their relationship to the copper *N,N'*-dicyanoquinonediimine (DCNQI) compounds, Cu(DCNQI)$_2$, some of which show a remarkably high electrical conductivity. X-ray crystallographic structural data indicate that in these compounds the copper ion is in a distorted tetrahedral environment coordinated by four cyanamide groups.[2] In some respects, anionic phenylcyanamides behave as pseudohalides in their ligating properties.[3–8] For example, they are ambidentate in nature exhibiting three different coordination modes, namely (i) monodentate *via* the cyano nitrogen, (ii) μ-1,3-bridging through both the amido and cyano nitrogens and (iii) μ-1,1-bridging *via* the cyano nitrogen. In this study earlier work on substituted anionic phenylcyanamides[1,4,5] is extended to include their interactions with silver(I) and some further observations on the their copper(I) chemistry. Of particular interest in this report is the isolation of the two complexes [{M(PPh$_3$)(4-Me$_2$Npcyd)}$_2$] (M = Cu or Ag) which, although they have the same formulations, have different structures.

EXPERIMENTAL

Infrared spectra were obtained on a BIORAD FTS-40 spectrophotometer and microanalyses (Table I) were performed by the Campbell Microanalytical Laboratory, University of Otago. All chemicals were reagent grade or better and solvents were dried by the usual methods. The phenylcyanamide ligands were prepared from the appropriate anilines *via* phenylthioureas following the literature method[9] for the unsubstituted compound or directly using cyanogen bromide.[10] [Cu(PPh$_3$)$_2$NO$_3$], [Cu(PPh$_3$)$_3$BF$_4$] and [Ag(PPh$_3$)$_3$NO$_3$] were prepared according to Refs. 11, 12 and 13 respectively and the silver(I) phenylcyanamide salts were obtained following the published method for [Ag(pcyd)].[8] Compounds were prepared under a dinitrogen atmosphere.

Preparation of the Complexes

[{Cu(PPh$_3$)$_2$L}$_2$] (L = 4-NO$_2$pcyd or 4-Me$_2$Npcyd)

The appropriate phenylcyanamide (0.2 mmol) was deprotonated by reaction with sodium (0.2 mmol) in ethanol (10 cm^3). The resulting solution was added to a stirred solution of [Cu(PPh$_3$)$_2$NO$_3$] (0.2 mmol) in dichloromethane (15 cm^3) and the reaction mixture gently heated for 30 min. The precipitate of NaNO$_3$ which formed was filtered off, the resulting filtrate reduced in volume using a rotary evaporator and then hexane was added to initiate crystallisation. The product was washed with hexane and dried *in vacuo*. In the case of L = 4-NO_2pcyd, the product was recrystallised from dichloromethane/hexane. Yields: *ca.* 50–75%.

[Cu(PPh_3)$_3$L] (L = pcyd or 4-NO_2-pcyd)

These were prepared following the method given above for [{Cu((PPh_3)$_2$L}$_2$], but without the recrystallisation step. Yields: *ca.* 50%. Attempts to purify the products by recrystallisation from dichloromethane/hexane solution, even in the presence of excess PPh_3, led to formation of the dimeric complexes. In the case of L = pcyd, use of [Cu(PPh_3)$_3$$BF_4$], as the copper precursor, did not improve the yield or purity of the product.

[Ag(PPh_3)$_3$L] (L = pcyd, 2-Clpcyd, 4-Clpcyd, 4-Brpcyd, 4-MeOpcyd, 4-NO_2pcyd or 4-Me_2Npcyd)

Triphenylphosphine (3 mmol), dissolved in dichloromethane (30 cm^3), was added to a suspension of the appropriate silver(I) phenylcyanamide salt (1 mmol) in dichloromethane (20 cm^3) and the mixture stirred until a clear solution was obtained. The volume of the resulting solution was reduced to *ca.* 25 cm^3 using a rotary evaporator and then hexane added to initiate crystallisation of the product. It was washed with ethanol and dried *in vacuo*. Yields: 30–75%.

[Ag(PPh_3)$_3$(4-Me_2Npcyd)]

4-Dimethylaminophenylcyanamide (0.033 g, 0.2 mmol) was deprotonated by reaction with sodium (0.005 g, 0.2 mmol) in ethanol (10 cm^3). The resulting solution was added to a stirred solution of [Ag(PPh_3)$_3$$NO_3$] (0.196 g, 0.2 mmol) in dichloromethane (10 cm^3) and the reaction mixture gently heated for 20 min. The precipitate of $NaNO_3$ which formed was filtered off, the resulting filtrate reduced in volume to *ca.* 10 cm^3 using a rotary evaporator and then hexane was added to initiate crystallisation. The product was washed with hexane and dried *in vacuo*. Yield: 75%. If the product was recrystallised from dichloromethane/hexane a few crystals of a second complex were obtained which was identified by X-ray crystal structural analysis as [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] (see below).

[Ag(Me_2phen)(2-Clpcyd)]

2,9-Dimethyl-1,10-phenanthroline (Me_2phen) (0.108 g, 0.52 mmol) dissolved in dichloromethane (10 cm^3), was added to a suspension of [Ag(2-Clpcyd)] (0.134 g, 0.52 mmol) in the same solvent (10 cm^3) and the resulting solution stirred for *ca.* 10 min. The cream precipitate of the product which formed was filtered off, washed with ethanol and dried *in vacuo*. Yield: 48%.

[Ag(dppm)(4-Brpcyd)]

To a suspension of [Ag(4-Brpcyd)] (0.388 g, 1.3 mmol) in hot acetonitrile (20 cm^3) was added a solution of bis(diphenylphosphino)methane (dppm) (0.494 g, 1.3 mmol) in hot acetonitrile (20 cm^3). The mixture was refluxed for 20 min and then the resulting cream precipitate of the product was filtered off, washed with ethanol and dried *in vacuo*. Yield: 89%.

TABLE I

Analytical, m.p., conductivity and IR spectral data for the complexes

Complex	Analysis (%)[a]				m.p. °C	Λ (S cm^2/mol)	ν(CN)[b] cm^{-1}
	C	H	N	P			
[Cu(PPh$_3$)$_3$(pcyd)]	73.4 (73.1)	5.4 (5.1)	2.7 (2.8)		87–90	5[c]	2120
[Cu(PPh$_3$)$_3$(4-NO$_2$pcyd)]	71.6 (72.4)	5.1 (4.9)	4.2 (4.2)		159–161	<1[c]	2145
[{Cu(PPh$_3$)$_2$(4-NO$_2$pcyd)}$_2$][d]	68.9 (68.8)	4.9 (4.6)	5.4 (5.6)		227–229	<1[c]	2162
[{Cu(PPh$_3$)$_2$(4-Me$_2$Npcyd)}$_2$][d]	71.2 (70.6)	5.3 (5.3)	5.5 (5.5)		201–204	<1[c]	2158
[Ag(PPh$_3$)$_3$(pcyd)][e]	67.2 (67.9)	4.7 (4.8)	2.2 (2.6)		174–177	–	2085
[Ag(PPh$_3$)$_3$(2-Clpcyd)]	69.2 (70.0)	4.6 (4.7)	2.6 (2.7)	8.7 (8.9)	188–190	13[f]	2100
[Ag(PPh$_3$)$_3$(4-Clpcyd)]	69.2 (70.0)	4.8 (4.7)	2.3 (2.7)	9.2 (8.9)	180–182	13[f]	2093
[Ag(PPh$_3$)$_3$(4-Brpcyd)]	67.3 (67.2)	4.5 (4.5)	2.3 (2.5)	8.5 (8.5)	153–155	11[f]	2110
[Ag(PPh$_3$)$_3$(4-MeOpcyd)]	70.8 (71.5)	4.9 (5.0)	2.3 (2.7)	9.4 (8.9)	168–171	4[f]	2100
[Ag(PPh$_3$)$_3$(4-NO$_2$pcyd)]	69.0 (69.3)	4.9 (4.7)	4.0 (4.0)	8.7 (8.8)	187–189	24[f]	2121
[Ag(PPh$_3$)$_3$(4-Me$_2$Npcyd)][d]	70.7 (70.6)	5.3 (5.2)	3.7 (3.9)		152–158	2[f]	2098
[Ag(Me$_2$phen)(2-Clpcyd)]	53.6 (53.9)	3.4 (3.5)	12.0 (12.0)		221–225	–	2134
[Ag(dppm)(4-Brpcyd)]	55.9 (55.8)	3.7 (3.8)	4.2 (4.1)	9.0 (9.1)	231–235	–	2107

[a] Calculated values given in parentheses.

[b] Recorded as nujol mulls.

[c] In CH_2Cl_2.

[d] Contains 0.25 molecule CH_2Cl_2.

[e] Contains one molecule CH_2Cl_2.

[f] In acetone.

Determination of the X-ray Crystal Structures of *[{Cu(PPh3)2(4-Me2Npcyd)}2] · CH2Cl2, [{Ag((PPh3)2(4-Me2Npcyd)}2], [Ag(PPh3)3(4-Brpcyd)] and [Ag(PPh3)3(4-MeOpcyd)]*

Suitable crystals were obtained as follows: $[\{Cu(PPh_3)_2(4\text{-}Me_2Npcyd)\}_2] \cdot CH_2Cl_2$ and $[\{Ag(PPh_3)_2(4\text{-}Me_2Npcyd)\}_2]$ from dichloromethane/hexane; $[Ag(PPh_3)_3$(4-Brpcyd)] from toluene/*n*-butanol; and $[Ag(PPh_3)_3$(4-MeOpcyd)] from dichloromethane/*n*-butanol solutions. Data collection, processing, structure analysis and refinement data are given in Table II. Structure solution was by Direct Methods[14] and refinement by a full-matrix least-squares method.[15] Anisotropic thermal motion was assumed for all non-hydrogen atoms except those referred to below. Hydrogen atoms were included in calculated positions (U = 0.08) riding on the atoms to which they were attached and were numbered accordingly. In the analysis of $[\{Cu\text{-}(PPh_3)_2\text{-}(4\text{-}Me_2Npcyd)\}_2] \cdot CH_2Cl_2$ two disordered sites (occupancy factors 0.43 and 0.57) were identified for the dicholoromethane molecule and the hydrogen and chlorine atoms were restrained to form a tetrahedron about their common carbon. Disordered sites (two of occupancy 0.43 and 0.57) were also apparent for the carbon atoms for the NMe_2 substituent and geometrical restraints were applied in the refinement of these atoms. Isotropic thermal motion was assumed for these terminal carbons. Tables of atomic coordinates, thermal parameters and complete listings of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. The deposition numbers are: 103168 $[Ag(PPh_3)_3$(4-Brpcyd)]; 103169 $[\{Ag(PPh_3)_2\text{-}(4\text{-}Me_2Npcyd)\}_2]$; 103170 $[Ag(PPh_3)_3$(4-MeOpcyd)]; and 103171 $[\{Cu(PPh_3)_2(4\text{-}Me_2\text{-}Npcyd)\}_2] \cdot CH_2Cl_2$.

RESULTS AND DISCUSSION

Preparation and Characterisation of the Complexes

The phenylcyanamidocopper(I) complexes $[\{Cu(PPh_3)_2L\}_2]$ (L = 4-NO_2pcyd or 4-Me_2Npcyd) were synthesised by anion displacement from $[Cu(PPh_3)_2NO_3]$. Microanalytical data are given in Table I and the dimeric formulation for the 4-Me_2Npcyd complex was established by single crystal X-ray structural analysis (see below). The 4-Mepcyd complex has a similar μ-1,3-bridged ligand structure[5] and thus it appears for a variety of substituted phenylcyanamides, X-pcyd, where X ranges from being strongly electron withdrawing to electron donating in character (*i.e.* X = 4-NO_2, 4-F, 4-Cl, 3-Cl, 4-Br, H, 4-Me, 4-MeO or 4-Me_2N), that the most readily isolated complexes can be formulated as dimers, namely $[\{Cu(PPh_3)_2L\}_2]$. However, in this study it has also been possible to isolate two complexes with the formulation, $[Cu(PPh_3)_3L]$ (L = pcyd or 4-NO_2pcyd), although IR spectroscopy indicates that there is a slight contamination with the dimeric analogues since the strong phenylcyanamide ν(CN) bands near 2000 cm^{-1} (Table I) can be used to distinguish between the two different complex types. For instance in the complex, $[Cu(PPh_3)_3$(pcyd)], the ν(CN) band is at 2120 cm^{-1}, whereas for the dimer, $[\{Cu(PPh_3)_2(pcyd)\}_2]$, it appears at higher wavenumbers (2163 cm^{-1}).

TABLE II

Crystallographic data

Compound	[{Cu(PPh$_3$)$_2$(4-Me$_2$-Npcyd)}$_2$] · CH$_2$Cl$_2$	[{Ag(PPh$_3$)$_2$–(4-Me$_2$Npcyd)}$_2$]	[Ag(PPh$_3$)$_3$(4-Brpcyd)]	[Ag (PPh$_3$)$_3$(4-MeOpcyd)]
Crystal data				
Empirical formula	$C_{46}H_{42}Cl_2CuN_3P_2$	$C_{45}H_{40}AgN_3P_2$	$C_{61}H_{49}AgBrN_2P_3$	$C_{62}H_{52}AgN_2OP_3$
Formula weight	833.21	792.61	1090.71	1041.84
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	14.024(3)	12.255(5)	9.927(2)	13.756(4)
b / Å	21.440(4)	13.560(4)	13.755(3)	14.116(2)
c / Å	14.174(3)	26.947(6)	20.256(4)	14.198(3)
α / °	90	101.66(2)	102.68(3)	87.87(2)
β / °	97.94(3)	87.99(2)	94.61(3)	103.68(2)
γ / °	90	116.20(2)	106.32(3)	101.87(2)
Volume / Å^3	4221(2)	3928(2)	2559.7(9)	2621(1)
Z	4	4	2	2
D_C / mg m^{-3}	1.311	1.340	1.415	1.320
μ(Mo-Kα) / mm^{-1}	0.755	0.630	1.310	0.519
F(000)	1728	1632	1112	1076
Crystal size / mm	0.50 × 0.35 × 0.32	0.27 × 0.20 × 0.13	0.48 × 0.28 × 0.24	0.40 × 0.22 × 0.20

TABLE II (continued)

Data collection, processing and refinement				
θ range / °	1.73 to 20.97*	1.55 to 21.48*	1.046 to 24.96	1.47 to 24.97
Index ranges	$0 \le h \le 14$, $0 \le k \le 21$, $-14 \le l \le 14$	$0 \le h \le 12$, $-13 \le k \le 12$, $-27 \le l \le 27$	$0 \le h \le 11$, $-16 \le k \le 15$, $-24 \le l \le 23$	$0 \le \mathrm{h} \le 16$, $-16 \le \mathrm{k} \le 16$, $-16 \le \mathrm{l} \le 16$
Independent reflections	4498	8941	8931	9186
Decay / %	2.0	1.8	0.1	1.6
Absorption corrections maximum, minimum	1.000, 0.927	0.999, 0.913	1.000, 0.926	1.000, 0.968
Data/restraints/ parameters	4461/12/510	8919/0/920	8925/0/614	9186/0/624
Observed data ($>2\sigma(I)$)	2602	5094	5681	3865
Goodness-of-fit on F^2	1.042	1.028	1.079	0.994
Least-squares weights a, b	0.0892, 0.0000	0.0323, 4.5824	0.0423, 0.5923	0.0975, 0.0000
$R1$, $wR2$ [$I>2\sigma(I)$]	0.0542, 0.1309	0.0376, 0.0755	0.0288, 0.0703	0.0488, 0.1207
$R1$, $wR2$ (all data)	0.1390, 0.2258	0.1276, 0.1069	0.0806, 0.0941	0.1840, 0.1827
Extinction coefficient	0.0013(5)	0.00024(10)	0.0085(4)	0.000(4)
Largest diff. map peak and hole / e Å^{-3}	0.461 and –0.425	0.431 and –0.399	0.426 and –0.471	0.624 and –0.858

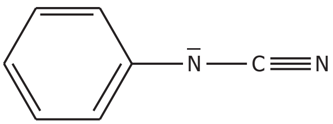
Common data:

CAD4 diffractometer; Temperature of data collection 293(2)°; Scan type ω-2θ; Absorption corrections by psi-scan method; Mo-Kα radiation, $\lambda = 0.71073$; Function miminised $\Sigma\, w(F_o^2 - F_c^2)^2$; $R1 = \Sigma\,|(\,|F_o| - |F_c|\,|/\Sigma\,|F_o|$; $wR2 = [\Sigma\, w\,(F_o^2 - F_c^2)^2 / \Sigma\, w\,(F_o^2)^2]^{0.5}$; $w = 1.0 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2) / 3$.

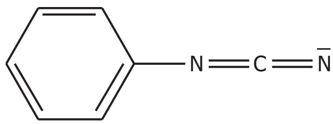
Data collection was discontinued at $\theta < 25°$ since data were weak.

A similar trend is seen for the analogous 4-NO_2pcyd complexes (*viz.* 2145 and 2162 cm^{-1}). It has not been possible to obtain suitable crystals of the [Cu(PPh_3)$_3$L] complexes for X-ray structural analysis, but monomeric tetrahedral structures, similar to those found for the silver(I) complexes (see below), are proposed. Attempts to purify the products using various solvents, even in the presence of excess triphenylphosphine, only led to an increased contamination by the dimeric complex.

In contrast, silver(I) affords the readily isolatable complexes, [Ag(PPh_3)$_3$L] (L = pcyd, 2-Clpcyd, 4-Clpcyd, 4-Brpcyd, 4-MeOpcyd, 4-NO_2pcyd or 4-Me_2Npcyd) (Table I) which, based on the structures of the 4-Brpcyd and 4-MeOpcyd complexes (see below), are all assumed to be tetrahedral monomers. These complexes were prepared from the reaction of triphenylphosphine in a 3:1 molar ratio with the appropriate phenylcyanamido silver(I) salts or by anion displacement from [Ag(PPh_3)$_3$$NO_3$]. The ν(CN) bands fall in the range 2085–2125 cm^{-1} (Table I) but there is no clear relationship between the wavenumbers and the nature of the substituent on the phenylcyanamide although it is noted that for the 4-NO_2pcyd complex the band falls at the top end of the range suggesting the importance of resonance structure (a) as a result of the strongly electron withdrawing substituent delocalising the negative charge on the amido nitrogen towards the aromatic ring.



(a)



(b)

Care is needed in accounting for the trends in the ν(CN) frequencies in these phenylcyanamido complexes. For the complexes, [M(PPh_3)$_3$L] (M = Cu or Ag, L = pcyd or 4-NO_2pcyd), the ν(CN) frequencies are over 20 cm^{-1} higher for the copper complexes which may reflect the greater influence of resonance structure (b) for the silver complexes. However, other factors such as the mass and size effect and enhanced soft-acid-soft-base interaction will also contribute to lower ν(CN) frequencies for the silver complexes. The apparent preference of phenylcyanamide ligands to bind to silver in a terminal fashion rather than in the μ-1,3-bridging mode, may be due to the greater influence of resonance structure (b) in these complexes. However, when the negative charge on the amido nitrogen is enhanced, as expected in 4-Me_2-Npcyd, it is possible to isolate the dimeric silver(I) complex, [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$], albeit in low yield, upon recrystallization of [Ag(PPh_3)$_3$(4-Me_2Npcyd)]. The larger silver(I) ion is able to stabilise this latter structural type for most of the substituted pcyd complexes studied, whereas for the smaller copper(I) ion, one triphenylphosphine is more readily lost and the dimeric complex is favoured. As noted for copper(I), the ν(CN) band is higher for the bridged 4-Me_2Npcyd ligand silver complex (2145 cm^{-1}) when compared with the monodentate ligand analogue (2098 cm^{-1}).

Molar conductivity data for the complexes are listed in Table I and fall well below the values expected for 1:1 electrolytes, confirming that in solution the phenylcyanamide ligands remain coordinated to the metal atom.

Two further complexes, characterised as [Ag(Me_2phen)(2-Clpcyd)] (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) and [Ag(dppm)(4-Brpcyd)] (dppm = bis(diphenyl-phosphino)methane, have been synthesised by the addition of the appropriate ligand, in a 1:1 molar ratio, to the corresponding silver(I) phenylcyanamide salt. The fact that the ν(CN) absorption for [Ag(Me_2phen)(2-Clpcyd)] is at higher wavenumbers (2134 cm^{-1}) than the value of 2100 cm^{-1} observed for the terminal phenylcyanamide in [Ag(PPh_3)$_3$(2-Clpcyd)], may suggest that in the Me_2phen complex, the 2-Clpcyd is bridged, binding through both the amido and cyano nitrogens in a μ-1,3 fashion but this requires structural verification. Further characterisation of these complexes was prevented by their low solubility in suitable solvents.

Crystal Structures of [{Cu(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] · CH_2Cl_2 and [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$]

The molecular structures of both [{Cu(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] · CH_2Cl_2 and [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] contain the 4-dimethylaminophenylcyanamide ligands bridging the metal atoms in a μ-1,3-fashion through the cyano and amido nitrogens. The structures are shown in Figures 1 and 2 and selected bond parameters are given in Tables III and IV. The copper complex is a centrosymmetric dimer but this is not the case for the silver complex, where the two metal atoms are non-equivalent.

Each metal atom has a distorted tetrahedral coordination sphere consisting of two triphenylphosphine phosphorus atoms, and two nitrogen atoms from 4-Me_2Npcyd ligands. In the centrosymmetric copper complex the copper atoms are bound to a terminal cyano nitrogen from one 4-Me_2Npcyd ligand and an amido nitrogen from the symmetry related cyanamide. In the silver complex, Ag(1) is bound to the cyano nitrogens [N(1) and N(2)] of two 4-Me_2Npcyd ligands and Ag(2) is bound to the amido nitrogens [N(3) and N(4)] of the same two phenylcyanamides. Angles around the metal range from 96.9(3) to 118.66(8)° for the copper complex and 89.4(2) to 121.35(6)° for the silver complex, with the largest being the P–M–P (M = Cu or Ag) angles in each case as expected for tetrahedral bis(triphenylphosphine)copper(I) or silver(I) centres,[5,13,16] presumably because of repulsions between

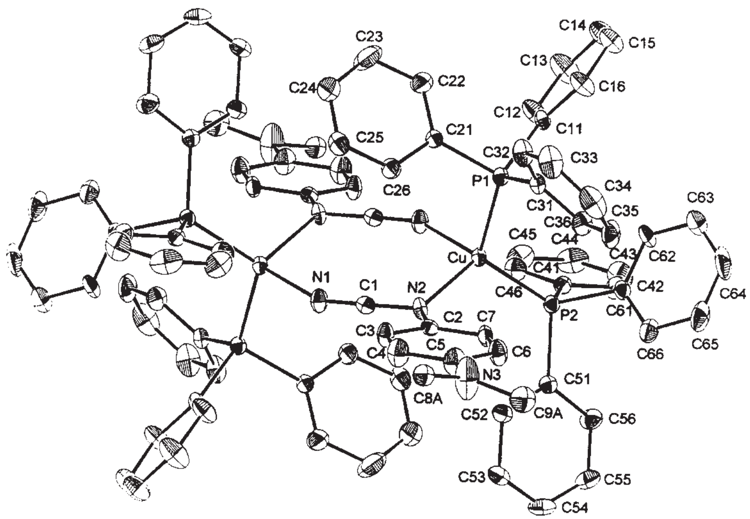


Figure 1. ZORTEP[18] diagram for [{Cu(PPh$_3$)$_2$(4-Me$_2$Npcyd)}$_2$] showing the numbering scheme used. Thermal ellipsoids are drawn at the 20% probability level.

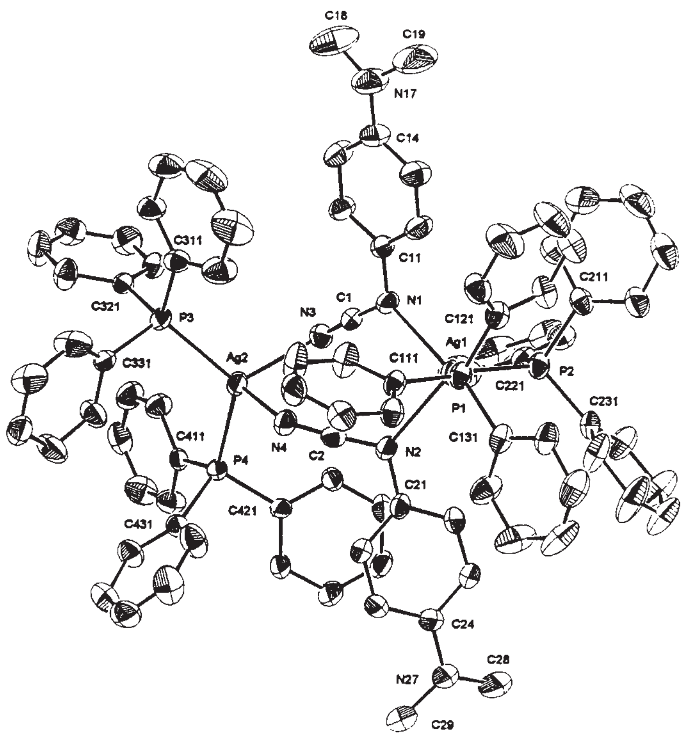


Figure 2. ZORTEP[18] diagram for [{Ag(PPh$_3$)$_2$(4-Me$_2$Npcyd)}$_2$] showing the numbering scheme used. Thermal ellipsoids are drawn at the 30% probability level.

TABLE III

Selected bond lengths and angles for $[\{Cu(PPh_3)_2(4\text{-}Me_2Npcyd)\}_2]\cdot CH_2Cl_2$

Bond lengths / Å	
Cu–N(1)#1	2.015(7)
Cu–N(2)	2.114(6)
Cu–P(2)	2.246(2)
Cu–P(1)	2.303(2)
N(1)–C(1)	1.152(9)
N(1)–Cu#1	2.015(7)
C(1)–N(2)	1.328(10)
N(2)–C(2)	1.411(8)
Bond angles / °	
N(1)#1–Cu–N(2)	96.9(3)
N(1)#1–Cu–P(2)	114.1(2)
N(2)–Cu–P(2)	117.2(2)
N(1)#1–Cu–P(1)	100.6(2)
N(2)–Cu–P(1)	106.0(2)
P(2)–Cu–P(1)	118.66(8)
C(1)–N(1)–Cu#1	152.7(6)
N(1)–C(1)–N(2)	177.0(8)
C(1)–N(2)–C(2)	118.3(6)
C(1)–N(2)–Cu	113.2(5)
C(2)–N(2)–Cu	124.8(5)

Symmetry transformations used to generate equivalent atoms: (#1) –*x*, –*y*, –*z*.

the phenyl rings of the PPh_3 ligands. For $[\{Cu(PPh_3)_2(4\text{-}Me_2Npcyd)\}_2]$, and the analogous 4-Mepcyd complex,[5] the Cu–N(cyano) distance is shorter than the Cu–N(amido) distance, although the difference is greater (0.1 compared with 0.4 Å) in the latter complex. However, both Cu–N distances lie in the range expected for complexes of this type as do the Cu–P distances.[5] In the case of the silver complex, $[\{Ag(PPh_3)_2(4\text{-}Me_2Npcyd)\}_2]$, the mean Ag–N(cyano) distances are not very different from the mean Ag–N(amido) distances (2.365 and 2.353 Å respectively). For the copper complex the centrosymmetric $(CuNCN)_2$ bridging unit forms an approximately planar eight-membered ring (maximum deviation 0.02 Å) but in the silver analogue the $(AgNCN)_2$ is far from planar with the deviations ranging up to 0.67 Å. Coupled with this, is the observation of much smaller Ag–N(cyano)–C bond angles [C(1)–N(3)–Ag(2) 119.6(6) and C(2)–N(4)–Ag(2) 117.6(5)°] as compared with 152.7(6)°

TABLE IV

Selected bond lengths and angles for $[\{Ag(PPh_3)_2(4\text{-}Me_2Npcyd)\}_2]$

Bond distances / Å			
Ag(1)–N(2)	2.339(5)	P(2)–C(231)	1.835(7)
Ag(1)–N(1)	2.367(5)	P(3)–C(321)	1.821(7)
Ag(1)–P(2)	2.483(2)	P(3)–C(311)	1.822(7)
Ag(1)–P(1)	2.498(2)	P(3)–C(331)	1.835(7)
Ag(2)–N(3)	2.336(6)	P(4)–C(411)	1.823(6)
Ag(2)–N(4)	2.394(6)	P(4)–C(421)	1.825(6)
Ag(2)–P(3)	2.462(2)	P(4)–C(431)	1.824(7)
Ag(2)–P(4)	2.483(2)	N(1)–C(1)	1.293(9)
P(1)–C(131)	1.816(8)	N(1)–C(11)	1.407(8)
P(1)–C(111)	1.824(7)	N(2)–C(2)	1.284(9)
P(1)–C(121)	1.826(8)	N(2)–C(21)	1.422(8)
P(2)–C(221)	1.812(7)	N(3)–C(1)	1.150(8)
P(2)–C(211)	1.834(7)	N(4)–C(2)	1.181(8)
Bond angles / °			
N(2)–Ag(1)–N(1)	93.3(2)	C(231)–P(2)–Ag(1)	118.2(3)
N(2)–Ag(1)–P(2)	119.5(2)	C(321)–P(3)–C(311)	103.8(3)
N(1)–Ag(1)–P(2)	106.2(2)	C(321)–P(3)–C(331)	103.2(3)
N(2)–Ag(1)–P(1)	100.5(2)	C(311)–P(3)–C(331)	104.7(3)
N(1)–Ag(1)–P(1)	114.9(2)	C(321)–P(3)–Ag(2)	114.6(2)
P(2)–Ag(1)–P(1)	119.70(6)	C(311)–P(3)–Ag(2)	119.1(3)
N(3)–Ag(2)–N(4)	89.4(2)	C(331)–P(3)–Ag(2)	110.0(2)
N(3)–Ag(2)–P(3)	114.4(2)	C(411)–P(4)–C(421)	104.2(3)
N(4)–Ag(2)–P(3)	110.5(2)	C(411)–P(4)–C(431)	104.4(3)
N(3)–Ag(2)–P(4)	112.8(2)	C(421)–P(4)–C(431)	101.5(3)
N(4)–Ag(2)–P(4)	102.8(2)	C(411)–P(4)–Ag(2)	117.6(2)
P(3)–Ag(2)–P(4)	121.35(6)	C(421)–P(4)–Ag(2)	113.2(2)
C(131)–P(1)–C(111)	102.6(3)	C(431)–P(4)–Ag(2)	114.2(2)
C(131)–P(1)–C(121)	105.0(3)	C(1)–N(1)–C(11)	118.0(6)
C(111)–P(1)–C(121)	103.8(3)	C(1)–N(1)–Ag(1)	116.8(4)
C(131)–P(1)–Ag(1)	109.6(3)	C(11)–N(1)–Ag(1)	124.8(4)
C(111)–P(1)–Ag(1)	117.1(2)	C(2)–N(2)–C(21)	116.7(6)
C(121)–P(1)–Ag(1)	117.1(3)	C(2)–N(2)–Ag(1)	116.6(4)
C(221)–P(2)–C(211)	102.9(3)	C(21)–N(2)–Ag(1)	126.5(4)
C(221)–P(2)–C(231)	104.0(3)	C(1)–N(3)–Ag(2)	119.6(6)
C(211)–P(2)–C(231)	104.5(3)	C(2)–N(4)–Ag(2)	117.6(5)
C(221)–P(2)–Ag(1)	112.9(2)	N(3)–C(1)–N(1)	176.7(7)
C(211)–P(2)–Ag(1)	112.8(2)	N(4)–C(2)–N(2)	175.6(8)

for C(1)–N(1)–Cu(#1). The fact that the angles around the cyano nitrogen are close to 120° in the silver complex is consistent with a greater contribution from resonance structure (b) to the molecular orbital description of the cyanamide anion than for the copper complex. This difference may arise from the greater polarizing power of the Ag(I) ion increasing the contribution of (b) as well as steric constraints associated with the packing of the asymmetric dimer. However, such conclusions must be treated with caution, since the mean N(cyano)–C bond distance at 1.166 Å is still closer to the value expected for a CN triple bond (1.16 Å) than a double bond (1.29 Å) and the mean value of the N(amido)–C bond distance is 1.289 Å. For [{$Cu(PPh_3)_2$(4-Me_2Npcyd)}$_2$], the values of the N(cyano)–C and N(amido)–C bond distances of 1.152(9) and 1.328(10) Å are consistent with the suggestion that resonance structure (a) is more important for the copper complex than for the silver complex, however, these differences between the two complexes are barely statistically significant. Other bond angles within the $(MNCN)_2$ (M = Cu or Ag) rings are not markedly different from the expected values;[3–7] for example, the N(cyano)–C–N(amido) angles are close to linear at *ca.* 176°.

Crystal Structures of [$Ag(PPh_3)_3$(4-Brpcyd)] and [$Ag(PPh_3)_3$(4-MeOpcyd)]

The silver(I) complexes, [$Ag(PPh_3)_3$(4-Brpcyd)] and [$Ag(PPh_3)_3$(4-MeOpcyd)], crystallise as discrete monomers, in which the Ag atoms adopt a distorted tetrahedral geometry with a 'P_3N' coordination sphere with the phenylcyanamide ligands binding in a terminal fashion through the cyano nitrogens. The structures are depicted in Figures 3 and 4 and selected bond parameters are listed in Tables V and VI. The Ag–P distances, which lie in the range 2.530(2) to 2.571(2) Å, are in good agreement with close structural analogues such as [$Ag(PPh_3)_3X$] (X = Cl, Br, I, NO_3 or BF_4)[13,16] but are longer than the Ag–P distances [2.462(2) to 2.498(2) Å] found in the dimeric complex, [{$Ag(PPh_3)_2$(4-Me_2Npcyd)}$_2$], thus fitting the observation that Ag–P bond distances lengthen as the number of bulky triphenylphosphine ligands coordinated to the central atom increases.[13,16,17] The angles about the silver atom deviate from the ideal tetrahedral angle with the P–Ag–P angles [104.2(2) to 116.74(4)°] generally being the larger and the N–Ag–P angles [97.54(9) to 104.83(10)°] more acute. The Ag–N(cyano) bond distances are similar at 2.280(3) Å for the 4-Brpcyd complex and 2.286(7) for the 4-MeOpcyd complex, however, the Ag–N(cyano)–C bond angles are markedly different, being 159.2(3)° for the former complex and 140.7(8)° for the latter. This would suggest that the substitution of an electron donating *para*-methoxy group, rather than an electron withdrawing bromo group, into the

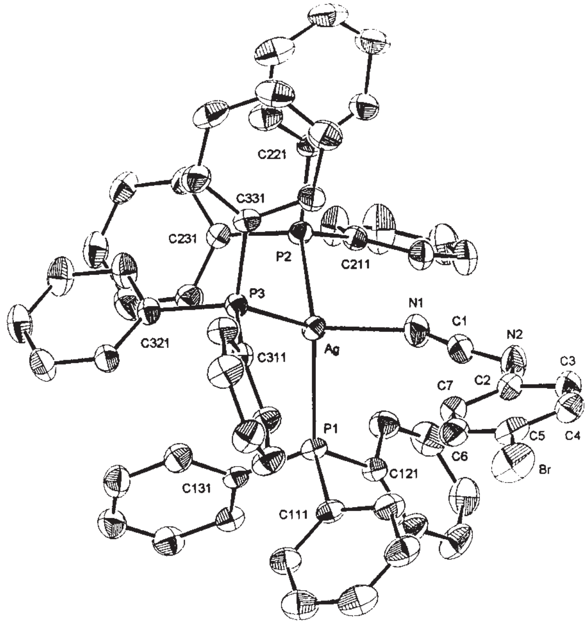


Figure 3. ZORTEP[18] diagram for $[Ag(PPh_3)_3(4\text{-Brpcyd})]$ showing the numbering scheme used. Thermal ellipsoids are drawn at the 30% probability level.

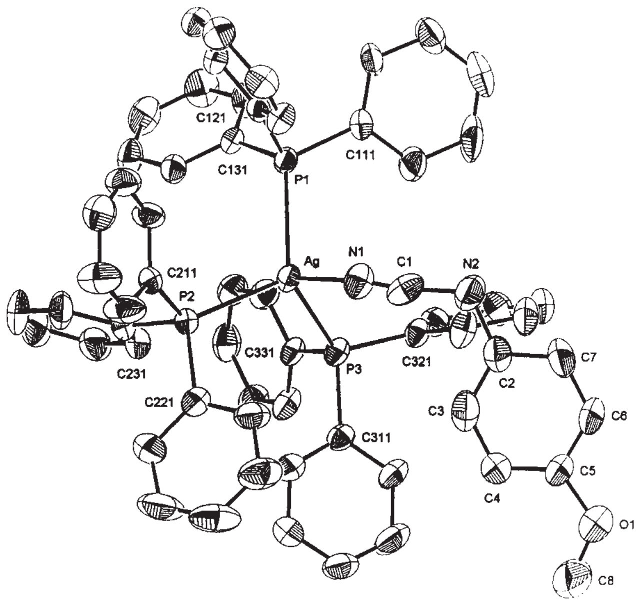


Figure 4. ZORTEP[18] diagram for $[Ag(PPh_3)_3(4\text{-MeOpcyd})]$ showing the numbering scheme used. Thermal ellipsoids are drawn at the 30% probability level.

TABLE V

Selected bond lengths and angles for
$[Ag(PPh_3)_3(4\text{-Brpcyd})]$

Bond lengths / Å	
Ag–N(1)	2.280(3)
Ag–P(3)	2.543(1)
Ag–P(1)	2.563(1)
Ag–P(2)	2.571(1)
Br–C(5)	1.903(4)
N(1)–C(1)	1.158(4)
C(1)–N(2)	1.286(5)
N(2)–C(2)	1.383(5)
Bond angles / °	
N(1)–Ag–P(3)	104.83(10)
N(1)–Ag–P(1)	97.54(9)
P(3)–Ag–P(1)	116.27(3)
N(1)–Ag–P(2)	112.76(9)
P(3)–Ag–P(2)	107.79(4)
P(1)–Ag–P(2)	116.74(4)
C(1)–N(1)–Ag	159.2(3)
N(1)–C(1)–N(2)	172.7(4)
C(1)–N(2)–C(2)	120.1(3)
N(2)–C(2)–C(7)	125.5(3)
N(2)–C(2)–C(3)	118.1(3)
C(7)–C(2)–C(3)	116.4(4)

aromatic ring causes the contribution from resonance structure (b) for the cyanamide ligand to increase. The N(cyano)–C and C–N(amido) distances point to both resonance structures being important with the former being closer to the value expected for a triple bond in both cases, however, it is noted that the N(1)–C(1) distance is markedly shorter, at 1.013(10) Å, for the 4-MeOpcyd than for the 4-Br compound [1.158(4) Å]. The C(1)–N(2) distances for the two compounds at 1.410(12) (4-MeOpcyd) and 1.286(5) Å (4-Brpcyd), reflect these differences and suggest that there is not a simple correlation between such bond lengths, metal-cyanamide bond angles, the *para*-substituent and the significance of either resonance structure (a) or (b). In particular, previous reports have shown, the metal-cyanamide angles for terminal pcyd ligands can vary from 171.4(10)° in the ruthenium(III) compound, $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]SO_4$,[6] and 170.7(5)° for the copper(I) com-

TABLE VI

Selected bond lengths and angles for $[Ag(PPh_3)_3(4\text{-MeOpcyd})]$

Bond lengths / Å	
Ag–N(1)	2.286(7)
Ag–P(1)	2.530(2)
Ag–P(2)	2.542(2)
Ag–P(3)	2.571(2)
O(1)–C(8)	1.273(14)
O(1)–C(5)	1.379(12)
N(2)–C(1)	1.410(12)
N(2)–C(2)	1.411(11)
N(1)–C(1)	1.013(10)
Bond angles / °	
N(1)–Ag–P(1)	102.4(2)
N(1)–Ag–P(2)	104.5(2)
P(1)–Ag–P(2)	114.59(6)
N(1)–Ag–P(3)	104.2(2)
P(1)–Ag–P(3)	115.69(6)
P(2)–Ag–P(3)	113.44(7)
C(8)–O(1)–C(5)	120.7(10)
C(1)–N(2)–C(2)	115.8(7)
C(1)–N(1)–Ag	140.7(8)
N(1)–C(1)–N(2)	172.9(11)
C(7)–C(2)–C(3)	116.6(9)
C(7)–C(2)–N(2)	117.4(9)
C(3)–C(2)–N(2)	126.0(8)

pound $[Cu_2(dppe)_3(4\text{-Clpcyd})_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane],[5] to between 141.4(7) and 165.3(9)° for two copper(II) complexes with 2,3-Cl_2pcyd.[3] For one of the copper(II) complexes, crystal packing forces were suggested to be important in determining some of the bond angles.

CONCLUSION

Phenylcyanamides readily react with both copper(I) and silver(I), however, their behaviour towards these metal ions differs. The most readily isolated complexes with copper are the centrosymmetric dimers, $[\{Cu(PPh_3)_2$-

L}$_2$] in which the cyanamide ligands (L) bridge in a μ-1,3-fashion through the cyano and amido nitrogen atoms, whereas for silver the preference is for complexes to be [Ag(PPh_3)$_3$L] monomers with the cyanamides bound terminally through the cyano nitrogen atoms (although it has been possible to isolate one binuclear silver complex, [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$], in very low yield). It is suggested that this difference in behaviour is mainly a result of the larger softer silver atom being more readily able to accommodate three bulky soft PPh_3 ligands in its coordination sphere that the smaller harder copper atom. However, further structural work and a range of complexes with different metals is required before a consistent relationship between the detailed bond parameters and the substituents on the phenyl rings can be given.

REFERENCES

1. M. L. Brader, E. W. Ainscough, E. N. Baker, and A. M. Brodie, *Polyhedron* **8** (1989) 2219–2221.
2. R. J. Crutchley and M. L. Naklicki, *Inorg. Chem.* **28** (1989) 1955–1958;
   M. L. Naklicki and R. J. Crutchley, *Inorg. Chem.* **28** (1989) 4226–4229 and references therein.
3. R. J. Crutchley , R. Hynes, and E. J. Gabe, *Inorg. Chem.* **29** (1990) 4921–4928.
4. M. L. Brader, E. W. Ainscough, E. N. Baker, A. M. Brodie, and S. L. Ingham, *J. Chem. Soc., Dalton Trans.* (1990) 2785–2792.
5. E. W. Ainscough, E. N. Baker, M. L. Brader, A. M. Brodie, S. L. Ingham, J. M. Waters, J. V. Hanna, and P. C. Healy, *J. Chem. Soc., Dalton Trans.* (1991) 1243–1249.
6. R. J. Crutchley, K. McCaw, F. L. Lee, and E. J. Gabe, *Inorg. Chem.* **29** (1990) 2576–2581.
7. M. A. S. Aquino, A. E. Bostick, and R. J. Crutchley, *Inorg. Chem.* **29** (1990) 3641–3644.
8. B. R. Hollebone and R. S. Nyholm, *J. Chem. Soc. (A)* (1971) 332–337.
9. F. Kurzer, *J. Chem. Soc*. (1949) 3034–3048; R. L. Frank and P. V. Smith, *Org. Synth*. (1955) Coll. vol. 3, 735–736.
10. G. Simig, K. Lempart, J. Tamás, and G. Czira, *Tetrahedron* **31** (1975) 1195–2000.
11. P. Simpson, *Organometallic Chemistry of the Main Group Elements*, Longman, London, 1970, p. 99.
12. A. P. Gaughan, Z Dori, and J. Ibers, *Inorg. Chem.* **13** (1974) 1657–1667.
13. P. F. Barron, J. C. Dyason, P. C. Healy, L. M. Englehardt, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.* (1986) 1965–1970.
14. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **46** (1990) 467–473.
15. G. M. Sheldrick, SHELXL–93, program for crystal structure determination and refinement, University of Göttingen, Germany, 1993.
16. A. Cassel, *Acta Crystallogr., Sect. B* **37** (1981) 229–231;
    L. M. Engelhardt, P. C. Healy, V. A. Patrick, and A. H. White, *Aust. J. Chem.* **40** (1987) 1873–1880;
    M. Camalli and F. Caruso, *Inorg. Chim. Acta* **127** (1987) 209–213.

17. B-K. Teo and J. C. Calabrese, *Inorg. Chem.* **15** (1976) 2467–2474;
M. R. Churchill, J. Donahue, and F. J. Rotella, *Inorg. Chem.* **15** (1976) 2752–2763;
D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *Inorg. Chem.* **13** (1974) 1191–1199;
F. A. Cotton and R. L. Luck, *Acta Crystallogr., Sect. C* **45** (1989) 1222–1224.
18. L. Zsolnai, ZORTEP, University of Heidelberg, Germany, 1994.

SAŽETAK

Fenilcianamidobakrovi(I) i srebrovi(I) kompleksi: Sinteza i strukturna istraživanja

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Fenilcianamidobakrovi(I) i srebrovi(I) kompleksi vrste [{M(PPh_3)$_2$L}$_2$] (M = Cu, L = 4-NO_2pcyd ili 4-Me_2Npcyd; M = Ag, L = 4-Me_2Npcyd), [Cu(PPh_3)$_3$L] (L = pcyd ili 4-NO_2-pcyd), [(PH_3)$_3$L] (L = pcyd, 2-Clpcyd, 4-Clpcyd, 4-Brpcyd, 4-MeOpcyd, 4-NO_2pcyd ili 4-Me_2Npcyd), [Ag(Me_2phen)(2-Clpcyd)] (Me_2 = 2,9-dimetil-1,10-fenantrolin) i [Ag(dppm)(4-Brpcyd)] (dppm = bis(difenilfosfino)metan) sintetizirani su i pobliže opisani, a difrakcijom rentgenskih zraka na monokristalu određena je kristalna i molekulska struktura četirima kompleksima. Cianamidni ligandi u molekulama kompleksa [{Cu(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] · CH_2Cl_2 i [{Ag(PPh_3)$_2$(4-Me_2Npcyd)}$_2$] premošćuju atome metala na μ-1,3 način koristeći pritom ciano- i amidne dušikove atome. Atomi metala u obje strukture posjeduju nepravilnu tetraedarsku geometriju u kojoj su dva fosforova atoma dva trifenilfosfina i dva dušikova atoma dva 4-Me_2N-pcyd liganada koordinirana na atome metala stvarajući na taj način koordinacijsku ljusku 'P_2N_2'. U slučaju bakrova dimernog kompleksa molekula posjeduje kristalografski centar inverzije, a u kompleksu srebra atomi metala nisu ekvivalentni. Za razliku od spomenutih spojeva kompleksi [Ag(PPh_3)$_3$(4-Brpcyd)] i [Ag(PPh_3)$_3$(4-MeOpcyd)] izgrađeni su od odvojenih monomernih molekula u kojima svaki srebrov atom poprima također nepravilnu tetraedarsku geometriju u kojoj je atom metala okružen s tri trifenilfosfinska fosforova atoma i terminalnim dušikovim atomom fenilcianamidnog liganda.