NEW COPPER(I) ISOCYANIDE COMPLEXES CONTAINING OTHER DONOR LIGANDS

J. BAILEY and M. J. MAYS

University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)

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SUMMARY

The preparation and physical properties of some new copper(I) isocyanide complexes containing other neutral donor ligands such as Ph_3P, pyridine (Py), 1,10-phenanthroline (Phen), bipyridine (Bipy), or 1,2-bis(diphenylphosphino)ethane (Diphos) are described. Possible structures for these new complexes, in the solid state and in solution, are discussed.

INTRODUCTION

Copper(I) isocyanide complexes which have been previously reported, have all been of the type $(RNC)_nCuX$, where X is halogen[2–5], CN[2], ClO_4[6], $C\equiv CPh$[2], C_5H_5[7], indenyl[7] or Acac[8] (Acac = acetylacetonate). The number of isocyanide ligands present in these complexes depends on the nature of X but, for a given X, two or more complexes with different values of n can often be synthesised.

In contrast to this wide range of known $(RNC)_nCuX$ complexes, there has been no report of the preparation of copper(I) complexes containing isocyanide together with other uncharged 2-electron donor ligands. This is despite the fact that such mixed ligand complexes have been postulated as intermediates in the copper catalysed reactions of isocyanides with alcohols[7]. In this paper, we report a series of such mixed ligand complexes containing isocyanide together with either phosphorus or nitrogen donor ligands. We also report some new complexes of the type $(RNC)_n$-CuX (X = halogen) which we have prepared in the course of our studies on the mixed complexes.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin–Elmer 257 Grating spectrometer using Nujol mulls between caesium bromide plates. Conductivity measurements were made using 10^{-3} M solutions in nitromethane with a Phillips GM 4249 bridge.

Molecular weights were determined osmometrically by the Alfred Bernhardt Mikroanalytisches Laboratorium and analyses were performed by the microanalytical department at Cambridge. Analytical data and some physical properties of the new complexes prepared are reported in Table 1.

TABLE 1

Compound	M.p. (°C)	Analysis found (calcd.) (%)				Mol. wt. found (calcd.)	$\nu(N{\equiv}C)$ (cm^{-1})	Λ (cm$^2 \cdot \Omega^{-1} \cdot$ mole)
		C	H	N	P			
(I) (p-MeOC$_6$H$_4$NC)CuCl	188–190	41.45 (41.36)	3.10 (3.04)	6.27 (6.04)		229[a] (232)	2155s(br)	[e]
(II) (p-MeOC$_6$H$_4$NC)CuBr	190–193	35.18 (34.72)	2.67 (2.55)	5.61 (5.07)		279[a] (276)	2173s(br)	[e]
(III) (p-MeOC$_6$H$_4$NC)CuI	148–150	29.91 (29.68)	2.17 (2.18)	4.09 (4.33)			2158s(br)	[e]
(IV) (p-MeOC$_6$H$_4$NC)$_2$CuCl	139–142	52.80 (52.59)	3.51 (3.86)	7.68 (7.67)		367[b] (365)	2141s(br) 2163(sh)	5.5
(V) (p-MeOC$_6$H$_4$NC)$_2$CuBr	129–131	46.55 (46.88)	3.40 (3.47)	6.70 (6.87)		408[b] (409)	2143s(br) 2161(sh)	7.5
(VI) (p-MeOC$_6$H$_4$NC)CuCl(Py)	131–137	50.54 (50.14)	3.77 (3.89)	8.71 (9.00)		309[b] (311)	2098vw 2133s(br)	3.2
(VII) (p-MeOC$_6$H$_4$NC)CuCl(PPh$_3$)	192–195	63.64 (63.15)	4.75 (4.49)	3.06 (2.83)			2094vw 2130s	[e]
(VIII) (p-MeOC$_6$H$_4$NC)CuBr(PPh$_3$)	201–205	57.53 (57.93)	4.19 (4.12)	2.51 (2.60)		528[b] (538)	2096vw 2133s	[o]
(IX) (p-MeOC$_6$H$_4$NC)CuBr(AsPh$_3$)	175–177	53.27 (53.56)	3.94 (3.81)	2.17 (2.40)			2099vw 2138s	2.8
(X) (C$_2$H$_5$NC)CuCl(PPh$_3$)	191–195	60.70 (60.56)	4.77 (4.84)	2.98 (3.36)			2168s 2184(sh)	[e]
(XI) (p-MeOC$_6$H$_4$NC)CuCl(Phen)	202–205	58.33 (58.24)	3.78 (3.67)	10.13 (10.19)			2127(br)	34.2
(XII) (p-MeOC$_6$H$_4$NC)CuBr(Phen)	206–211	51.91 (52.56)	3.41 (3.31)	9.41 (9.20)			2131(br)	31.6
(XIII) (p-MeOC$_6$H$_4$NC)CuBr(Diphos)	230–235	60.27 (60.48)	4.69 (4.63)	2.09 (2.08)		668[b] (674)	2138s	33.1
(XIV) [(p-MeOC$_6$H$_4$NC)Cu(PPh$_3$)Phen]PF$_6$	255–260 (decomp)	58.23 (58.19)	4.01 (3.86)	5.63 (5.36)	8.04 (7.90)	408[c] (7.84)	2161s 2166(sh)	97.5
(XV) [(C$_2$H$_5$NC)Cu(PPh$_3$)$_3$]PF$_6$	161–165	65.13 (65.14)	4.88 (4.80)	1.20 (1.33)	12.00 (11.80)	528[b] (1050)	2193m	83.8

(XVI) [(p-MeOC₆H₄NC)₂Cu(PPh₃)₂]PF₆	93–95	62.39 (62.47)	4.92 (4.44)	2.76 (2.80)	9.21 (9.31)		2156s 2168(sh)	77.5
(XVII) [(p-MeOC₆H₄NC)₂Cu(Diphos)]PF₆	176–179	58.16 (57.75)	4.60 (4.39)	3.13 (3.21)		864[b] (872)	2152s 2162(sh)	83.2
(XVIII) [(p-MeOC₆H₄NC)₂Cu(Bipy)]PF₆	131–138	49.71 (49.48)	3.45 (3.52)	9.01 (8.88)		638[b] 333[c] (631)	2142s 2166(sh)	87.0
(XIX) [(p-MeOC₆H₄NC)₄Cu]PF₆	183–184	51.57 (51.84)	3.60 (3.81)	7.37 (7.56)			2144(sh) 2169s	102.8

[a] Dimethylformamide. [b] Chloroform. [c] Acetone. [d] Nitromethane. [e] Insufficiently soluble.

Chloro(p-methoxyphenyl isocyanide)copper(I)

A suspension of cuprous chloride (1.38 g, 14.0 mmol) and *p*-methoxyphenyl isocyanide (1.86 g, 14.0 mmole) in $CHCl_3$ (150 ml) was stirred overnight at room temperature. The white solid product was filtered off and recrystallised from $CHCl_3$. Further product was obtained by the addition of light petroleum to the filtrate. Yield 85%.

The corresponding bromo complex was similarly prepared.

Iodo(p-methoxyphenyl isocyanide)copper(I)

A suspension of cuprous iodide (0.2 g, 1.1 mmol) in water (10 ml) was treated with a solution of *p*-methoxyphenyl isocyanide (0.14 g, 1.1 mmol) in absolute alcohol (5 ml). The mixture was stirred overnight and the white solid product was filtered off and recrystallised from $CHCl_3$. Yield 40%.

Chlorobis(p-methoxyphenyl isocyanide)copper(I)

A solution of $CuCl_2$ (1.0 g, 7.5 mmol) in water (10 ml) was treated with a solution of *p*-methoxyphenyl isocyanide (3.0 g, 22.5 mmol) in absolute alcohol (25 ml). After refluxing for 1 h, the white solid produced was filtered off and recrystallised from $CHCl_3$. Yield 72%.

The bromo complex was similarly prepared.

Chloro(p-methoxyphenyl isocyanide)pyridinecopper(I)

A solution of $(p\text{-MeOC}_6\text{H}_4\text{NC})\text{CuCl}$ (0.2 g, 0.85 mmol) in DMF (5 ml) was treated with a 3-fold excess of pyridine. Light petroleum was added to effect precipitation. Yield 95%.

Chloro(p-methoxyphenyl isocyanide)(1,10-phenanthroline)copper(I)

To a solution of $(p\text{-MeOC}_6\text{H}_4\text{NC})\text{CuCl}$ (0.2 g, 0.86 mmol) in DMF (5 ml) cooled to $0°$ was added, dropwise, 1,10-phenanthroline hydrate (0.17 g, 0.86 mmol) in $CHCl_3$ (5 ml). The solution was stirred while being allowed to warm to room temperature and was then filtered through a No. 4 sinter. Light petroleum was added to the filtrate to effect precipitation and the yellow solid so obtained was recrystallised from $CHCl_3$. Yield ca. 90%.

The bromo complexes with Phen and Diphos were similarly prepared.

(p-Methoxyphenyl isocyanide)(triphenylphosphine)(1,10-phenanthroline)copper(I)-hexafluorophosphate

A suspension of $p\text{-MeOC}_6\text{H}_4\text{NC(Phen)CuCl}$ (0.17 g, 0.41 mmol) in acetone (10 ml) was treated with $AgPF_6$ (0.11 g, 0.42 mmol). After shaking vigorously for 2 h, the precipitated AgCl was centrifuged off and Ph_3P (0.11 g, 0.41 mmol) was added to the supernatant liquid. After shaking this mixture for a further 1 h, light petroleum was added to effect precipitation. The yellow solid produced was recrystallised from acetone. Yield 73%.

Chloro(p-methoxyphenyl isocyanide)(triphenylphosphine)copper(I)

(*a*). To a suspension of $(p\text{-MeOC}_6\text{H}_4\text{NC})\text{CuCl}$ (0.25 g, 1.1 mmol) in $CHCl_3$ (20 ml) was added Ph_3P (0.29 g, 1.1 mmol) in $CHCl_3$ (5 ml). After being stirred over-

night, light petroleum was added to the colourless solution to effect precipitation and the white solid produced was recrystallised from CHCl$_3$. Yield 82%.

The bromo complexes with Ph$_3$P and Ph$_3$As were similarly prepared.

(b). To a solution of Ph$_3$PCuCl (0.76 g, 2.1 mmol) in CHCl$_3$ (25 ml) was added p-MeOC$_6$H$_4$NC (0.28 g, 2.1 mmol). After stirring the solution for 1 h light petroleum was added to effect precipitation and the product was recrystallised as above.

Bis(p-methoxyphenyl isocyanide)bis(triphenylphosphine)copper(I) hexafluorophosphate

To a suspension of (p-MeOC$_6$H$_4$NC)$_2$CuCl (0.2 g, 0.55 mmol) in acetone (10 ml) was added AgPF$_6$ (0.14 g, 0.55 mmol). This mixture was stirred for 1 h after which the precipitated AgCl was centrifuged off. Ph$_3$P (0.32 g, 1.2 mmol) was added to the supernatant liquid and, after shaking for a further 1 h, the solvent was evaporated off. Diethylether (100 ml) was added to the oily residue and the mixture stirred for several hours. The resulting white solid was recrystallised from acetone. Yield 65%. The corresponding complex with Diphos was similarly prepared, using 0.6 mmol of Diphos in place of the Ph$_3$P. Yield 71%.

Bis(p-methoxyphenyl isocyanide)(2,2'-bipyridine)copper(I) hexafluorophosphate

A suspension of (p-MeOC$_6$H$_4$NC)$_2$CuBr (0.2 g, 0.48 mmol) in acetone (10 ml) was treated with AgPF$_6$ (0.12 g, 0.48 mmol). After stirring for 3 h the precipitated AgBr was centrifuged off and 2,2'-bipyridine (0.08 g, 0.49 mmol) was added to the colourless supernatant liquid. Light petroleum was added to effect precipitation and the resulting yellow solid was recrystallised from acetone. Yield 93%.

Chloro(ethyl isocyanide)(triphenylphosphine)copper(I)

A suspension of Ph$_3$PCuCl (0.92 g, 2.5 mmol) in CHCl$_3$ (15 ml) was stirred for several hours with EtNC (0.14 g, 2.5 mmole). Light petroleum was added to the colourless solution to effect precipitation and the white solid produced was recrystallised from CHCl$_3$. Yield 90%.

(Ethyl isocyanide)tris(triphenylphosphine)copper(I) hexafluorophosphate

To a suspension of (EtNC)(Ph$_3$P)CuCl (0.2 g, 0.48 mmol) in acetone (10 ml) was added AgPF$_6$ (0.12 g, 0.48 mmol). After shaking for 1 h the precipitated AgCl was filtered off and Ph$_3$P (0.25 g, 0.96 mmol) was added to the supernatant liquid. Addition of light petroleum to effect precipitation was followed by recrystallisation from acetone. Yield 89%.

Tetrakis(p-methoxyphenyl isocyanide)copper(I) hexafluorophosphate

A suspension of (p-MeOC$_6$H$_4$NC)$_2$CuBr (0.15 g, 0.37 mmol) and AgPF$_6$ (0.09 g, 0.37 mmol) in acetone (10 ml) was stirred for several hours. The precipitated AgBr was centrifuged off and p-MeOC$_6$H$_4$NC (0.10 g, 0.75 mmol) was added to the supernatant liquid. Light petroleum was added to effect precipitation and the product recrystallised from CHCl$_3$.

RESULTS AND DISCUSSION

The new complexes reported in this paper are all crystalline materials which

are air-stable both in the solid state and in solution. All are soluble in chloroform to some extent, the complexes RNCCuX being the least soluble and the complexes $[(RNC)_2CuL_2]PF_6$ the most soluble. The mixed ligand complexes are apparently stable with respect to disproportionation, since their solid state IR spectra are unchanged after repeated recrystallisation from $CHCl_3$.

Copper may be 2-, 3-, or 4-coordinate in Cu^I complexes[9,10] and this range of possibilities means that it is rather difficult, in the absence of X-ray data, to assign solid-state structures to most of the complexes which we have prepared. An additional complication is that, in solution, related organophosphine complexes of Cu^I have been shown to undergo ligand dissociation[11]. Thus the dimeric complex: $L_2Cu\overset{Cl}{\underset{Cl}{\diagdown\diagup}}CuL_2$ [L = tri-p-tolylphosphine] dissociates above $-100°$ to give the complex L_2-$Cu\overset{Cl}{\underset{Cl}{\diagdown\diagup}}CuL$, while significant concentrations of the species L_3CuCl and monomeric L_2CuCl are also present in solution. However, provided these complicating factors are borne in mind, it is possible, on the basis of stoichiometries, solid-state IR spectra, and molecular weight and conductivity measurements in solution, to assign probable structures, both in the solid state and in solution, to most of the complexes we have prepared. In the following discussion, complexes which appear from the available data to be structurally analogous are considered in groups.

(p-MeOC$_6$H$_4$NC)CuX (X = Cl, Br or I)

Although R_3MCuX (M = As or P; X = Cl, Br or I) complexes are tetrameric in the solid state[12,13,14] with tetrahedrally coordinated copper atoms, it seems more probable that the corresponding isocyanide complexes reported here are 2-coordinate. The evidence for this is that the solid-state IR spectra of the copper–isocyanide complexes (4000–400 cm^{-1}) are virtually identical [aside from the position of the one $v(N\equiv C)$ band] with those of the corresponding gold complexes which are almost certainly 2-coordinate[15]. In contrast, the IR spectra of $[Ph_3PCuX]_4$ complexes in this region are quite different from those for the 2-coordinate Ph_3PAuX species. However, $(CH_3NC)CuI$, the only copper–isocyanide complex which has been the subject of an X-ray study[16], does contain 4-coordinate copper and an analogous structure for the p-MeOC$_6$H$_4$NC complexes cannot be ruled out, although the presence of only one infrared band due to $v(N\equiv C)$ suggests that it is unlikely.

In dimethylformamide solution the measured molecular weight of p-MeOC$_6$-H$_4$NCCuX (X = Cl and Br) is exactly that required for a monomeric formulation. This observation could be accounted for by the presence of a dimeric species with complete dissociation of one p-MeOC$_6$H$_4$NC ligand but, since this would leave one copper atom without any coordinated isocyanide ligands, it seems more probable that the complex is indeed monomeric in solution.

(p-MeOC$_6$H$_4$NC)$_2$CuX (X = Cl or Br) and (p-MeOC$_6$H$_4$NC)LCuX (X = Cl, L = Py, Ph$_3$P; X = Br, L = Ph$_3$P, Ph$_3$As)

In the solid state these complexes are probably dimeric and halogen-bridged. Such a halogen-bridged structure has been established by X-ray analysis for the complex $(Ph_3P)_3Cu_2Cl_2$[10]. If indeed the complexes are halogen-bridged in the solid state, then for (p-MeOC$_6$H$_4$NC)LCuX the possibility of *cis–trans* isomerism exists.

Although the observation of two infrared active bands due to $v(N\equiv C)$ is as required for the *cis*-isomer, it has been previously shown[17,18] that the number of such bands is not a reliable guide to the symmetry of isocyanide complexes, particularly in the solid state.

In chloroform solution, apparent molecular weights for $(p\text{-MeOC}_6\text{H}_4\text{NC})_2$-CuX (X = Cl or Br) and for $(p\text{-MeOC}_6\text{H}_4\text{NC})\text{CuBr(PPh}_3)$ are in each case very close to those required for monomeric formulations. This is in contrast to the apparent molecular weight in this solvent for, *e.g.* $(\text{Ph}_3\text{P})_2\text{CuCl}$, which is very much lower (*ca.* 276) than that required for a monomeric formulation (623)[14]. In this latter case, ligand dissociation and the existence of several different species in solution has been demonstrated by ^{31}P NMR studies[11], but for the isocyanide complexes the molecular weight measurements suggest that these various equilibria are less important. It is not, however, possible to say whether the complexes are genuinely 3-coordinate or whether the coordination number is raised by coordination of solvent molecules.

p-MeOC$_6$H$_4$NCCu(X)L(X = Cl; L = Phen: X = Br; L = Phen or Diphos)

These complexes most probably contain 4-coordinate copper atoms in the solid state. Lower coordination numbers could only be achieved if either the complexes were ionic or if the bidentate ligands were coordinated through only one donor atom. Neither possibility seems very likely. In nitromethane solution conductivity data indicate that complexes of this type are partially ionised.

[(p-MeOC$_6$H$_4$NC)Cu(PPh$_3$)Phen]PF$_6$, [(EtNC)Cu(PPh$_3$)$_3$]PF$_6$, [(p-MeOC$_6$H$_4$-NC)$_2$CuL$_2$]PF$_6$ (L = Ph$_3$P, p-MeOC$_6$H$_4$NC; L$_2$ = Diphos, Bipy)

Again these complexes probably contain 4-coordinate copper atoms in the solid state. In this solvent, molecular weight measurements indicate that the EtNC complex is ionised while the complexes with $p\text{-MeOC}_6\text{H}_4\text{NC}$ are present as ion pairs. In the more polar solvent, acetone, $[(p\text{-MeOC}_6\text{H}_4\text{NC})_2\text{Cu(Bipy)}]\text{PF}_6$ is also fully ionised as are presumably the other complexes of this type. Conductivity data indicate that all the complexes are also extensively ionised in nitromethane solution.

The IR spectrum of $[(p\text{-MeOC}_6\text{H}_4\text{NC})_4\text{Cu}]\text{PF}_6$ exhibits two bands in the $v(N\equiv C)$ region rather than the one band expected for a molecule of T_d symmetry. One possible explanation of this observation is that the CNC grouping in the isocyanide ligands is bent at the nitrogen atom[17].

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