Structurally Diversified Neutral Copper(I) Isocyanide Complexes: Mono- and Bi-nuclear Complexes from the Reaction of Copper(I) Halides with *p*-Tolyl Isocyanide†

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The reaction of copper(I) iodide with *p*-tolyl isocyanide (RNC) led to different compounds depending on the stoicheiometric ratio and the presence of ancillary ligands. A large excess of RNC in the presence of $NaBPh_4$ yields the complex $[Cu(RNC)_4]BPh_4$, (**2**) [ν(C=N) (Nujol) 2 147 cm^{-1}]. Using a lower RNC:Cu ratio, the neutral complex $[CuI(RNC)_3]$, (**3**) [ν(C=N) (Nujol) broad band centred at 2 135 cm^{-1}] was isolated. In the presence of 2,2'-bipyridine (bipy) the mononuclear complex [CuI(bipy)(RNC)], (**4**) [ν(C=N) (Nujol) 2 124 cm^{-1}], was isolated, while the use of a monodentate sterically demanding ligand, 1-benzyl-2-phenylbenzimidazole (bpbzim), afforded the asymmetric binuclear complex $[Cu_2(\mu\text{-}I)_2(bpbzim)_2(RNC)_2]$, (**5**) [$\nu$(C=N) (Nujol) 2 127 cm^{-1}] [Cu $\cdots$ Cu 3.362(2), Cu–I 2.697(2) and 2.801(2) Å]. The reaction of CuCl in tetrahydrofuran with RNC led to the analogous binuclear complex $[Cu_2(\mu\text{-}Cl)_2(RNC)_4]$, (**6**) [$\nu$(C=N) (Nujol) 2 137 and 2 159 cm^{-1}] [Cu $\cdots$ Cu 3.234(1) Å], having like (**5**) a slightly asymmetric bridged structure [Cu–Cl 2.382(1) and 2.419(1) Å]. Crystallographic details: complex (**3**), space group $P2_1/c$ (monoclinic), a = 11.022(3), b = 11.288(2), c = 20.363(5) Å, β = 102.52(2)°, Z = 4, R 0.045 (R' = 0.050) for 1 831 observed reflections; (**4**), space group $P\bar{1}$ (triclinic), a = 11.226(3), b = 11.935(3), c = 9.011(2) Å, α = 110.08(3), β = 101.07(3), γ = 80.22(3)°, Z = 2, R 0.041 (R' = 0.048) for 2 291 observed reflections; (**5**), space group $P\bar{1}$ (triclinic), a = 12.526(2), b = 10.257(2), c = 11.144(3) Å, α = 109.16(2), β = 114.92(2), γ = 81.94(2)°. Z = 1, R 0.041 (R' = 0.038) for 2 131 observed reflections; (**6**), space group $P2_1/n$ (monoclinic), a = 21.041(4), b = 6.325(1), c = 13.184(2) Å, β = 104.28(1)°, Z = 2, R 0.043 (R' = 0.050) for 2 750 observed reflections.

Copper(I) isocyanide adducts formed from the reaction of Cu_2O and isocyanides have an unusual versatility in catalysing a variety of organic reactions:[1–6] (*i*) the dimerization of α,β-unsaturated carbonyl and nitrile compounds;[1] (*ii*) reaction of cyclopentadiene with ketones leading to fulvenes;[2] (*iii*) cycloaddition reactions of isocyanides to C=C leading to Δ^1-pyrroline and Δ^2-oxazoline;[4] (*iv*) formamidation of amines, alcohols, and amides by vinyl isocyanide;[4] (*v*) cyclopropanation of activated olefins using α-halogeno ketones, nitriles, *etc.*;[5] and (*vi*) Michael-type additions.[3]

A common denominator of the reactions listed above is, very probably, the intermediate formation of Cu–C and Cu=C bonds[1–6] from a rather unusual reaction like that starting from a metal oxide. We are presently focusing our attention on the structural variety of complexes formed from the reaction of copper(I) complexes with isocyanides and the reactivity of the Cu–CNR functionality.[7] The reaction between copper(I) halides and isocyanides has been described,[8] but with little or no information on the structure and on the structural variety of the products. The objective of this report is to describe structurally diversified isocyanide derivatives derived from the reaction of copper(I) iodide and chloride with *p*-tolyl isocyanide under slightly different conditions. In previous papers we reported the structure of some copper(I) isocyanide derivatives[9] containing different types of ancillary ligands.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The compounds CuCl,[10] CuI,[10] *p*-tolyl isocyanide,[11] and 1-benzyl-2-phenylbenzimidazole[12] were prepared by published procedures. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Synthesis.—Tetrakis(p-*tolyl isocyanide*)*copper*(I) *tetraphenylborate*, $[Cu(RNC)_4]BPh_4$ (**2**; R = $p\text{-}MeC_6H_4$). To a tetrahydrofuran (thf) (20 cm^3) suspension of CuI (0.3 g, 1.58 mmol) was added neat *p*-tolyl isocyanide (0.8 cm^3, 6.56 mmol). A white precipitate suddenly formed. By the addition of solid $NaBPh_4$ (0.57 g, 1.67 mmol) a greenish solution formed. The i.r. spectrum (solution) showed three bands at 2 160, 2 140, and 2 120 cm^{-1}. The solution is very air-sensitive. It was partially evaporated then Et_2O (50 cm^3) was added. A microcrystalline white solid was obtained which was recrystallized from thf–Et_2O (Found: C, 78.50; H, 6.05; N, 6.70. Calc. for $C_{56}H_{48}BCuN_4$: C, 79.00; H, 5.65; N, 6.60%); ν(CN) (Nujol) 2 147br cm^{-1}.

Iodotris(p-*tolyl isocyanide*)*copper*(I), $[CuI(RNC)_3]$ (**3**; R = $p\text{-}MeC_6H_4$). *p*-Tolyl isocyanide (1.0 cm^3, 8.20 mmol) was added to a thf (20 cm^3) suspension of CuI (0.5 g, 2.63 mmol). A

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

greenish yellow solution formed. The solution was concentrated to 10 cm^3, then Et_2O (30 cm^3) was added. A white solid crystallized (*ca.* 48%). Colourless transparent needle-like crystals suitable for *X*-ray analysis were obtained from the filtrate after a few days (Found: C, 53.00; H, 3.85; N, 7.75. Calc. for $C_{24}H_{21}CuIN_3$: C, 53.20; H, 3.90; N, 7.75%); ν(CN) (Nujol) band centred at 2 135 cm^{-1} (2 130 cm^{-1} in thf solution).

2,2′-Bipyridineiodo(p-*tolyl isocyanide*)*copper*(I), [CuI(bipy)(RNC)] (**4**; R = *p*-MeC_6H_4). 2,2′-Bipyridine (0.43 g, 2.75 mmol) was added to a thf (20 cm^3) suspension of CuI (0.50 g, 2.62 mmol). A reddish brown precipitate formed. By the addition of *p*-tolyl isocyanide (0.34 cm^3, 2.79 mmol) the suspension became yellow-orange and was kept on stirring for 4 h. The yellow solid (*ca.* 80%) was filtered off, and the mother-liquor allowed to stand. Orange prismatic crystals were obtained after a few days (Found: C, 46.75; H, 3.70; N, 8.75. Calc. for $C_{18}H_{15}CuIN_3$: C, 46.60; H, 3.25; N, 9.05%); ν(CN) (Nujol) 2 124 cm^{-1}.

Bis(1-*benzyl-2-phenylbenzimidazole*)*-di-μ-iodo-bis*(p-*tolyl isocyanide*)*dicopper*(I), $[Cu_2(\mu\text{-}I)_2(bpbzim)_2(RNC)_2]$ (**5**; R = *p*-MeC_6H_4). 1-Benzyl-2-phenylbenzimidazole (1.57 g, 5.51 mmol) was added to a thf suspension (20 cm^3) of CuI (0.50 g, 2.63 mmol) and stirred for 3 h. The CuI dissolved and suddenly a white powder formed. Then *p*-tolyl isocyanide (0.34 cm^3, 2.79 mmol) was added and the suspension stirred for several hours. The white powder was removed by filtration and the solution on standing for several days gave colourless crystals (*ca.* 50%). ν(CN) (Nujol): broad band centred at 2 127 cm^{-1} (Found: C, 57.50; H, 3.95; N, 7.05. Calc. for $C_{56}H_{46}Cu_2I_2N_6$: C, 56.80; H, 3.90; N, 7.10%).

Di-μ-chloro-tetrakis(p-*tolyl isocyanide*)*dicopper*(I), $[Cu_2(\mu\text{-}Cl)_2(RNC)_4]$ (**6**; R = *p*-MeC_6H_4). The addition of *p*-tolyl isocyanide (1.75 cm^3, 14.35 mmol) to a thf (30 cm^3) suspension of CuCl (0.726 g, 7.33 mmol) gave a light yellow solid (*ca.* 73%) (Found: C, 57.55; H, 4.60; N, 10.80. Calc. for $C_{32}H_{28}Cl_2Cu_2N_4$: C, 57.65; H, 4.20; Cl, 10.65%); ν(CN) (Nujol) 2 137 and 2 159 cm^{-1}. The solid was removed by filtration, and the solution gave by addition of benzene (5 cm^3) and on standing light yellow crystals suitable for *X*-ray analysis. Such crystals contain benzene of crystallization.

X-*Ray Crystallography for Complexes* (**3**)—(**6**).—Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using SHELX 76.[13] The crystals selected for study were sealed in glass capillaries under nitrogen and mounted in a random orientation on a single-crystal four-circle diffractometer. Crystal data and details of the data collection and structure refinement parameters are given in Table 1. The reduced cells quoted were obtained with use of TRACER.[14] Intensity data were collected at room temperature

Table 1. Experimental data for the *X*-ray diffraction studies

Complex	(**3**)	(**4**)	(**5**)	(**6**)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Cell parameters[a]				
a/Å	11.022(3)	11.226(3)	12.526(2)	21.041(4)
b/Å	11.288(2)	11.935(3)	10.257(2)	6.325(1)
c/Å	20.363(5)	9.011(2)	11.144(3)	13.184(2)
α/°	90	110.08(3)	109.16(2)	90
β/°	102.52(2)	101.07(3)	114.92(2)	104.28(1)
γ/°	90	80.22(3)	81.94(2)	90
U/Å^3	2 473(1)	1 105.7(5)	1 226.5(5)	1 700.4(5)
Z	4	2	1	2
D/g cm^{-3}	1.455	1.393	1.603	1.455
M	541.9	463.8	1 183.9	744.7
Crystal dimensions, mm	0.22 × 0.24 × 0.62	0.29 × 0.40 × 0.58	0.13 × 0.13 × 0.43	0.32 × 0.36 × 0.50
μ/cm^{-1}	21.3	23.7	21.6	32.5
A[b]	1.48—1.52	1.72—2.09	1.23—1.23	2.12—2.21
Diffractometer	Philips PW 1100	Philips PW 1100	Philips PW 1100	Siemens AED
Diffraction geometry	Equatorial	Equatorial	Equatorial	Equatorial
Scan type	ω	ω	ω–2θ	θ–2θ
Scan speed	0.075° s^{-1}	0.075° s^{-1}	0.050° s^{-1}	3—12° min^{-1}
Scan width/°	1.50	1.50	1.00	*c*
Radiation	*d*	*d*	*d*	*e*
2θ range/°	6—52	6—48	6—48	6—140
Reflections measured	$\pm h \pm k\ l$	$\pm h \pm k\ l$	$\pm h \pm k\ l$	$\pm h\ k\ l$
Total data measured	8 290	3 434	3 727	3 226
Unique data	4 420	3 434	3 727	3 226
Unique observed data	1 831 [$I > 3\sigma(I)$]	2 291 [$I > 3\sigma(I)$]	2 131 [$I > 3\sigma(I)$]	2 750 [$I > 2\sigma(I)$]
Agreement between equiv. observed reflections	0.037			
No. of variables	262	208	298	208
Overdetermination ratio	7.0	11.0	7.2	13.2
Max. shift/error in last cycle	0.3	0.3	0.1	0.2
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.045	0.041	0.041	0.043
$R' = \Sigma w^{\frac{1}{2}}\lvert\Delta F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.050	0.048	0.038	0.050
Goodness of fit = $[\Sigma w\lvert\Delta F\rvert^2/(N_o - N_v)]^f$	0.90	0.73	1.10	0.80

[a] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25—30 carefully centred reflections chosen from diverse regions of reciprocal space. [b] A minimum and maximum absorption correction factor. [c] $(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]°$; $\Delta\theta = (\lambda\alpha_2 - \lambda\alpha_1)/\lambda$. [d] Graphite-monochromated Mo-K_α (λ = 0.7107 Å). [e] Nickel-filtered Cu-K_α (λ = 1.5418 Å). [f] N_o = Number of observations, N_v = number of variables.

Table 2. Fractional atomic co-ordinates (× 10^4) for complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I	2 371(1)	1 647(1)	1 112(0)	C(4B)	3 844(10)	8 535(9)	738(6)
Cu	1 080(1)	3 324(1)	336(1)	C(5B)	5 084(10)	8 465(10)	740(5)
N(1A)	−1 162(8)	3 641(7)	990(4)	C(6B)	5 605(10)	7 369(11)	684(7)
C(1A)	−343(10)	3 561(9)	714(6)	C(7B)	4 932(10)	6 352(9)	626(6)
C(2A)	−2 155(9)	3 774(9)	1 328(5)	C(8B)	5 881(12)	9 586(11)	828(7)
C(3A)	−3 178(11)	3 049(10)	1 157(6)	N(1C)	807(8)	1 976(8)	−992(5)
C(4A)	−4 133(11)	3 205(12)	1 500(6)	C(1C)	813(9)	2 549(10)	−539(7)
C(5A)	−4 042(10)	4 021(13)	1 996(6)	C(2C)	923(9)	1 173(10)	−1 507(5)
C(6A)	−2 999(11)	4 717(13)	2 162(6)	C(3C)	1 373(9)	1 596(10)	−2 051(6)
C(7A)	−2 037(10)	4 600(11)	1 829(6)	C(4C)	1 568(9)	787(10)	−2 546(5)
C(8A)	−5 112(14)	4 214(18)	2 342(8)	C(5C)	1 321(9)	−398(10)	−2 481(5)
N(1B)	2 939(8)	5 393(7)	527(4)	C(6C)	815(10)	−759(10)	−1 944(6)
C(1B)	2 232(11)	4 618(9)	439(6)	C(7C)	625(10)	2(11)	−1 455(6)
C(2B)	3 678(10)	6 434(8)	619(5)	C(8C)	1 628(12)	−1 279(12)	−2 987(7)
C(3B)	3 109(9)	7 514(10)	676(6)				

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I	−2 175(1)	−1 201(0)	1 712(1)	C(8)	1 111(10)	6 301(8)	2 046(13)
Cu	−2 459(1)	999(1)	3 650(1)	C(9)	−1 482(9)	632(8)	6 883(11)
N(1)	−1 209(6)	2 809(6)	3 040(8)	C(10)	−1 583(14)	625(11)	8 407(14)
N(2)	−2 466(6)	898(5)	5 891(7)	C(11)	−2 762(17)	921(12)	8 881(13)
N(3)	−4 304(5)	1 386(5)	3 836(7)	C(12)	−3 693(11)	1 220(8)	7 902(11)
C(1)	−1 664(7)	2 102(8)	3 289(9)	C(13)	−3 568(8)	1 198(6)	6 408(8)
C(2)	−641(7)	3 648(7)	2 763(8)	C(14)	−4 587(7)	1 463(6)	5 255(8)
C(3)	−1 087(9)	4 837(8)	3 254(13)	C(15)	−5 802(9)	1 753(7)	5 543(11)
C(4)	−518(9)	5 672(7)	3 002(11)	C(16)	−6 711(8)	1 974(10)	4 367(16)
C(5)	472(8)	5 359(7)	2 263(9)	C(17)	−6 406(9)	1 861(9)	2 921(13)
C(6)	895(7)	4 156(7)	1 719(10)	C(18)	−5 190(8)	1 597(8)	2 704(11)
C(7)	353(7)	3 398(6)	1 963(10)				

Table 4. Fractional atomic co-ordinates (× 10^4) for complex (**5**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I	3 766(1)	1 218(1)	839(1)	C(7)	6 923(7)	2 569(9)	2 774(9)
Cu	4 963(1)	1 134(1)	−816(1)	C(8)	6 826(6)	3 104(8)	1 772(8)
N(1A)	3 038(6)	1 140(7)	−3 640(7)	C(9)	7 440(7)	4 309(8)	2 073(9)
C(1A)	3 773(7)	1 122(8)	−2 595(9)	C(10)	5 996(6)	3 384(8)	−1 683(8)
C(2A)	2 123(7)	1 140(8)	−4 915(8)	C(11)	5 379(7)	4 464(9)	−2 199(9)
C(3A)	965(8)	1 084(9)	−5 083(9)	C(12)	4 955(7)	4 268(10)	−3 632(11)
C(4A)	86(7)	1 100(9)	−6 369(10)	C(13)	5 161(8)	3 059(11)	−4 507(9)
C(5A)	316(7)	1 105(8)	−7 468(9)	C(14)	5 763(7)	2 003(9)	−3 985(8)
C(6A)	1 467(7)	1 148(8)	−7 272(9)	C(15)	6 161(7)	2 161(9)	−2 585(9)
C(7A)	2 389(7)	1 162(9)	−5 979(9)	C(16)	7 629(7)	5 751(8)	705(8)
C(BA)	−705(8)	1 053(9)	−8 834(9)	C(17)	8 971(7)	5 805(8)	1 312(8)
N(1)	6 190(5)	2 656(6)	298(6)	C(18)	9 483(8)	7 102(8)	1 762(9)
C(2)	6 430(6)	3 541(8)	−184(8)	C(19)	10 711(9)	7 185(11)	2 225(9)
N(3)	7 181(5)	4 560(6)	838(6)	C(20)	11 396(8)	6 026(11)	2 280(9)
C(4)	8 162(8)	5 001(9)	3 448(9)	C(21)	10 876(8)	4 740(10)	1 803(9)
C(5)	8 252(8)	4 440(10)	4 443(9)	C(22)	9 656(8)	4 635(9)	1 306(9)
C(6)	7 636(7)	3 235(9)	4 120(9)				

using the profile measurement technique[15] for complex (**6**) and the 'three-point' technique for (**3**)—(**5**). The structure amplitudes were obtained after the usual Lorentz and polarization corrections. The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected for complex (**4**), so an absorption correction was made following ref. 16. No absorption corrections were applied for complexes (**3**), (**5**), and (**6**).

The structure solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was by full-matrix least squares minimizing the function $\Sigma w|\Delta F|^2$. The reflections were weighted according to $w = k/[\sigma^2(F_o) + |g|F_o^2]$. At convergence the values for k and g were 0.8479 and 0.002 53 respectively for complex (**3**), 0.6245 and 0.003 47 for (**4**), 1.0536 and 0.000 00 for (**5**), 1.0000 and 0.006 99 for (**6**). Scattering factors for neutral atoms were taken from ref. 17*a* for non-hydrogen atoms and ref. 18 for H. Anomalous scattering corrections were included in all structure-factor calculations.[17b] Among the low-angle reflections no

Table 5. Fractional atomic co-ordinates (× 10^4) for complex (**6**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	201.6(2)	−2 820.2(6)	638.7(3)
Cl	−367.0(3)	−3 572(1)	−1 154.3(4)
C(1A)	−372(1)	−1 398(4)	1 342(2)
N(1A)	−673(1)	−370(4)	1 767(2)
C(2A)	−1 036(1)	1 001(4)	2 242(2)
C(3A)	−1 186(2)	3 007(4)	1 843(2)
C(4A)	−1 545(1)	4 335(5)	2 331(2)
C(5A)	−1 742(1)	3 698(5)	3 213(2)
C(6A)	−1 590(2)	1 684(6)	3 583(2)
C(7A)	−1 232(2)	320(5)	3 121(2)
C(8A)	−2 121(2)	5 188(6)	3 748(2)
C(1B)	1 029(1)	−1 456(4)	737(2)
N(1B)	1 502(1)	−479(3)	876(2)
C(2B)	2 043(1)	892(4)	1 030(2)
C(3B)	2 649(1)	208(4)	1 618(2)
C(4B)	3 184(1)	1 547(5)	1 767(2)
C(5B)	3 112(1)	3 596(5)	1 337(2)
C(6B)	2 502(1)	4 218(5)	764(2)
C(7B)	1 956(1)	2 895(4)	602(2)
C(8B)	3 694(2)	5 051(6)	1 500(3)
C(1S)	−13(6)	3 596(20)	5 619(7)
C(2S)	323(6)	3 391(13)	5 017(12)
C(3S)	284(5)	4 704(24)	4 284(8)

Table 6. Selected bond distances (Å) and angles (°) for complex (**3**)

Cu–I	2.670(2)	C(1B)–N(1B)	1.16(1)
Cu–C(1A)	1.91(1)	C(1C)–N(1C)	1.13(2)
Cu–C(1B)	1.92(1)	N(1A)–C(2A)	1.42(1)
Cu–C(1C)	1.95(1)	N(1B)–C(2B)	1.42(1)
C(1A)–N(1A)	1.17(2)	N(1C)–C(2C)	1.41(1)
I–Cu–C(1C)	100.3(3)	C(1A)–N(1A)–C(2A)	178.4(10)
I–Cu–C(1B)	102.7(4)	Cu–C(1A)–N(1A)	174.1(10)
I–Cu–C(1A)	103.9(4)	C(1B)–N(1B)–C(2B)	173.1(10)
C(1B)–Cu–C(1C)	114.0(5)	Cu–C(1B)–N(1B)	177.4(10)
C(1A)–Cu–C(1C)	117.2(5)	C(1C)–N(1C)–C(2C)	172.6(11)
C(1A)–Cu–C(1B)	115.6(5)	Cu–C(1C)–N(1C)	168.5(10)

Table 7. Selected bond distances (Å) and angles (°) for complex (**4**)

Cu–I	2.613(1)	N(3)–C(18)	1.34(1)
Cu–N(2)	2.065(7)	C(10)–C(11)	1.42(2)
Cu–N(3)	2.070(6)	C(11)–C(12)	1.32(2)
Cu–C(1)	1.85(1)	C(12)–C(13)	1.37(1)
N(1)–C(1)	1.16(1)	C(13)–C(14)	1.46(1)
N(1)–C(2)	1.39(1)	C(14)–C(15)	1.40(1)
N(2)–C(9)	1.35(1)	C(15)–C(16)	1.39(2)
N(2)–C(13)	1.35(1)	C(16)–C(17)	1.37(2)
N(3)–C(14)	1.35(1)	C(17)–C(18)	1.38(1)
I–Cu–C(1)	115.9(3)	Cu–N(2)–C(13)	115.1(5)
I–Cu–N(3)	106.0(2)	Cu–N(2)–C(9)	126.2(6)
I–Cu–N(2)	107.2(2)	C(9)–N(2)–C(13)	118.7(7)
N(3)–Cu–C(1)	119.2(4)	Cu–N(3)–C(18)	125.5(6)
N(2)–Cu–C(1)	123.5(3)	Cu–N(3)–C(14)	114.8(5)
N(2)–Cu–N(3)	78.8(3)	C(14)–N(3)–C(18)	119.6(7)
C(1)–N(1)–C(2)	178.7(8)	Cu–C(1)–N(1)	177.4(8)

Table 8. Selected bond distances (Å) and angles (°) for complex (**5**)

Cu–I	2.801(2)	C(2)–C(10)	1.48(1)
Cu–I′	2.697(2)	N(3)–C(9)	1.38(1)
Cu–C(1A)	1.911(8)	N(3)–C(16)	1.49(1)
Cu–N(1)	2.033(6)	C(4)–C(5)	1.37(2)
N(1A)–C(1A)	1.15(1)	C(4)–C(9)	1.40(1)
N(1A)–C(2A)	1.40(1)	C(5)–C(6)	1.41(1)
N(1)–C(2)	1.32(1)	C(6)–C(7)	1.37(1)
N(1)–C(8)	1.387(9)	C(7)–C(8)	1.40(2)
C(2)–N(3)	1.366(8)	C(8)–C(9)	1.40(1)
Cu ··· Cu	3.362(2)		
Cu–I–Cu′	75.4(1)	C(1A)–N(1A)–C(2A)	178.6(9)
I–Cu–N(1)	106.1(2)	Cu–C(1A)–N(1A)	177.8(9)
I–Cu–C(1A)	105.9(3)	Cu–N(1)–C(8)	128.1(6)
I–Cu–I′	104.6(1)	Cu–N(1)–C(2)	125.9(5)
C(1A)–Cu–N(1)	121.3(3)	C(2)–N(1)–C(8)	105.5(7)
I′–Cu–N(1)	104.2(2)		
I′–Cu–C(1A)	113.4(3)		

Symmetry equivalent position: (′) $1 - x, \bar{y}, \bar{z}$.

Table 9. Selected bond distances (Å) and angles (°) for complex (**6**)

Cu–Cl	2.419(1)	C(1A)–N(1A)	1.146(4)
Cu–Cl′	2.382(1)	C(1B)–N(1B)	1.147(3)
Cu–C(1A)	1.918(3)	N(1A)–C(2A)	1.401(4)
Cu–C(1B)	1.918(2)	N(1B)–C(2B)	1.405(3)
Cu ··· Cu′	3.234(1)		
Cu–Cl–Cu′	84.7(1)	Cu–C(1A)–N(1A)	172.9(2)
C(1A)–Cu–C(1B)	115.2(1)	Cu–C(1B)–N(1B)	171.9(2)
Cl–Cu–Cu(1B)	112.1(1)	C(1A)–N(1A)–C(2A)	176.1(3)
Cl–Cu–C(1A)	110.2(1)	C(1B)–N(1B)–C(2B)	174.5(3)
Cl–Cu–Cl′	95.3(1)		

Symmetry equivalent position: (′) $-x, -1 - y, z$.

correction for the effects of secondary extinction was deemed necessary.

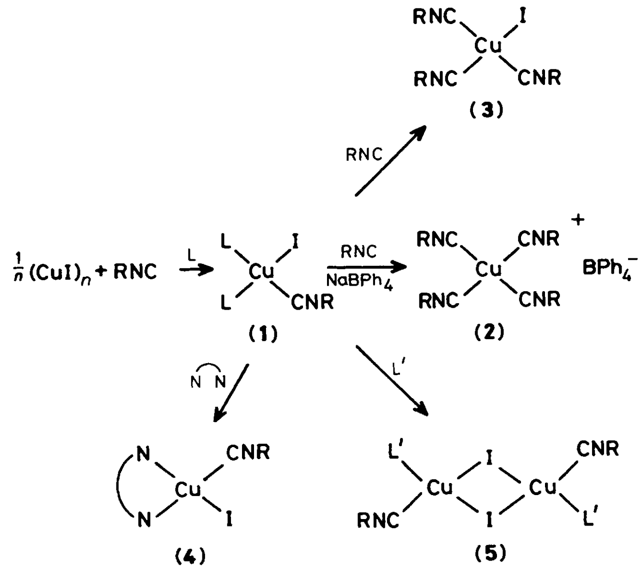
The hydrogen atoms were located from ΔF syntheses and introduced in calculations as fixed contributors prior to the final refinement (U_{iso} = 0.10 Å). The final difference maps showed no unusual feature, with no significant peak above the general background of about 0.3 e $Å^{-3}$ except for a few peaks in the proximity of iodine atoms. For complex (**6**) the *X*-ray analysis revealed the presence of a benzene molecule of crystallization in the molar ratio complex : benzene of 1 : 1. This molecule lies on a centre of symmetry and shows high thermal motion (or disorder) as normally found in situations like this.

Final atomic co-ordinates are listed in Tables 2—5, selected bond distances and angles in Tables 6—9. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

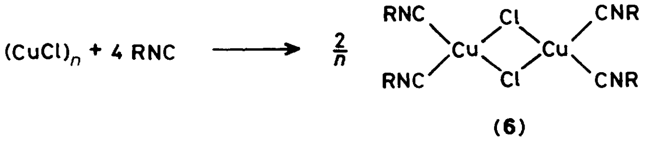
Results and Discussion

The reaction of copper(I) iodide with *p*-tolyl isocyanide in thf afforded different compounds depending on the Cu : RNC (R = *p*-MeC_6H_4) molar ratio and the presence of mono- or bi-dentate ligands, as in Scheme 1. Analogous reactions carried out treating $(CuCl)_n$ with *p*-tolyl isocyanide in thf produced complex (**6**) (Scheme 2).

The choice of the complexes reported is based on the fact that they have been structurally characterized and they represent



Scheme 1. R = p-MeC$_6$H$_4$, $\overset{\frown}{\text{NN}}$ = bipy, L′ = 1-benzyl-2-phenylbenzimidazole, L = thf



Scheme 2.

diversified structural models for copper(I) isocyanide derivatives. Reaction of carbon monoxide or isocyanide ligands with copper(I) halides produces, very probably, and as reported for similar reactions, the solvated 1 : 1 adduct (**1**), which is the likely precursor of the species in Scheme 1.[9b,19–21] The complete substitution of solvent molecules by RNC afforded (**3**), while in the presence of an ionizing agent the excess of RNC led to the tetrakis(isocyanide) derivative (**2**). The addition of RNC to CuI in the presence of 2,2′-bipyridine led to the mononuclear complex (**4**), while in the presence of a monodentate crowded ligand like 1-benzyl-2-phenylbenzimidazole[12] the binuclear halogen-bridged species (**5**) was isolated. The nature of the halogen has a significant influence on the nature of the isolable compound. The reaction of RNC with CuCl led to the binuclear complex (**6**) rather than to (**2**) or (**3**), independently of the Cu:RNC molar ratio.

Analytical and spectroscopic data (i.r.) do not give sufficient insight into the structure of complexes (**2**)—(**6**). The i.r. spectra show very broad bands in the solid state, on the other hand, in solution they are different and free isocyanide (2 120 cm^{-1}) is always present. This is expected from the kinetic lability of copper(I); such lability is, on the the other hand, interesting for potential catalytic activity. Several CuX·RNC adducts have been analytically characterized,[8d] without any structural assignment because of the inconclusive spectroscopic data. Common features of the complexes reported are the four-co-ordination of copper(I) and the terminal bonding mode of the isocyanide group. The C≡N stretching vibrations higher than in the free p-tolyl isocyanide are due to an electrophilic activation of the carbon, and this for some of the most interesting copper(I) isocyanide-catalysed reactions, *i.e.* those involving formation of a metal–carbene intermediate.[8a] The Cu–CNR functionality has quite similar structural features for all complexes reported and for those in the literature.[8e,8f,9] Table 10 gives a complete list of the copper(I) isocyanide complexes with their structural parameters.

Table 10. Comparison of bond distances (Å) and angles (°) for copper(I) isocyanide complexes

Complex	Cu–C	C–NR	Cu–C–N	c.n.	Ref.
[CuI(RNC)$_3$], (**3**)	1.93(1)	1.15(2)	173(2)	4	This work
[CuI(bipy)(RNC)], (**4**)	1.85(1)	1.16(1)	177.4(8)	4	This work
[Cu$_2$(μ-I)$_2$(bpzim)$_2$-(RNC)$_2$], (**5**)	1.911(8)	1.15(1)	177.8(9)	4	This work
[Cu$_2$(μ-Cl)$_2$(RNC)$_4$], (**6**)	1.918(3)	1.147(4)	172.4(2)	4	This work
[{CuI(CNMe)}$_n$]	1.81	1.24	n.r.	4	8*e*
[Cu(CNMe)$_4$]$^+$	1.97(2)	1.11(3)	176(2)	4	8*f*
[Cu(tmen)(C$_6$H$_{11}$NC)$_2$]$^+$	1.897(8)	1.14(1)	172.6(7)	4	9*a*
[CuI(H$_2$ben)(RNC)]	1.858(9)	1.17(1)	167.9(7)	4	9*b*
[Cu$_2$(μ-OPh)$_2$(RNC)]	1.906(7)	1.146(9)	172.7(7)	4	9*c*
[Cu(2,6-Bu$^t_2$C$_6$H$_3$O)-(RNC)$_2$]	1.891(4)	1.157(5)	172.8(4)	3	9*c*
[Cu$_2$(μ-PhCO$_2$)$_2$(RNC)$_2$]	1.824(6)	1.159(8)	176.9(8)	3	9*d*
[Cu$_2$(μ-PhCO$_2$)$_2$(RNC)$_3$]	1.89(1)	1.15(1)	171.6(7)	4	9*d*
	1.831(6)	1.146(7)	178.2(6)	3	9*d*

c.n. = Co-ordination number, n.r. = not reported; tmen = *NNN′N′*-tetramethylethylenediamine, R = p-MeC$_6$H$_4$.

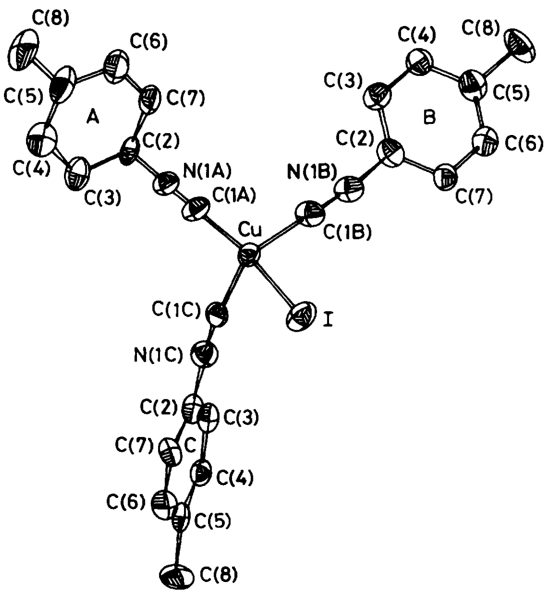


Figure 1. ORTEP drawing for [CuI(RNC)$_3$], (**3**) (40% probability ellipsoids)

The structure of complex (**2**) has been determined,[22] but the structural parameters are very similar to those reported for [Cu(CNMe)$_4$]BF$_4$.[8f] The copper co-ordination spheres for complexes (**3**)—(**6**) are shown in Figures 1—4. In all these complexes copper exhibits a pseudo-tetrahedral co-ordination, particularly distorted in (**4**) because of the narrow bite of the bipyridine ligand. This probably accounts for the significant shortening observed for the Cu–C and Cu–I distances with respect to those found in (**3**), (**5**), and (**6**) where the Cu–C bond lengths are not significantly different. It is worth noting that the Cu–C (Table 10) and Cu–I bond distances for complex (**4**) compare very well with those found in [CuI(H$_2$ben)(RNC)][9b] [Cu–I 2.619(3) Å] where H$_2$ben [*NN'*-ethylenebis(benzylideneimine)] exhibits a bonding mode similar to 2,2'-bipyridine. The Cu–N distances fall in the usual range.[9b] The Cu–C–N system is essentially linear in all complexes and the values observed are in good agreement with those quoted in Table 10 for other compounds. These data indicate a regular trend of bond distances and angles with the Cu–CNR system without remarkable differences except for a significant shortening of the Cu–C bond lengths in three-co-ordinate copper(I) derivatives. Further comment is warranted on the two μ-halogen-bridged complexes (**5**) and (**6**). The dimers have an imposed crystallographic C_i symmetry and contain a Cu ••• Cu unit separated by 3.362(2) and 3.234(1) Å respectively. The Cu–X bond distances show an asymmetry of the binuclear unit which is remarkable for (**5**) but small, even if significant, for (**6**). Complex (**5**) contains a quite unusual substituted benzimidazole derivative,[12] which has been used as a particularly crowded monodentate ligand.

The adducts CuX•RNC adopt a variety of structural forms, indicating the high lability of copper(I). A more difficult problem to elucidate is the solid state–solution relationship. Future studies of the reactivity of the Cu–CNR functionality can now take advantage of the present knowledge obtained of the various co-ordination environments and molecular complexities for copper(I) isocyanides.

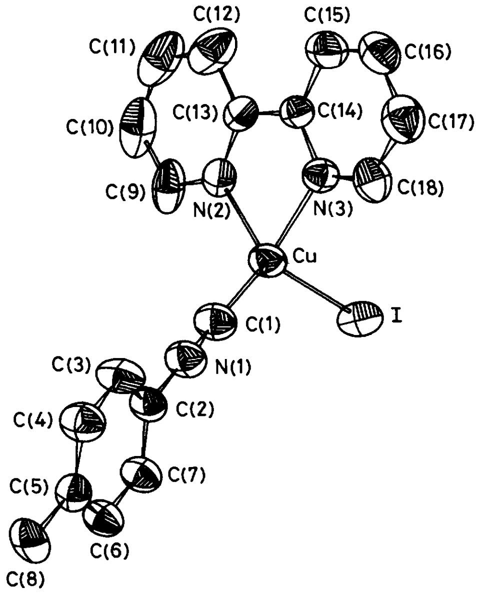


Figure 2. ORTEP drawing for [CuI(bipy)(RNC)], (**4**) (40% probability ellipsoids)

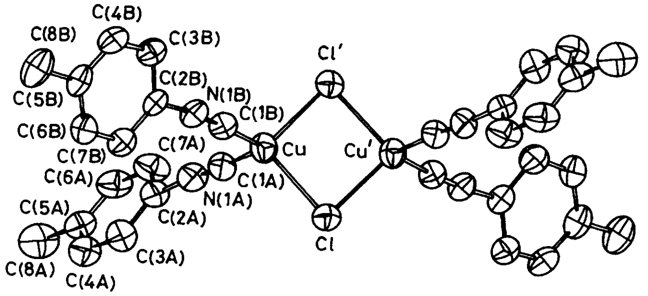


Figure 4. ORTEP drawing for [Cu$_2$(μ-Cl)$_2$(RNC)$_4$], (**6**) (60% probability ellipsoids). Prime indicates a transformation of $-x$, $-1-y$, $-z$

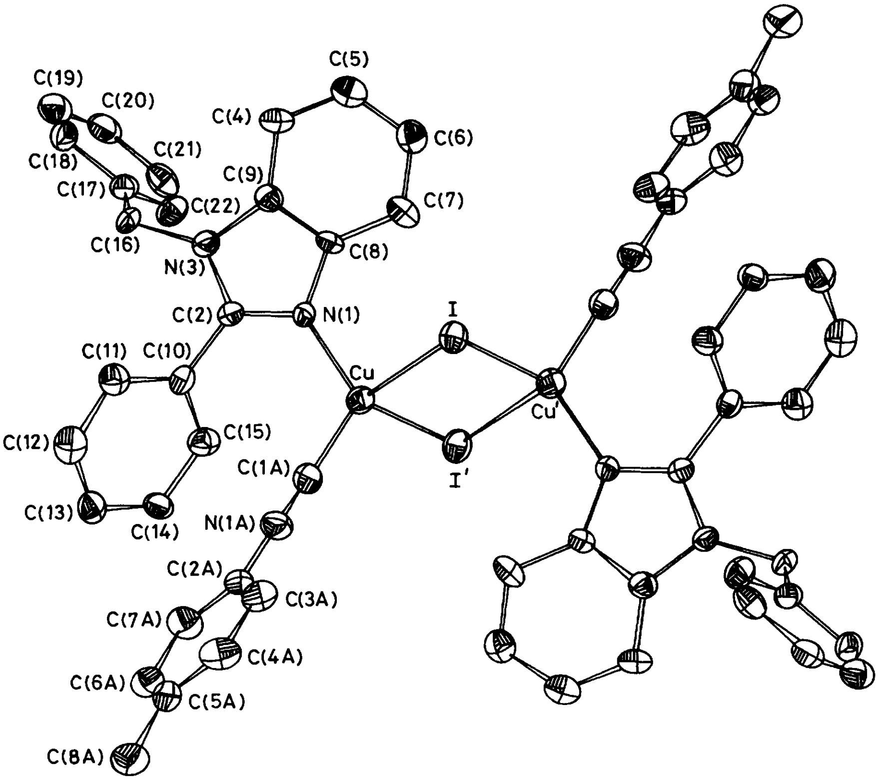


Figure 3. ORTEP drawing for [Cu$_2$(μ-I)$_2$(bpbzim)$_2$(RNC)$_2$], (**5**) (40% probability ellipsoids). Prime indicates a transformation of $1-x$, $-y$, $-z$

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