Cu...Cu in the latter complex is shorter than in the chloride or bromide and shorter than in the remainder of the other iodide complexes with 2-substituted ligands, presumably a consequence of a steric interaction varied by diminished carbon–carbon distance and constrained hydrogen position in the quinoline ligand. In chloride and bromide $\angle$N–Cu–N angles are particularly large. The precision of determination of ligand geometries is better in the iodide, and it is noted that Cu–N (2.104 (5), 2.076 (5) Å; mean 2.090 Å) distances are above the corresponding distances in those other structures where precision permits a confident estimate (CuCl, Br/2-methylpyridine, mean 2.029 Å; CuCl, -Br, -I/2,4-dimethylpyridine, mean 2.023, 2.031, 2.044 Å, respectively; CuI/3,5-dimethylpyridine, mean 2.058 Å), a result perhaps unexpected in view of the relatively minor differences in base strengths (pK_a for 2-methyl- and 2,4-dimethylpyridine and quinoline are 5.9, 6.8, and 4.9 respectively). It would, however, be expected that increased Cu–X bond order might be reflected in increased X–Cu–X angles, while Cu–N bond order and $\angle$N–Cu–N should diminish in parallel. While this is true of the quinoline/iodide complex, it does not appear to be the case for the 3,5-dimethylpyridine/iodide adduct.

The theme of the above discussion is that, in the present array of complexes of type $L_2CuX_2CuL_2$, the presence of a 2-substituent on the pyridine base L leads to steric interactions between the base substituent and the halide that have the effect of distorting the CuX_2Cu core so that the Cu...Cu distance is enlarged relative to its value in the complex unconstrained in this manner, i.e. by the presence of substituents of this type. For the iodide, the "unstrained" distance can be less than 2.7 Å (e.g., CuI/3,5-dimethylpyridine, 2.683 (1) Å), while in the "strained" state the maximum Cu...Cu observed is 3.140 (3) Å (CuI/2,4-dimethylpyridine (**5**)). Comparable unstrained values for chloride and bromide complexes are not, so far, available; evidence from the polymeric ···CuX_2CuX_2Cu··· anions suggests Cu...Cu estimates of ~2.7 and 2.85 Å, respectively.[13] The maximum strained values observed for the chloride are remarkably similar to the value observed in the iodide, being 3.145 (3) Å; for the bromide, as discussed already, the maximum observed in the copper(I) bromide/2-methylpyridine adduct (3.351 (3) Å) is extraordinarily long. Values obtained for the 2,4-dimethylpyridine and quinoline analogues of the latter (3.091 (3), 3.140 (3) Å) conform well to the chloride and iodide maxima. The odd bromide value, nevertheless, taken in conjunction with the considerable variability generally observed, e.g., 3.145 (3) and 2.995 (3) Å for the 2-methyl and 2,4-dimethylpyridine/chloride derivatives, suggests that in the "stretched" state steric control of the CuX_2Cu dimensions by the halide...halide van der Waals contact is lost, particularly as halide size decreases, and the core geometry becomes unstable. For three-coordinated copper in $NCuX_2CuX$ systems, minimum Cu...Cu is less, being 2.535 (9) Å (Table VI).

It remains to be finally demonstrated that 2-substituent–halide contacts are the effective cause of the CuX_2Cu core stretch. In the 3,5-dimethylpyridine/iodide adduct where there is no such substituent, it has already been noted that the complex is of high symmetry. In this complex contacts between the 2-carbons of the ligand rings with the iodine are snuggly disposed at 3.881 (5) and 3.877 (5) Å, close to the Pauling aromatic molecule/iodide van der Waals sum of 3.85 Å.[12] In the presence of 2-methyl substituents, rotation of the ligand about the Cu–N bond occurs; consideration of the 2-methyl/iodide contact distances of Table V suggests that this is done in such a manner as to maintain these distances at or near to the van der Waals halide...methyl sum (estimates: 3.8, 3.95, and 4.15 Å for chloride, bromide, and iodide, respectively).[12] Significantly, in a considerable number of cases, the value is *less* (by ~0.15 Å) rather than greater than the estimate. Interligand methyl–methyl contacts in all cases are considerably greater than their van der Waals sum. In the case of **1**, the observed hydrogen atom dispositions are such that within each methyl group H(21c) lies 0.2 Å out of the ligand plane and directed toward H(3), while H(21a,b) lie 0.6–0.7 Å to either side of the plane and H(3). The complexes of quinoline differ from the main pattern; consideration of the molecular projections shows a considerably different ligand disposition in which the substituent ring is oriented so that the 2-carbon of the pyridine ring, rather than the C_6 ring, contacts the halide at distances at or near the aromatic ring/halide contact estimate (3.5, 3.65, and 3.95 Å for chloride, bromide, and iodide, respectively).[12] The increased $\angle$N–Cu–N angles in the chloride and bromide complexes may be a consequence of the relatively awkward ligand disposition in these complexes, in which the ligand twist about the Cu–N bond is at its greatest; the more "normal" value of $\angle$N–Cu–N in the iodide together with the decrease in Cu...Cu in that complex presumably indicates some relaxation of strain.

Conclusion

The results of the present study show clearly the steric role of the halide and 2-methyl substituents in pyridine base complexes of copper(I) halides of stoichiometry $XCuL_2$; however, in spite of considerable variation in base profile, dissociation of the binuclear species into a monomer by this means has not yet been achieved.

Note Added in Proof. Recent work,[17-19] which has become available to us since the acceptance of this paper, describes the structure determinations of **1**,[17] **2**,[18] and $[CuI(quin)_2]_2CH_3CN$.[19] Bond length and angle data for the CuX_2Cu cores of these compounds have been included in Table VI for comparison. Data for **1** and **2** are in substantial agreement with the present work. There is a noticeable variation in the core *angular* geometry of quinoline and acetonitrile solvates of the $[CuI(quin)_2]_2$ dimer, emphasizing the ease with which parameters such as Cu···Cu distances can respond to minor changes in chemical environment.

Registry No. **1**, 95675-77-7; **2**, 93581-91-0; **3**, 95675-78-8; **4**, 95675-79-9; **5**, 95675-80-2; **6**, 95694-53-4; **7**, 95675-82-4.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positional parameters, distances and angles, least-squares planes, and observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

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Lewis Base Adducts of Group 11 Metal Compounds.† 15. Structural Studies of Mononuclear Adducts of Copper(I) Halides with Pyridine Bases of Stoichiometry $XCuL_{2,3}$

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In the preceding paper[2] we reported single-crystal structural studies on various pyridine base adducts of the copper(I) halides. $[XCuL_2]_2$, which are binuclear with a four-coordinate metal atom. Elsewhere,[3] we have noted that in the context of the sterically hindered base 2,6-dimethylpyridine (2,6-Me_2py) 1:2 CuI:base adducts may be isolated as mononuclear species, rather than the

0020-1669/85/1324-1957$01.50/0

Table I. Crystal Data

	compound				
	1	2	3	4	5
formula	CuCl(2,6-Me_2py)$_2$ ($C_{14}H_{18}ClCuN_2$)	CuBr(2,6-Me_2py)$_2$ ($C_{14}H_{18}BrCuN_2$)	CuCl(3-Mepy)$_3$ ($C_{18}H_{21}ClCuN_3$)	CuBr(3-Mepy)$_3$ ($C_{18}H_{21}BrCuN_3$)	CuI(3-Mepy)$_3$ ($C_{18}H_{21}CuIN_3$)
M_r	313.3	357.8	378.4	422.8	469.8
cryst syst	monoclinic	monoclinic	rhombohedral	rhombohedral	rhombohedral
space gp	$P2_1/n$ (C_{2h}^5, No. 14)	$C2/c$ (C_{2h}^6, No. 15)	$R3$ (C_3^4, No. 146)	$R3$ (C_3^4, No. 146)	$R3m$ (C_{3v}^5, No. 160)
a/Å	8.350 (1)	15.549 (8)	8.661 (4)	8.738 (5)	8.860 (3)
b/Å	14.317 (3)	7.456 (3)			
c/Å	12.304 (3)	14.222 (8)			
α/deg			112.15 (3)	112.05 (5)	111.37 (2)
β/deg	99.99 (2)	117.79 (4)			
V/Å^3	1451.8 (6)	1459 (1)	444.6 (3)	457.9 (4)	494.3 (2)
D_{calcd}/g cm^{-3}	1.44	1.63	1.41	1.53	1.58
Z	4	4	1	1	1
F(000)	648	720	196	214	232
μ_{Mo}/cm^{-1}	22.5	41	14.6	33.8	26.2
specimen/mm	~0.1 dia[b]	0.07 × 0.47 × 0.05	0.2 × 0.2 × 0.3	0.15 × 0.15 × 0.30	0.20 × 0.20 × 0.33
range A[a]		1.21–1.34	[c]	1.58–1.62	1.55–1.59
$2\theta_{max}$/deg	45	50	50	50	50
N	1974	1296	518	523	342
N_0	871	853	499	507	342
R'[a]	0.047	0.032	0.033	0.028	0.026
R[a]	0.047	0.037	0.041	0.036	0.032

[a] Preferred chirality for 3–5. [b] No absorption correction. [c] Not recorded.

Table II. Non-Hydrogen Atom Coordinates for [$XCuL_2$]

	X = Cl (1)			X = Br (2)		
	x	y	z	x	y	z
Cu	0.0438 (2)	0.1212 (1)	0.2307 (1)	$^1/_2$	−0.2259 (1)	$^1/_4$
X	0.1869 (4)	0.1912 (2)	0.3833 (2)	$^1/_2$	0.1026 (1)	$^1/_4$
			Ligand 1			
N(1)	0.1571 (10)	0.1244 (6)	0.1007 (6)	0.4195 (3)	−0.3105 (5)	0.3159 (3)
C(2)	0.1929 (14)	0.2071 (8)	0.0565 (9)	0.3300 (3)	0.3768 (6)	0.2520 (4)
C(21)	0.1231 (20)	0.2932 (11)	0.0949 (13)	0.3077 (5)	−0.4106 (12)	0.1394 (5)
C(3)	0.2858 (17)	0.2074 (10)	−0.0277 (10)	0.2633 (4)	−0.4091 (8)	0.2885 (5)
C(4)	0.3429 (16)	0.1275 (12)	−0.0658 (9)	0.2881 (4)	−0.3721 (8)	0.3925 (5)
C(5)	0.3065 (19)	0.0446 (11)	−0.0202 (12)	0.3793 (4)	−0.3076 (8)	0.4585 (5)
C(6)	0.2135 (14)	0.0455 (8)	0.0637 (8)	0.4444 (3)	−0.2796 (7)	0.4196 (4)
C(61)	0.1767 (20)	−0.0446 (11)	0.1166 (12)	0.5442 (4)	−0.2131 (10)	0.4886 (5)
			Ligand 2			
N(1)	−0.1673 (10)	0.0789 (5)	0.2707 (6)			
C(2)	−0.3022 (12)	0.1292 (8)	0.2403 (7)			
C(21)	−0.2929 (18)	0.2108 (9)	0.1676 (13)			
C(3)	−0.4446 (14)	0.1068 (9)	0.2810 (9)			
C(4)	−0.4444 (15)	0.0304 (10)	0.3512 (9)			
C(5)	−0.3082 (15)	−0.0194 (8)	0.3790 (9)			
C(6)	−0.1707 (12)	0.0038 (7)	0.3380 (8)			
C(61)	−0.0172 (20)	−0.0522 (9)	0.3682 (13)			

Table III. Non-Hydrogen Atom Coordinates for [$XCuL_3$]

	X = Cl (3)			X = Br (4)			X = I (5)		
atom	x	y	z	x	y	z	x	y	z
Cu	0	0	0	0	0	0	0	0	0
X	−0.3295 (8)	[a]	[a]	0.3422 (11)	[a]	[a]	0.3391 (11)	[a]	[a]
N(1)	−0.0841 (10)	0.1540 (10)	0.1489 (10)	0.0898 (13)	−0.1440 (13)	−0.1469 (13)	0.0077 (14)	−0.2253 (15)	[b]
C(2)	0.0497 (12)	0.3272 (12)	0.3487 (12)	−0.0431 (14)	−0.3377 (15)	−0.3210 (15)	−0.1411 (16)	−0.4168 (18)	[b]
C(3)	−0.0084 (15)	0.4313 (13)	0.4473 (14)	0.0115 (20)	−0.4382 (21)	−0.4274 (20)	−0.1456 (18)	−0.5754 (19)	[b]
C(31)	0.1552 (15)	0.6264 (17)	0.6732 (15)	−0.1467 (24)	−0.6616 (24)	−0.6167 (25)	−0.3138 (30)	−0.7822 (24)	[b]
C(4)	−0.2139 (14)	0.3569 (14)	0.3385 (15)	0.2128 (19)	−0.3316 (19)	−0.3524 (18)	0.0146 (23)	−0.5344 (26)	[b]
C(5)	−0.3538 (15)	0.1805 (16)	0.1351 (16)	0.3552 (26)	−0.1299 (26)	−0.1770 (27)	0.1685 (21)	−0.3348 (27)	[b]
C(6)	−0.2835 (12)	0.0848 (12)	0.0446 (12)	0.2846 (15)	−0.0451 (16)	−0.0805 (16)	0.1592 (16)	−0.1938 (18)	[b]

[a] $x = y = z$. [b] $x = z$.

usual binuclear bis(μ-halo)-bridged forms obtained with less hindered pyridine bases. By recrystallization of CuCl and CuBr from the parent base, we have now obtained the adducts

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 thorugh 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

(1) (a) Griffith University. (b) University of Western Australia.

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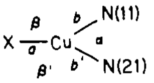
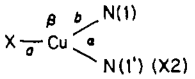
Table IV. $XCuN_2$ Core Geometries (I Values from Ref 3)



	X = Cl (1)	X = Br (2)	*I* (α and β phases)	
		Distances (Å)		
a	2.276 (3)	2.449 (2)	2.681 (2)	2.642 (2)
b	1.995 (8)	1.984 (5)	1.984 (5)	1.984 (4)
b'	2.004 (9)			
		Angles (deg)		
α	139.7 (3)	142.9 (2)	149.6 (2)	143.5 (1)
β	113.4 (2)	108.6 (1)	105.2 (1)	108.26 (8)
β'	106.8 (2)			
θ^a	67.2	71.0	87.6	71.7
θ'^a	76.4			

[a] θ (θ') is the dihedral angle between the ligand plane and the $XCuN_2$ plane. The latter is exact in the bromide and iodide; for the chloride, σ is 0.013 Å.

Table V. $XCuN_3$ Core Geometries



	Cl (3)	Br (4)	I (5)
		Distances (Å)	
a	2.451 (4)	2.585 (6)	2.710 (3)
b	2.029 (10)	2.032 (13)	2.046 (14)
H(6)···X	2.88	2.93	3.11
		Angles (deg)	
α	113.1 (4)	114.0 (5)	112.8 (4)
β	105.5 (2)	104.4 (3)	105.9 (2)

$[CuCl(2,6\text{-}Me_2py)_2]$ (**1**) and $[CuBr(2,6\text{-}Me_2py)_2]$ (**2**) as colorless crystalline solids that rapidly lose their integrity as base is lost on exposure to the atmosphere. Single-crystal X-ray structure determinations have been carried out at 295 K and are reported here, showing the species to be mononuclear also and completing the series of molecular geometrical parameters for $[CuX(2,6\text{-}Me_2py)_2]$ (X = Cl, Br, I).

No structural confirmation as yet exists for species of the type $XCuL_3$ (L = nitrogen base) in contrast to the well-established triphenylphosphine systems of this type. Recent work[4] describes the synthesis of adducts of this type with pyridine bases unhindered in the 2-position, by recrystallization of copper(I) halides from the neat pyridine base. For the copper(I) iodide:pyridine adduct obtained in this way, 1:2 stoichiometry of the $L_2CuX_2CuL_2$ dimer type was found in a single-crystal X-ray study,[5] rather than a 1:3 adduct. With 3-methylpyridine, however, we find that for all X (chloride (**3**), bromide (**4**), iodide (**5**)) mononuclear $XCuL_3$ are obtained; the results of this study are also reported here.

Experimental Section

Synthesis. Compounds were prepared as described in the preceding paper.[2]

Crystallography. General crystallographic detail and ligand labeling are given in the preceding paper;[2] specific details for each compound are given in Table I.

Particular Features. In **1** and **2** $(x, y, x)_H$ were successfully refined, together with $(U_{iso})_H$ in **2**. In **3**–**5**, $(x, y, z, U_{iso})_H$ were constrained after location of the hydrogen atom in difference maps; in **5**, the methyl hydrogen atoms were disordered over two sets of sites. In **3**–**5**, thermal motion is highest at the methyl group, possibly precursive of an $R3 \leftrightarrow R3m$ phase transition. Residuals are quoted for the preferred chirality.

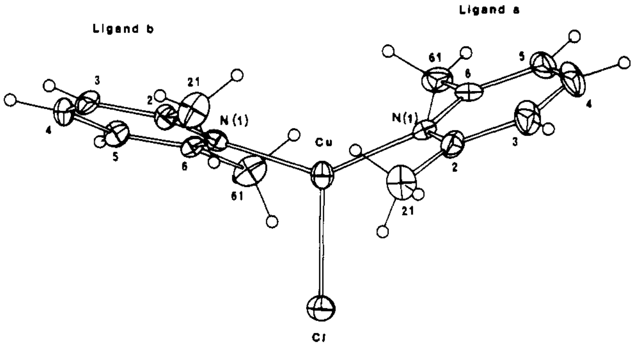


Figure 1. Single molecule of $[ClCu(2,6\text{-}Me_2py)_2]$. Hydrogen atoms have an arbitrary radius of 0.1 Å. Projection is normal to the $ClCuN_2$ plane.

Non-hydrogen atom coordinates are given in Tables II and III and molecular core geometries in Tables IV and V.

Discussion

1 and 2. The structure determination in each case establishes the presence of a mononuclear $[XCu(2,6\text{-}Me_2py)_2]$ species with pseudo-trigonal-planar coordination about the metal atom. The asymmetric unit of the structure in the chloride is the single molecule. For the iodide analogue with the existence of two *C*2/*c* phases has been established,[3] the orientation of the molecules in the β phase being such as to permit dimer formation were it not, presumably, for the steric effects of the methyl substitutents on the pyridine rings. The bromide species is isomorphous with the iodide β form and displays a similar molecular disposition: in the iodide, the close Cu···X distances along *b* are 4.752 (1) Å, while in the bromide they are 5.007 (2) Å. As in the iodide, the molecule of the bromide lies on a crystallographic twofold axis. The chloride is not isomorphous with the bromide or iodide, and the molecule contains no crystallographically imposed symmetry; it is depicted in Figure 1.

In refinement of the hydrogen atom parameters of the methyl groups in binuclear $[L_2(CuCl)_2L_2]$ (L = 2-methylpyridine) (preceding paper), a disposition was obtained whereby one hydrogen atom lay close to the ring plane (both ligands) and directed toward the 3-hydrogen, while the other two lay to either side of the plane. In the mononuclear bromide, $[BrCu(2,6\text{-}Me_2py)_2]$ (**2**), in which the precision of the determination and order of the structure allows satisfactory refinement of the methyl hydrogen atoms of the ligand, a similar disposition is observed in spite of the sterically more relaxed environment of the methyl group in the monomer.

Comparative molecular parameters are given for chloride (**1**), bromide (**2**), and iodide are given in Table IV. Deviations from internal symmetry and/or consistency are evident from the nonequality of angles β, β' in the chloride and between the parameters of the two iodide phases, as might be expected in molecules of low coordination number and polarizable components; in the iodide, the two different α angles are consistent with the expected and observed changes in the distance *a*. Throughout the three complexes, distance *b* does not change appreciably, and 1.99 Å may be considered as a representative mean, in agreement with that observed in the X_2CuN system $[[CuI(2,6\text{-}Me_2py)]_2]$ (1.99 Å).[6]

Angle α and the distance *a* both increase uniformly along the series from chloride to iodide; we adopt 146.5° and 2.66 Å as the mean values of the two iodide phases. The value for the chloride of Cu–Cl (2.276 (3) Å) is in contrast with that observed in the 1:1 adduct of CuCl with 2,9-dimethyl-1,10-phenanthroline (2.126 (2) Å),[7] this difference, although large, is consistent with expectations concomitant on a reduction in the N–Cu–N angle of

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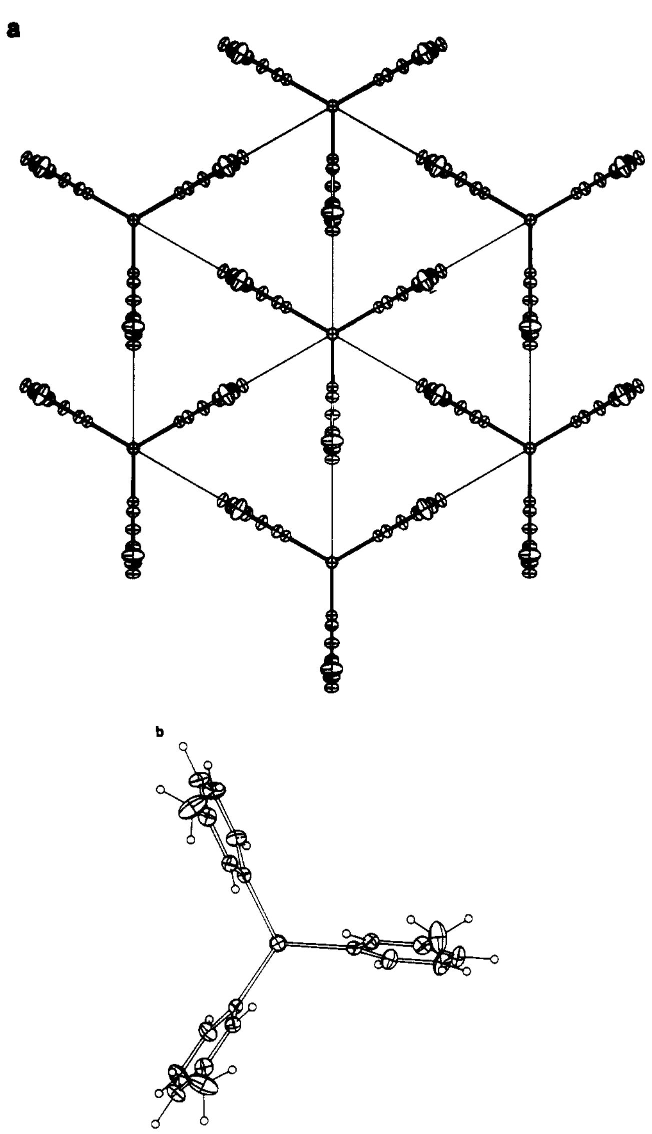

Figure 2. (a) Unit cell contents (and neighboring cells) of [ICu(3-Mepy)$_3$] projected down the threefold axis. (b) A single molecule of [ClCu(3-Mepy)$_3$] projected down the Cl–Cu bond.

139.7 (3)° (in the present complex) to 81.8 (2)°. In the latter compound, Cu–N is increased to 2.060 (6) Å (cf. 2.00 Å in the present complex). For Cu–N in the three-coordinate cation [Cu(2-Mepy)$_3$]$^+$, a value of 1.99 Å is reported.[8]

Also of interest is the relationship of the present parameters with those of bis(2,6-dimethylpyridine)copper(I) perchlorate and nitrate;[9] in the former, the cation is centrosymmetric, ∠N–Cu–N necessarily being 180° and Cu–N are 1.936 (5) Å. In the nitrate, with the distant approach of the quasi-bidentate nitrate group to the copper, ∠N–Cu–N is reduced to 165.9 (2)° while Cu–N increases to 1.966 (5) and 1.956 (5) Å. In the present case, with genuine three-coordination, N–Cu–N is further reduced while Cu–N are further increased, as documented above.

Comparison is also invited with the analogous compounds with tertiary phosphine bases.[10,11] For XCuL'$_2$ (L' = triphenylphosphine) the angle subtended by the two ligand atoms at the copper is largely independent of halide (125.48 (7), 126.0 (1), and 126.9 (1)° for chloride, bromide, and iodide), while copper–phosphine distances range from 2.260 (2) to 2.282 (3) Å. Halide–copper–phosphine angles are symmetry constrained in the iodide to 116.55 (7)°; in the chloride and bromide, this constraint is lost, the values being 113.76 (7), 120.74 (6)° (chloride) and 112.8 (1), 121.0 (1)° (bromide). Apart from the latter disparity, the behavior of the system strongly suggests that steric considerations are less relevant in determination of molecular geometry than was the case for the 2,6-dimethyl-substituted pyridine bases. For the phosphine adducts, copper–chloride, –bromide, and –iodide, distances are 2.208 (2), 2.346 (2), and 2.515 (2) Å, all very substantially shorter than their nitrogen base counterparts, in accord with the smaller opposed angle between the two base atoms.

3–5. The archetypal structure of this series is the iodide (**5**). The unit cell contents comprise a single molecule in space group *R*3*m*, so that one-sixth of the molecule comprises the asymmetric unit of the structure. The copper atom is four-coordinated by the halide and the nitrogen atoms of the three ligands. The copper–halide vector is coincident with the crystallographic threefold axis; this also contains three mirror planes, and the symmetry of the structure thus requires that the three ligands lie in these planes and therefore parallel to the unique crystallographic (1, 1, 1) axis and the three axes of the hexagonal setting normal to it (Figure 2a).

As we proceed from iodide (**5**) to bromide (**4**) and chloride (**3**) in interesting descent in symmetry occurs from space group *R*3*m* to *R*3, the three intramolecular mirror planes being lost in the process. This is occasioned by a twist of each of the ligands in the same direction about the Cu–N axis, so that the methyl substituent moves to one side of the potential mirror plane (Figure 2b), accompanied by a twist about the threefold axis of the XCuN$_3$ system in the opposite sense. Seemingly, the cause of this distortion is the decrease in metal–halide distance accompanied by increased steric interaction between the nearby ligand hydrogen atoms and the halide. Mean X–Cu–N–C(2,6) torsion angles for **3** and **4** are (modulli) 11.0 and 9.5°, respectively.

Changes in the copper(I)–nitrogen distances and angles about the copper atom (Table IV) are of limited significance and trivial in nature for the three complexes. The mean copper–nitrogen distance for the three complexes (2.03_6 Å) is longer than its counterpart for the XCuL$_2$ system, as might be expected, and similar to the value observed for the tetrakis(pyridine)copper(I) cation (2.046 (4) Å).[12] The copper angular geometry is less closely tetrahedral than that of the analogous tris(triphenylphosphine)copper(I) halide counterparts.[13] As in complexes of the type XCuL$_2$, we find the copper(I)–halide distances in the phosphorus base adducts to be appreciably shorter than their counterparts in the nitrogen base complexes; for [XCu(PPh$_3$)$_3$], the copper–halide distances (mean) are 2.34, 2.48, and 2.69 Å; for the iodide, however, the difference is quite minor.

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Note Added in Proof. A recent publication[14] that has become available to us since the acceptance of this paper also describes the structure of **1**, with results in essential agreement with the present.

Registry No. **1**, 95740-44-6; **2**, 95740-45-7; **3**, 36537-50-5; **4**, 36537-51-6; **5**, 36537-52-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positional parameters, distances and angles, least-squares planes, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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