Dicyanoimidazole Complexes of Cu(I): a Carbonyl Assisted Alcoholysis of Nitrile

P. G. RASMUSSEN*, LIN RONGGUANG, W. M. BUTLER
Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48109, U.S.A.
and J. C. BAYÓN*
Departament de Química Inorgànica, Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain

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Abstract

We describe a series of compounds which result from the reaction of Cu(I) with 4,5-dicyanoimidazole. This ligand is far more acidic than imidazole and in all cases forms complexes as the anion. The presence of carbon monoxide with Cu(I) assists in the rapid alcoholysis of one of the nitrile groups. The resulting imino-ester remains coordinated to the copper in the phosphine derivative as confirmed by X-ray crystallography. The composition $CuC_{42}H_{35}N_4P_2$ crystallizes in the space group *Pbca* with $a = 14.140(4)$, $b = 21.466(7)$, $c = 24.577(8)$ Å and $Z = 8$ molecules per cell. The copper is four coordinate and the bidentate imino-ester imidazole is nearly planar.

Introduction

As part of a program to investigate the coordination properties of cyanoimidazoles, we have previously reported on a group of complexes of Cu(I) with tetracyanobiimidazole [1]. In this paper we extend that study to complexes of Cu(I) with dicyanoimidazole (HDicy). We also report an interesting reaction in which a copper(I) carbonyl complex assists in the facile alcoholysis of a nitrile group, resulting in a coordinated imino-ester. The presence of this group was confirmed by an X-ray crystal structure on a triphenylphosphine derivative.

Dicyanoimidazole was first prepared by Woodward [2] and its organic chemistry explored by Sheppard and Webster [3]. It is somewhat surprising, in view of the widespread interest in imidazole complexes, that it seems never to have been investigated in any reactions with metal ions. The cyano groups confer unusual acidity on the imidazole ring system $pK_a = 5.5$, and a variety of salts and complexes are readily formed. The pi accepting tendencies of the dicyanoimidazole anion (Dicy), favor coordination to larger metal ions with low charge and some pi donor ability, and in this article we describe reactions and structures with various Cu(I) moieties.

Experimental

$Cu(CH_3CN)_4BF_4$ was prepared by standard techniques. Dicyanoimidazole was prepared by the method of Woodward [2]. The sodium salt NaDicy was prepared by careful addition of $NaOCH_3$ (avoid excess) to HDicy in methanol. It was precipitated by addition of ether, recrystallized from methanol, and dried *in vacuo*. Solvents were freshly distilled from appropriate drying agents before use and stored under nitrogen. All copper complexes were prepared using standard Schlenk techniques. Triphenylphosphine was used as obtained from Aldrich Chemical Co. Elemental analysis were performed by Spang or Galbraith microanalytical laboratories. Infrared spectra were recorded on Perkin-Elmer 1330 or Nicolet 60 SX-FT spectrometers. NMR spectra were obtained on a JEOL FX-90Q spectrometer, peak positions relative to TMS.

Preparation of CuDicy

0.5 mM of $Cu(CH_3CN)_4BF_4$ was dissolved in 15 ml of a 1:1 mixture of methanol and chloroform and slowly added to a solution of 4 mM of HDicy in 5 ml of methanol. This produced a white precipitate which was filtered off, washed with chloroform and diethyl ether, dried *in vacuo*. Yield: 90%. *Anal.* Calc. for CuC_5N_4H: C, 35.18; H, 0.56; N, 31.02. Found: C, 34.66; H, 0.80; N, 31.24%.

The IR spectrum shows two sharp C≡N peaks at 2238 cm^{-1}, 2248 cm^{-1}. The peak characteristic for BF_4^- did not appear in the spectrum.

Preparation of Cu(Dicy)(PPh$_3$)$_2$

To 1.12 g (3.6 mM) of $Cu(CH_3CN)_4BF_4$, dissolved in 25 ml of CH_3OH was added 1.88 g (7.2 mM) of

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*Author to whom correspondence should be addressed.

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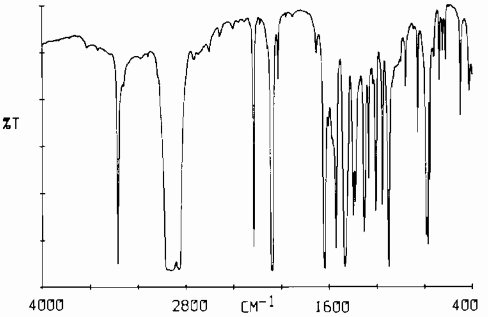

Fig. 1. Infrared spectrum of Cu(CO)(Dicyie) run in nujol.

PPh_3. After stirring 5 min, 15 ml of methanolic NaDicy (0.5 g, 3.6 mM) was added. 5 min later, a white solid forms. After 1 h of stirring, an air stable product was collected by filtration. Yield: 85%. *Anal.* Calc. for $C_{41}H_{31}N_4P_2Cu$: C, 69.83; H, 4.43; N, 7.94; P, 8.78; Cu, 9.01. Found: C, 70.01; H, 4.51; N, 7.86; P, 9.04; Cu, 9.24%.

The IR spectrum showed a single peak in the C≡N region at 2224 cm^{-1}. The peak characteristic for BF_4^- did not appear in the spectrum.

Preparation of [Cu(CO)(Dicyie)]

To 15 ml of a solution of $Cu(CH_3CN)BF_4$ (0.67 g, 2.13 mM) in CH_3OH was slowly added a quantity of methanolic NaDicy (0.3 g). This was then bubbled with carbon monoxide for 0.5 h and the reaction mixture was stirred at room temperature for an additional 30 min under carbon monoxide atmosphere. The white solid that formed was filtered, then washed with methanol and dried *in vacuo*. The compound was stable in N_2 atmosphere and did not lose CO even *in vacuo* but was sensitive to air and moisture. *Anal.* Calc. for $CuC_7H_5N_4O_2$: C, 34.91; H, 2.08; N, 23.28. Found: C, 35.31; H, 2.14; N, 23.76%. The IR spectrum is shown in Fig. 1.

Preparation of Cu(Dicyie)(PPh$_3$)$_2$

0.1 g of Cu(CO)(Dicyie) was suspended in 15 ml of dichloromethane under N_2 atmosphere. Triphenylphosphine (0.2 g, 0.8 mM) in 5 ml of CH_2Cl_2 was slowly added to the suspension. The addition of PPh_3 gave a colorless solution. Fast evolution of carbon monoxide was observed at the same time. After layering with hexane for 2 days, white needles of crystalline product were obtained. *Anal.* Calc. for $CuC_{42}H_{35}N_4P_2$: C, 69.94; H, 4.89; N, 7.77; P, 8.59; Cu, 8.81. Found: C, 68.77; H, 4.67; N, 7.61; P, 8.69; Cu, 8.83%.

The IR spectrum showed a single strong peak for C≡N at 2224 cm^{-1} and one medium broad peak for NH at 3200 cm^{-1}. There is a sharp singlet in the NMR spectrum at 3.77 ppm assigned to the imino-ester methyl group.

Preparation of Cu(Dicy)PPh$_3$

$Cu(PPh_3)_2NO_3$ was prepared by reduction of $Cu(NO_3)_2\cdot3H_2O$ with excess PPh_3 in alcohol. The product precipitates on cooling to ice temperature and can be filtered off in good yield. The treatment of 1.08 g of $Cu(PPh_3)_2NO_3$ (1.66 mmol) with 195 mg of HDicy (1.66 mmol) in 50 ml THF with stirring for 12 h yields 260 mg $Cu(Dicy)PPh_3$ which precipitates in a few minutes. *Anal.* Calc. for $CuC_{23}N_4H_{16}P$: C, 62.37; N, 12.65; H, 3.64. Found: C, 61.8; N, 12.65; H, 3.67%.

This compound could also be converted to the $Cu(Dicy)(PPh_3)_2$ compound described above by treatment with stoichiometric PPh_3 and excess NaDicy in methanol.

TABLE I. Summary of Crystal Data Conditions and Results. Compound $Cu(Dicyie)(PPh_3)_2$:$CuC_{42}H_{35}N_4P_2$

Space group	*Pbca*
a (Å)	14.140(4)
b (Å)	21.466(7)
c (Å)	24.577(8)
V (Å^3)	7460(4)
Molecular weight	737.3
Z	8
D_c (g/ml)	1.313
Crystal dimensions (mm)	0.230 × 0.071 × 0.356
Absorption coefficient (1/cm)	7.01
Scan range (deg)	Mo Kα – 0.8 to Mo Kα + 0.9
Background time ratio	0.8
2 theta (deg)	40
Data collected	4217
Data >2σ(*I*)	1888
Final R_1	0.067
Final R_2	0.049
Residual (e/Å^3)	0.52

X-ray Structure Determination

A single crystal was mounted on a Syntex $P2_1$ diffractometer. Table I contains a summary of data collection conditions and results. Lattice parameters were determined from a least-squares refinement of 15 reflection settings obtained from an automatic centering routine.

Intensity data were obtained using Mo Kα radiation monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The data were reduced and corrected for absorption by procedures previously described*. The structure was solved using

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*Computations were carried out on an Amdahl 5860 computer, using programs for structural analysis from the SHEL-EX package by G. Sheldrick, Institut für Anorganische Chemie der Universitat Göttingen, F.R.G. Other programs used include ORTEP, a thermal ellipsoidal drawing program by C. K. Johnson, and the direct methods program MULTAN 78 by P. Main.

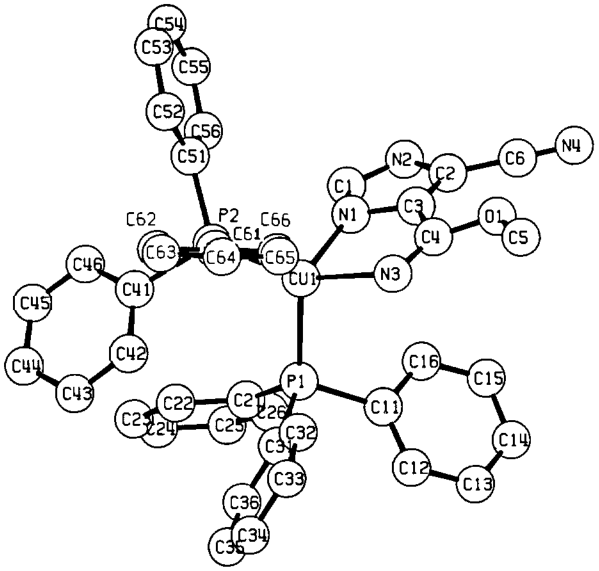

Fig. 2. Molecular structure and numbering scheme for Cu(Dicyie)(PPh$_3$)$_2$.

MULTAN. In the subsequent refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where F_o and F_c are the observed and calculated structure factor amplitudes. The agreement indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and the weighted $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were used to evaluate the results. The atomic scattering factors are from the International Tables for X-ray Crystallography [4].

Least-squares refinement results using anisotropic thermal parameters for all non-hydrogen atoms are shown in Table I. Positions of all phenyl hydrogen atoms were calculated and not refined. A difference fourier then gave the methyl hydrogen positions and indicated a possible hydrogen position of intensity 0.52 e/Å^3 located 1.34 Å from Cl. There was a possible hydrogen peak of intensity 0.34 e/Å^3, 1.31 Å from N3. All hydrogens were given fixed U values (isotropic temperature factors) of 0.05.

Figure 2 shows the atom arrangement. Final positional parameters with estimated standard deviations are shown in Table II. Anisotropic thermal parameters with their estimated standard deviations are listed in Table III. Tables IV and V list the crystallographically determined bond distances and angles.

Refinement of the final model to least squares convergence with all atoms isotropic gave $R_1 = 0.0785$, $R_2 = 0.0675$, $U(\mathrm{O1}) = 0.020$, and $U(\mathrm{N3}) = 0.051$. The same model assuming O1 is a nitrogen atom and N3 is an oxygen atom gave $R_1 = 0.0798$, $R_2 = 0.0686$, $U(\mathrm{O1}) = 0.066$, and $U(\mathrm{N3}) = 0.019$. The final values of $U(\mathrm{O1}) = 0.053$ and $U(\mathrm{N3}) = 0.034$ indicate correct assignment.

TABLE II. Fractional Atomic Coordinates

Atom	x	y	z	U
Cu1	0.3716(01)	0.1790(01)	0.1720(01)	0.0397
P1	0.4201(03)	0.2749(02)	0.2007(01)	0.0380
P2	0.3481(02)	0.1615(02)	0.0830(01)	0.0407
N1	0.2777(08)	0.1435(05)	0.2288(04)	0.0334
C1	0.1919(11)	0.1536(06)	0.2503(06)	0.0469
N2	0.1773(07)	0.1219(05)	0.2972(05)	0.0402
C2	0.2611(11)	0.0900(06)	0.3040(06)	0.0352
C3	0.3238(11)	0.1023(06)	0.2623(06)	0.0271
C4	0.4230(10)	0.0858(07)	0.2473(06)	0.0326
N3	0.4649(07)	0.1142(05)	0.2099(04)	0.0328
O1	0.4514(06)	0.0391(05)	0.2820(04)	0.0529
C5	0.5442(10)	0.0140(06)	0.2709(06)	0.0653
C6	0.2811(11)	0.0532(07)	0.3517(07)	0.0493
N4	0.2938(10)	0.0236(06)	0.3906(05)	0.0813
C11	0.4597(10)	0.2729(06)	0.2719(05)	0.0394
C12	0.5474(10)	0.2963(06)	0.2880(06)	0.0543
C13	0.5778(10)	0.2920(08)	0.3414(06)	0.0697
C14	0.5186(11)	0.2643(07)	0.3787(06)	0.0575
C15	0.4341(12)	0.2380(06)	0.3637(06)	0.0527
C16	0.4034(09)	0.2429(06)	0.3099(06)	0.0468
C21	0.3429(09)	0.3422(06)	0.1978(07)	0.0465
C22	0.3170(11)	0.3682(07)	0.1472(06)	0.0605
C23	0.2611(12)	0.4201(08)	0.1431(07)	0.0726
C24	0.2227(11)	0.4474(08)	0.1890(08)	0.0720
C25	0.2442(13)	0.4226(08)	0.2393(07)	0.0667
C26	0.3035(10)	0.3724(07)	0.2438(06)	0.0434
C31	0.5261(09)	0.3004(07)	0.1640(05)	0.0336
C32	0.5858(10)	0.2522(06)	0.1480(05)	0.0422
C33	0.6694(11)	0.2661(09)	0.1221(07)	0.0718
C34	0.6914(10)	0.3259(11)	0.1073(06)	0.0722
C35	0.6299(14)	0.3737(07)	0.1216(07)	0.0791
C36	0.5490(11)	0.3607(07)	0.1505(06)	0.0604
C41	0.3338(13)	0.2336(06)	0.0426(05)	0.0392
C42	0.4123(12)	0.2706(08)	0.0339(06)	0.0628
C43	0.4058(13)	0.3274(08)	0.0079(06)	0.0672
C44	0.3140(20)	0.3481(08)	−0.0093(07)	0.0951
C45	0.2426(14)	0.3098(10)	0.0(07)	0.0860
C46	0.2471(12)	0.2538(08)	0.0252(06)	0.0596
C51	0.2413(09)	0.1169(06)	0.0685(06)	0.0133
C52	0.2323(10)	0.0736(07)	0.0271(05)	0.0481
C53	0.1501(13)	0.0404(07)	0.0218(06)	0.0603
C54	0.0754(11)	0.0483(08)	0.0569(07)	0.0654
C55	0.0831(11)	0.0907(08)	0.0971(06)	0.0666
C56	0.1638(11)	0.1243(07)	0.1044(05)	0.0562
C61	0.4421(09)	0.1216(06)	0.0445(06)	0.0368
C62	0.4487(10)	0.1273(06)	−0.0118(06)	0.0507
C63	0.5205(12)	0.0959(07)	−0.0391(06)	0.0599
C64	0.5829(11)	0.0596(07)	−0.0114(08)	0.0638
C65	0.5762(11)	0.0546(07)	0.0441(08)	0.0580
C66	0.5066(11)	0.0853(07)	0.0727(05)	0.0419

Results and Discussion

The tetrakisacetonitrile complex of copper(I) reacts immediately with dicyanoimidazole in methanol, to produce a white insoluble solid of 1:1

TABLE III. Thermal Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.0417(09)	0.0426(10)	0.0348(10)	−0.0003(10)	−0.0033(11)	−0.0055(11)
P1	0.0397(26)	0.0399(26)	0.0344(28)	−0.0025(22)	0.0028(22)	−0.0011(22)
P2	0.0453(28)	0.0418(29)	0.0351(25)	−0.0028(20)	−0.0065(21)	0.0012(22)
N1	0.0456(84)	0.0296(78)	0.0249(75)	−0.0027(62)	0.0010(69)	−0.0017(67)
C1	0.0428(13)	0.0688(22)	0.0290(97)	−0.0070(91)	0.0209(85)	−0.0243(96)
N2	0.0145(67)	0.0485(88)	0.0577(93)	−0.0074(73)	0.0042(66)	−0.0066(66)
C2	0.0468(19)	0.0275(07)	0.0312(98)	0.0120(84)	−0.0003(99)	−0.0107(92)
C3	0.0464(20)	0.0092(91)	0.0258(02)	−0.0026(79)	−0.0121(96)	−0.0127(84)
C4	0.0162(98)	0.0301(09)	0.0514(23)	−0.0121(92)	−0.0224(94)	0.0130(90)
N3	0.0466(84)	0.0313(80)	0.0205(80)	0.0175(64)	−0.0002(64)	−0.0178(65)
O1	0.0317(68)	0.0626(76)	0.0644(78)	0.0197(63)	0.0049(59)	0.0148(60)
C5	0.0486(23)	0.0736(25)	0.0738(24)	0.0313(97)	0.0111(95)	0.0141(01)
C6	0.0504(16)	0.0448(24)	0.0526(33)	−0.0069(01)	0.0213(05)	0.0131(96)
N4	0.0999(18)	0.0771(18)	0.0668(21)	0.0263(90)	0.0291(94)	0.0338(92)
C11	0.0274(99)	0.0486(08)	0.0423(14)	−0.0140(86)	−0.0169(82)	−0.0007(86)
C12	0.0455(14)	0.0756(30)	0.0418(13)	−0.0079(88)	−0.0018(92)	−0.0201(91)
C13	0.0294(03)	0.1345(69)	0.0451(29)	−0.0147(11)	0.0020(97)	−0.0330(99)
C14	0.0430(18)	0.0900(35)	0.0394(15)	−0.0325(97)	−0.0339(01)	0.0102(04)
C15	0.0834(35)	0.0602(19)	0.0146(12)	−0.0084(84)	−0.0001(99)	−0.0047(06)
C16	0.0372(02)	0.0480(12)	0.0552(30)	−0.0034(87)	0.0114(87)	−0.0320(82)
C21	0.0438(00)	0.0422(08)	0.0536(07)	−0.0103(93)	−0.0007(91)	−0.0017(82)
C22	0.0754(23)	0.0652(37)	0.0410(17)	−0.0059(98)	−0.0176(92)	0.0216(04)
C23	0.0722(29)	0.0763(50)	0.0692(41)	0.0170(16)	−0.0230(15)	0.0343(12)
C24	0.0464(11)	0.0606(38)	0.1091(86)	−0.0032(35)	0.0162(22)	0.0211(94)
C25	0.0722(27)	0.0448(20)	0.0832(39)	−0.0122(21)	0.0307(29)	0.0359(01)
C26	0.0531(06)	0.0394(07)	0.0377(10)	−0.0139(93)	0.0042(88)	0.0005(87)
C31	0.0287(91)	0.0478(02)	0.0244(91)	−0.0180(86)	−0.0047(80)	−0.0105(81)
C32	0.0344(97)	0.0544(10)	0.0377(02)	0.0102(80)	0.0140(8)	−0.0132(94)
C33	0.0465(30)	0.0835(47)	0.0854(43)	0.0078(16)	0.0203(11)	0.0086(08)
C34	0.0416(09)	0.1241(85)	0.0508(18)	0.0098(45)	0.0182(89)	−0.0153(38)
C35	0.0737(34)	0.0761(45)	0.0875(40)	0.0230(16)	0.0368(32)	−0.0304(32)
C36	0.0792(33)	0.0267(12)	0.0754(45)	0.0028(93)	0.0121(06)	−0.0107(96)
C41	0.0830(29)	0.0140(93)	0.0205(98)	−0.0127(74)	−0.0015(94)	0.0090(04)
C42	0.1054(54)	0.0224(10)	0.0607(33)	0.0062(93)	−0.0126(11)	−0.0047(11)
C43	0.1095(61)	0.0385(34)	0.0537(21)	−0.0070(03)	0.0413(10)	0.0004(22)
C44	0.2102(74)	0.0312(32)	0.0438(26)	0.0088(04)	0.0192(62)	0.0556(63)
C45	0.1263(88)	0.0653(71)	0.0665(44)	−0.0033(27)	−0.0273(33)	0.0407(45)
C46	0.0647(31)	0.0636(43)	0.0505(18)	0.0034(01)	−0.0005(04)	0.0298(10)
C51	0.0400(40)	0.0 ( )	0.0 ( )	0.0 ( )	0.0 ( )	0.0 ( )
C52	0.0477(19)	0.0470(11)	0.0496(09)	−0.0216(97)	−0.0087(93)	0.0024(90)
C53	0.0682(42)	0.0468(09)	0.0660(34)	−0.0198(95)	−0.0213(16)	−0.0041(10)
C54	0.0329(17)	0.0949(57)	0.0685(41)	0.0030(17)	−0.0250(11)	−0.0175(17)
C55	0.0455(11)	0.1149(68)	0.0395(16)	−0.0280(08)	−0.0014(97)	−0.0125(17)
C56	0.0504(06)	0.0909(31)	0.0273(01)	−0.0357(90)	−0.0029(85)	−0.0077(99)
C61	0.0334(97)	0.0381(06)	0.0389(09)	−0.0041(83)	−0.0032(88)	−0.0080(83)
C62	0.0568(09)	0.0575(20)	0.0377(07)	0.0076(91)	0.0148(91)	0.0119(92)
C63	0.0691(23)	0.0547(23)	0.0558(29)	0.0044(03)	0.0319(11)	0.0158(01)
C64	0.0451(11)	0.0509(31)	0.0954(59)	−0.0254(18)	0.0427(21)	−0.0062(95)
C65	0.0431(10)	0.0512(17)	0.0797(45)	−0017(11)	−0.0004(12)	−0.0020(96)
C66	0.0437(05)	0.0533(15)	0.0287(04)	−0.0098(94)	−0.0088(94)	0.0 (90)

stoichiometry, irrespective of the ratios of the starting reagents. This material is likely to be a polymer in which the copper links by intermolecular bonds to the nitrile functionalities as well as to both the one and three positions of Dicy$^-$. Although it is polymeric, the IR peaks are sharp and the analytical data good. The facile formation of this compound gives good indication of the affinity between cyanoimidazolate and Cu(I). If triphenylphosphine is added prior to the addition of Dicy$^-$ in the synthetic procedure, a new compound, Cu(Dicy)(PPh$_3$)$_2$, precipitates. The insolubility of this species, unusual

TABLE IV. Bond Distances (A)

Bond	Distance
Cu1–P1	2.280(05)
Cu1–P2	2.246(05)
Cu1–N1	2.072(14)
Cu1–N3	2.131(14)
P1–C11	1.838(18)
P1–C21	1.813(19)
P1–C31	1.833(18)
P2–C41	1.849(18)
P2–C51	1.823(18)
P2–C61	1.843(18)
N1–C1	1.340(20)
N1–C3	1.372(19)
C1–N2	1.353(20)
N2–C2	1.379(21)
C2–C3	1.381(22)
C2–C6	1.442(23)
C3–C4	1.494(22)
C4–N3	1.254(21)
C4–O1	1.374(20)
O1–C5	1.445(20)
C6–N4	1.161(22)
C11–C12	1 394(22)
C11–C16	1.387(22)
C12–C13	1.386(23)
C13–C14	1.376(23)
C14–C15	1.373(23)
C15–C16	1.396(22)
C21–C22	1.412(22)
C21–C26	1.416(22)
C22–C23	1 369(24)
C23–C24	1.384(24)
C24–C25	1.379(25)
C25–C26	1.371(25)
C31–C32	1.391(21)
C31–C36	1.376(21)
C32–C33	1.375(24)
C33–C34	1.369(27)
C34–C35	1.392(28)
C35–C36	1.374(26)
C41–C42	1.381(24)
C41–C46	1.369(24)
C42–C43	1.381(25)
C43–C44	1.435(31)
C44–C45	1.322(32)
C45–C46	1.354(28)
C51–C52	1.385(21)
C51–C56	1.415(22)
C52–C53	1.369(24)
C53–C54	1.374(26)
C54–C55	1.347(25)
C55–C56	1.362(23)
C61–C62	1.390(21)
C61–C66	1.386(22)
C62–C63	1.392(23)
C63–C64	1.358(25)
C64–C65	1.372(25)

TABLE V. Bond Angles (°)

Atoms	Angle	Atoms	Angle
P1–Cu1–P2	119.8(2)	C33–C34–C35	119(2)
P1–Cu1–N1	108.5(4)	C34–C35–C36	120(2)
P2–Cu1–N1	120.0(4)	C31–C36–C35	121(2)
P1–Cu1–N3	105.5(4)	P2–C41–C42	118(2)
P2–Cu1–N3	114.1(4)	P2–C41–C46	122(2)
N1–Cu1–N3	82.1(6)	C42–C41–C46	119(2)
Cu1–P1–C11	111.4(7)	C41–C42–C43	122(2)
Cu1–P1–C21	121.8(6)	C42–C43–C44	118(2)
C11–P1–C21	103.8(9)	C43–C44–C45	117(2)
Cu1–P1–C31	111.3(6)	C44–C45–C46	127(3)
C11–P1–C31	103.0(9)	C41–C46–C45	118(2)
C21–P1–C31	103.6(9)	P2–C51–C52	125(2)
Cu1–P2–C41	113.5(6)	P2–C51–C56	118(2)
Cu1–P2–C51	113.6(7)	C52–C51–C56	118(2)
C41–P2–C51	104(1)	C51–C52–C53	120(2)
Cu1–P2–C61	118.1(7)	C52–C53–C54	122(2)
C41–P2–C61	101.1(9)	C53–C54–C55	119(2)
C51–P2–C61	104.7(9)	C54–C55–C56	121(2)
Cu1–N1–C1	142(2)	C51–C56–C55	121(2)
Cu1–N1–C3	110(1)	P2–C61–C62	121(2)
C1–N1–C3	107(2)	P2–C61–C66	119(2)
N1–C1–N2	113(2)	C62–C61–C66	120(2)
C1–N2–C2	103(2)	C61–C62–C63	119(2)
N2–C2–C3	112(2)	C62–C63–C64	121(2)
N2–C2–C6	123(2)	C63–C64–C65	120(2)
C3–C2–C6	126(2)	C64–C65–C66	121(2)
N1–C3–C2	105(2)	C61–C66–C65	119(2)
N1–C3–C4	117(2)		
C2–C3–C4	138(2)		
C3–C4–N3	121(2)		
C3–C4–O1	107(2)		
N3–C4–O1	132(2)		
Cu1–N3–C4	110(1)		
C4–O1–C5	115(2)		
C2–C6–N4	178(3)		
P1–C11–C12	122(2)		
P1–C11–C16	119(2)		
C12–C11–C16	119(2)		
C11–C12–C13	121(2)		
C12–C13–C14	118(2)		
C13–C14–C15	122(2)		
C14–C15–C16	120(2)		
C11–C16–C15	120(2)		
P1–C21–C22	120(2)		
P1–C21–C26	125(2)		
C22–C21–C26	115(2)		
C21–C22–C23	122(2)		
C22–C23–C24	121(2)		
C23–C24–C25	119(2)		
C24–C25–C26	121(2)		
C21–C26–C25	122(2)		
P1–C31–C32	114(2)		
P1–C31–C36	126(2)		
C32–C31–C36	119(2)		
C31–C32–C33	119(2)		
C32–C33–C34	122(2)		

for phosphine complexes, again suggests a polymeric structure and implies that the copper may be four coordinate. The sharp single peak in the cyanide stretching region implies a symmetrically bridging imidazolate ligand.

The tendency toward four coordination showed up in an unusual way in the preparation of the carbonyl complex. In a procedure similar to that which produced Cu(Dicy)(PPh_3)$_2$, a monocarbonyl complex precipitated which we formulated based on analytical data with a methanol of solvation *viz.* [Cu(CO)(Dicy)•(CH_3OH)]. The IR spectrum, which we reproduce as Fig. 1, was particularly well resolved, but had several inexplicable features. The very sharp peak at 3364 cm^{-1} could only be N–H not involved in hydrogen bonding, and the O–H of the methanol seemed not to be present. The C≡N and C≡O peaks left very clear signatures but the peak at 1634 cm^{-1} was also unexplained. Although this compound had insolubility similar to those described above, it did react with triphenylphosphine in methylene chloride to produce a soluble species with loss of carbon monoxide. Layering the solution with hexane produced crystals suitable for diffraction and the solved structure is shown in Fig. 2. The four coordinate copper has picked up two phosphine ligands, presumably by releasing from coordination one of the imidazole nitrogens, as well as the C≡O. The surprising feature is the formation of a methyl imino ester functionality on the ring system, and its participation in a bidentate chelation to the copper. In order to be certain that this group was indeed present, and not the isomeric *N*-methyl amide function, several tests were performed on the X-ray data. The positions of N3 and O1 were interchanged. This resulted, after re-refinement, in a very slightly poorer *R* factor, and significantly poorer temperature factors for the two atoms. In addition, the difference map calculated with all hydrogens present except that on N3, showed a definite residual in the vicinity of N3 and none around O1. There was also a smaller residual near N2 so some tautomerism between N3 and N2 could not be ruled out from the X-ray data, but the IR data favors a single location, most likely at N3. Thus the Cu(I)CO moiety appears to promote rapid and quantitative alcoholysis of one of the nitrile functions. There is some precedence for such a reaction in both alkyne [5] and nitrile [6] chemistry, and based on these observations as well as our own, we suggest a mechanism in which precoordination of nitrile occurs, followed by polarization and nucleophilic attack by the alcohol. Rate enhancement is typically large in cases of metal assisted solvolysis [7].

The stabilization of the imino ester by coordination is an interesting aspect of this work since the isomerism to the alkyl amide is favored thermodynamically [8]. In previous studies of similar reactions, the imino ester group was adduced mainly from IR and NMR evidence although another crystal structure was recently reported [9]. Our data for the C=N and C–O lengths of 1.254 Å and 1.374 Å agree closely with the previously reported data for the imino ester group as does the observed IR band at 1634 cm^{-1}. The imidazole ring, the nitrile, and N4 are coplanar within experimental error while N3 and O1 are twisted slightly out of this plane. In the light of the crystal structure, the IR spectrum of Fig. 1 is perfectly understandable and we now formulate the precursor as Cu(CO)(Dicyie), where Dicyie designates the mono-iminoester of dicyanoimidazole.

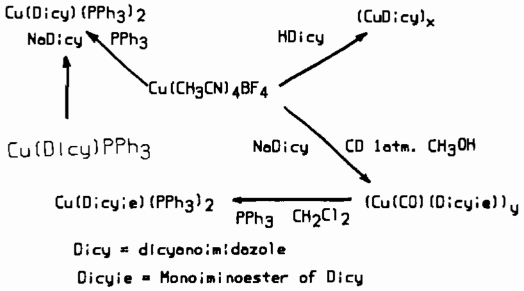

Fig. 3. Summary of synthesis.

The reactions we have observed are summarized in Fig. 3. We are continuing the investigation of Cu(I) chemistry with ligands of greater sigma donor strength in combination with various imidazoles.

Conclusion

It is well known that Cu(I) shows a strong affinity for ligands that are weak sigma donors and good pi acceptors. Indeed, as the donor strength increases, so does the tendency toward disproportionation. Thus strongly basic amines destabilize Cu(I) relative to Cu(II) [1]. On the other hand, Cu(I) normally can only bind one carbon monoxide and may reduce its coordination number if the pi acceptors are too numerous or too strong. This latter generalization is less well documented however and the several of the cases we have examined by X-ray crystallography show retention of four coordination. It may be that average Cu(I) coordination numbers will increase as more structures are determined as happened some years ago for Sn(II) which is seldom 'carbene-like' in its coordination shell.

Supplementary Material

Listings of observed and calculated structure factor amplitudes are available from the authors on request.

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