Heterolytic Cleavage of the C–C Bond of Acetonitrile with Simple Monomeric Cu^{II} Complexes: Melding Old Copper Chemistry with New Reactivity**

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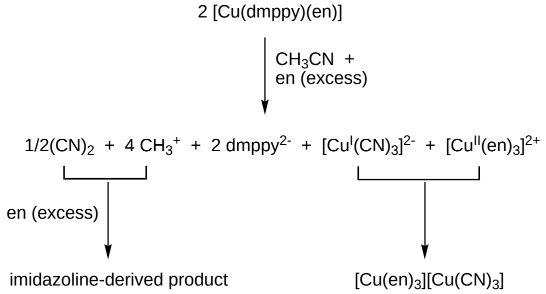
The reduction of Cu^{II} ion with cyanide (CN$^-$) to form stable cyanocopper(I) complexes (such as the trigonal-planar $[Cu(CN)_3]^{2-}$ species) and gaseous cyanogen has been known for quite some time.[1, 2] In this reaction, CN$^-$ in excess acts as both the reductant for the conversion of Cu^{II} to Cu^I and as the ligand for Cu^I, and is itself oxidized to cyanogen gas, $(CN)_2$. Historically, the rich reaction chemistry of cyanogen (including but not limited to that produced by Cu^{II} and KCN) with various organic compounds such as amines dates back well over a century.[2] The reaction of $(CN)_2$ with aliphatic diamines to produce imidazolines and polymeric amidines among other products is well documented.[2] In addition, the Cu^I cyanide complexes mentioned above also have their own interesting chemistry. The Sandmeyer reaction, for example, utilizes CuCN in the formation of aryl nitriles from their corresponding aryl diazonium salts.[3] Also, Cu^I cyanide complexes are known to form large extended structures in the presence of amines.[4, 5] Despite the reactivity of Cu^{II} with CN$^-$ (to form $[Cu^I(CN)_x]^{x-1}$ complexes), simple Cu^{II} salts in the presence of nitriles (alkyl cyanides) such as acetonitrile (CH_3CN) are generally quite stable, and hence salts of the $[Cu(CH_3CN)_4]^{2+}$ ion are common Cu^{II} starting materials for syntheses of other Cu^{II} complexes.[1] The Cu^I salts of CH_3CN are also stable, and the use of $[Cu(CH_3CN)_4]^+$ salts in syntheses of Cu^I complexes has been equally exploited.[1] In fact, metal-mediated splitting of the C–CN bond in alkyl cyanides (e.g. CH_3CN) has so far only been shown to occur with the aid of reactive low-valent metal complexes such as those containing a Pt^0 or Ni^0 metal center.[6, 7] To our knowledge, the reaction of Cu^{II} with CH_3CN to produce $[Cu^I(CN)_3]^{2-}$ (and a methylated product) has not been demonstrated as yet.

We have recently reported the syntheses and structures of several monomeric Cu^{II} complexes coordinated to the deprotonated tridentate ligand *N,N'*-dimethylpyridine-2,6-dicarboxamide (dmppyH$_2$, where the H atoms represent the dissociable carboxamido hydrogen atoms), and also commented on the instability of most of these complexes in solution. We speculated that the instability and/or reactivity of [Cu^{II}(dmppy)(L)] complexes in solution may be due to severe out-of-plane distortion of the Cu^{II} ion from the dmppy^{2-} plane.[8] The highly basic nature of the dmppy^{2-} ligand could be another contributing factor for this reactivity. Here we report the synthesis and structure of [Cu(dmppy)(en)] (en = ethylenediamine) and describe its reactivity toward CH_3CN. When [Cu(dmppy)(en)] is added to a mixture of CH_3CN and en, crystalline $[Cu(en)_3][Cu(CN)_3]$ is isolated in nearly quantitative yield (based on Cu) in addition to intact dmppyH$_2$, and a methylated imidazoline-derived polymeric material (Scheme 1). In this chemistry, the formation of the cyanocopper(I) complex $[Cu(CN)_3]^{2-}$ and the methylated polymeric product must be a result of the heterolytic cleavage of CH_3CN into CH_3^+ and CN$^-$.



Scheme 1. Reaction of [Cu(dmppy)(en)] with CH_3CN in the presence of ethylenediamine initally produces $[Cu(en)_3][Cu(CN)_3]$, dmppyH$_2$, and cyanogen, which slowly reacts to yield a imidazoline-derived product.

The complex [Cu(dmppy)(en)] was synthesized from $[\{Cu(dmppy)(py)\}_2]$[8] and ethylenediamine in DMF. [Cu(dmppy)(en)] has only partial solubility in DMF and crystals suitable for an X-ray structure analysis of this complex are obtained upon careful layering a DMF/en solution onto a solution of $[\{Cu(dmppy)(py)\}_2]$ also in DMF. The structure of [Cu(dmppy)(en)] shows that the dmppy^{2-} ligand coordinates to the Cu^{II} ion in the basal plane of a distorted square-pyramidal geometry; the en ligand occupies the remaining two sites (Figure 1).[9] When [Cu(dmppy)(en)] is suspended in a mixture of CH_3CN and en (10:1 v/v), large

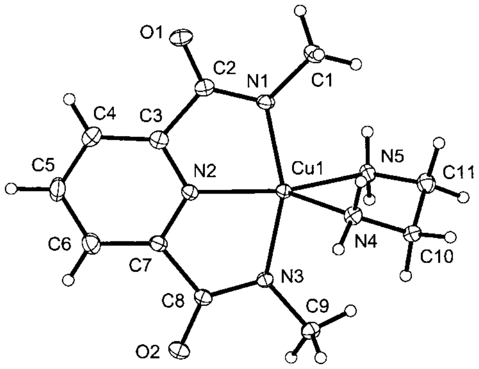


Figure 1. Structure of [Cu(dmppy)(en)] showing 50% thermal ellipsoids and selected atom labels. Selected bond lengths [Å] and angles [°]: Cu1-N1 2.0206(17), Cu1-N2 1.9455(18), Cu1-N3 2.0421(17), Cu1-N4 2.210(3), Cu1-N5 2.073(2); N2-Cu1-N1 79.20(6), N2-Cu1-N3 79.20(6), N1-Cu1-N3 158.23(7), N2-Cu1-N5 148.89(8), N1-Cu1-N5 99.28(9), N3-Cu1-N5 97.81(8), N2-Cu1-N4 127.98, N1-Cu1-N4 95.61(8), N3-Cu1-N4 99.76(8), N5-Cu1-N4 83.12(7).

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crystals of [Cu(en)$_3$][Cu(CN)$_3$] (Figure 2)[10] appear over a period of 1–2 weeks along with a flocculent white precipitate. Although [Cu(en)$_3$][Cu(CN)$_3$] has been synthesized previously,[11] and the structures of the individual ions [Cu(en)$_3$]$^{2+}$[12, 13] and [Cu(CN)$_3$]$^{2-}$[14, 15] have been determined separately in other crystal lattices, the structure of [Cu(en)$_3$][Cu(CN)$_3$] (Figure 2) as a unit had not been determined until now. The reaction of [Cu(dmppy)(en)] with CH$_3$CN and ethylenediamine is slow mainly due to its low solubility under the conditions used, and also appears to be quite complex in nature (Scheme 1). Analogous complexes such as [Cu(dmppy)-(bpy)],[8] which are soluble in CH$_3$CN, react faster in the en/CH$_3$CN mixture and cleave CH$_3$CN at a faster rate (1–2 days). The isolation of [Cu(en)$_3$][Cu(CN)$_3$] indicates that cleavage of CH$_3$CN must be heterolytic due to the presence of CN$^-$ in the products. As mentioned above, the reduction of Cu^{II} to Cu^{I} and subsequent formation of [Cu(CN)$_3$]$^{2-}$ is well established. In fact, Cu^{II} complexes of CN$^-$ are not particularly common.[16]

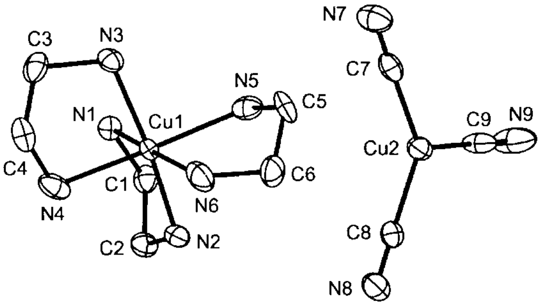
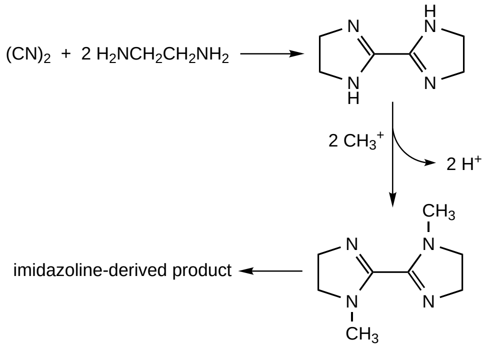


Figure 2. Structure of [Cu(en)$_3$][Cu(CN)$_3$] showing 50 % thermal ellipsoids and selected atom labels. Selected bond lengths [Å] and angles [°]: Cu1-N1 2.367(4), Cu1-N2 2.047(4), Cu1-N3 2.040(3), Cu1-N4 2.097(4), Cu1-N5 2.120(4), Cu1-N6 2.320(4), Cu2-C7 1.930(5), Cu2-C8 1.934(4), Cu2-C9 1.924(5), C9-N9 1.151(6); N1-Cu1-N6 172.08(14), N4-Cu1-N5 169.48(14), N2-Cu1-N3 170.62(15), C9-Cu2-C7 119.98(17), C9-Cu2-C8 119.95(17), C7-Cu2-C8 120.01(16).

Determination of the exact fate of the CH$_3^+$ group produced from the heterolytic cleavage of CH$_3$CN, however, is a less trivial task. We were successful in recovering the intact dmppyH$_2$ ligand from the solution after the reaction was complete.[17] ^{1}H NMR and mass spectra data reveal that the recovered dmppyH$_2$ ligand does not contain any additional methyl groups derived from the heterolytic cleavage of CH$_3$CN, as had been initially expected. Cyanogen is known to react with ethylenediamine to yield 2,2′-bis(2-imidazoline) (Scheme 2).[2] Data from ^{1}H NMR, IR, and mass spectral analysis on the white precipitate[18] led us to conclude that the expected imidazoline product is formed in our case, and that it is also methylated, presumably by the methyl groups from CH$_3$CN cleavage (Scheme 2). Although we were not able to determine the exact structure of this species, the gradual conversion in the mass spectra of high molecular weight peaks (at *m*/*z* 274.7 and 168.1) to a single peak at *m*/*z* 83.1, which is consistent with the degredation of a polymeric species to an *N*-methylimidazoline monomer, supports the assignment of a methylated imidazoline. Furthermore, ^{1}H NMR data reveal only three peak positions in the methyl and methylene region ([D$_6$]DMSO: $\delta = 2.7$, 2.9, and 3.3). The IR spectrum of this material is dominated by a band at 1592 cm^{-1} which is assigned to the C=N stretching frequency. In addition, absorptions in the range expected for C–H stretches (3452 cm^{-1}) are also present. It should be noted that the reaction depicted in Scheme 2 is only one possibility (or only part of what may be occurring) and this scheme does not account for all the methyl groups produced by CH$_3$CN cleavage.



Scheme 2. Possible scheme for the reaction of cyanogen with ethylenediamine to produce 2,2′-bis(2-imidazoline) which may be subsequently methylated by CH$_3^+$ and react further to produce the imidazoline-derived product.

In conclusion, we have prepared a very simple Cu^{II} complex that cleaves CH$_3$CN heterolytically into CN$^-$ and CH$_3^+$. This reaction is quite novel for Cu^{II}, although the reactivity subsequent to CH$_3$CN clevage is well established in copper chemistry. The reactivity of [Cu(dmppy)(en)] and related species toward CH$_3$CN appears to be dictated by the highly basic nature of the dmppy^{2-} ligand.[19] Further work directed at evaluating the mechanism of the CH$_3$CN cleavage is currently underway in our laboratory.

Experimental Section

[Cu(dmppy)(en)]: A solution of [{Cu(dmppy)(py)}$_2$] (0.10 g, 0.15 mmol) in DMF (3 mL) was carefully layered on a solution of en (0.09 g, 1.5 mmol) in DMF (1 mL). Within 48 h, large blue-green crystalline blocks had formed on the walls of the vial which were filtered off, washed with CH$_3$CN, and dried under vacuum (0.06 g, 63 % yield). Crystals suitable for an X-ray structure determination of [Cu(dmppy)(en)] were grown in a capillary tube by the same method. FT-IR (KBr): $\tilde{\nu} = 3262$ (m), 3173 (m), 2934 (w), 2861 (w), 1619 (m), 1592 (s), 1572 (s), 1384 (m), 1363 (m), 1296 (m), 1068 (m), 1047 (m), 1017 (m), 835 (w), 750 (m), 740 (m), 684 (m), 572 (w); EPR (100 K, DMF/Tol (1:1 v/v), 9.43 GHz): $g_{\parallel} = 2.22$, $g_{\perp} = 2.06$, $A_{\parallel} = 178$ G.

Reaction of [Cu(dmppy)(en)] with en and CH$_3$CN: en (0.3 mL) was added to a suspension of [Cu(dmppy)(en)] (0.020 g, 0.06 mmol) in CH$_3$CN (3 mL) and the mixture was sealed and stored at 25 °C for 1–2 weeks. During this time, all the suspended [Cu(dmppy)(en)] had been replaced by large crystals of [Cu(en)$_3$][Cu(CN)$_3$] (0.018 g, 80 % yield based on copper) and a flocculent white precipitate. The latter was collected by centrifugation and dried under vacuum. FT-IR of [Cu(en)$_3$][Cu(CN)$_3$] (KBr): $\tilde{\nu} = 3310$ (s), 3248 (s), 2950 (CN, m), 2884 (m), 2066 (s), 1586 (m), 1323 (w), 1101 (w), 1037 (s), 973 (m), 707 (w), 527 (w).

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[9] a) Crystal data for [Cu(dmppy)(en)]: Blue plates of dimensions $0.35 \times 0.13 \times 0.06$ mm^3; monoclinic, space group $P2_1/n$, $a = 7.022(2)$, $b = 16.136(5)$, $c = 11.313(4)$ Å, $\beta = 93.11(2)^\circ$, $V = 1280.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.634$ Mg m^{-3}, $2\theta_{max} = 63^\circ$, $\mu(Mo_{K\alpha}) = 1.713$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; the data were collected at 92(2) K on a Bruker SMART 1000 diffractometer; a total of 34867 reflections were measured, of which 9910 were independent ($R_{int} = 0.067$) and included in the refinement; mim./max. transmission = 0.5855/0.9042; solution by direct methods (SHELXS-97, Sheldrick, **1990**); refinement by full-matrix least-squares based on F^2 (SHELXTL 6.1, Sheldrick, **2001**); 175 parameters, $R1 = 0.0641$, $wR2 = 0.1254$ for all data; $R1 = 0.0460$ computed for 7282 observed data ($I > 2\sigma(I)$). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-167732 [Cu(dmppy)(en)] and CCDC-167733 [Cu(en)$_3$][Cu(CN)$_3$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] Crystal data for [Cu(en)$_3$][Cu(CN)$_3$]: Blue parallelpiped crystals of dimensions $0.50 \times 0.38 \times 0.28$ mm^3; Monoclinic, space group $P2_1/n$, $a = 7.6690(9)$ Å, $b = 17.2770(19)$ Å, $c = 12.4609(13)$ Å, $\beta = 95.038(9)^\circ$, $V = 1644.7(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.557$ Mg m^{-3}, $2\theta_{max} = 55^\circ$, $\mu(Mo_{K\alpha}) = 2.591$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; the data were collected at 130(2) K on a Siemens P3 diffractometer; a total of 4171 reflections were measured, of which 3769 were independent ($R_{int} = 0.044$) and included in the refinement; mim./max. transmission = 0.3574/0.5307; solution by direct methods (SHELXS-97, Sheldrick, **1990**); refinement by full-matrix least squares based on F^2 (SHELXTL 6.10, XL, Sheldrick, **2000**); 217 parameters, $R1 = 0.0811$, $wR2 = 0.1109$ for all data; $R1 = 0.0463$ computed for 2532 observed data ($I > 2\sigma(I)$).[9b]

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[17] Solvent from the filtrate was removed under vacuum, and the residue was dissolved in H$_2$O and extracted with CH$_2$Cl$_2$. The organic layer was collected, dried, and solvent removed under vacuum to yield pure dmppyH$_2$.

[18] The floculent white precipitate formed upon reaction of [Cu(dmppy)(en)] with CH$_3$CN and ethylenediamine was seperated by centrifugation and dried under vacuum.

[19] One of the reviewers has suggested that a amide-bound Cu^{III} could be involved in the mechanism of the C–C bond cleavage of acetonitrile. Although this appears to be plausible, we do not have any spectroscopic evidence of an intermediate containing trivalent copper at this time.

Pt^{II}-Catalyzed Intramolecular Reaction of Furans with Alkynes[**]

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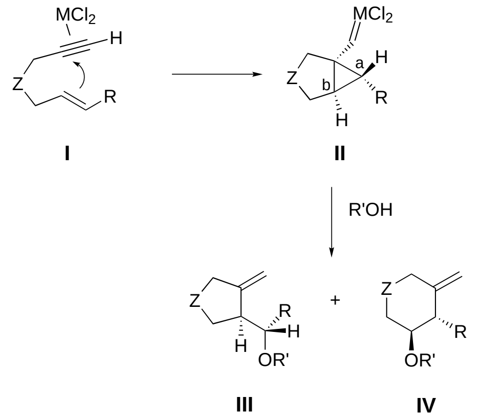
The coordination of electrophilic PtCl$_2$ to the C≡C bond of an enyne (**I**, Scheme 1) promotes intramolecular reaction of the alkene to form a cyclopropyl Pt carbene intermediate **II**.[1, 2] Subsequent attack of an alcohol or water at the cyclopropyl carbon atoms C$_a$ and C$_b$ of **II** leads to the formation of five- or six-membered carbo- or heterocyclic rings under catalytic conditions.[1]



Scheme 1. Metal-induced reaction of enynes to yield five- or six-membered rings.

These cyclizations are also catalyzed by AuCl$_3$ and some Ru^{II} complexes.[1] In this regard, the recent finding that the intramolecular reaction of furans with alkynes can be catalyzed by AuCl$_3$ to afford phenols is of considerable interest.[3, 4] The reaction was proposed to proceed by a [4+2] cycloaddition of the furan to the alkyne followed by cleavage of the resulting oxabicyclic adduct.[3] Although this mechanistic proposal is reasonable, the related intramolecular reaction of arenes with alkynes with catalysis by Pt^{II} or Ru^{II}[5] was proposed to take place by electrophilic aromatic substitution with an (η^2-alkyne)metal electrophile.

We have found that 5-furyl-1-alkynes are also cyclized by PtCl$_2$ as catalyst. Several intermediate products could be obtained by conducting the reaction in an aqueous solvent. A clearer picture of the mechanism was obtained by performing

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