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Only the Cu^+ Coordinated to the π-System of the C$\equiv$N Group Activates upon Collision C—H and C—C Bonds of Nitriles

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Summary: Collision-induced dissociations of organometallic complexes $Cu(RCN)^+$, generated by the reaction of Cu^+ with linear nitriles in the gas phase, generates products distinct from that of $M(RCN)^+$ complexes (M = Fe, Co, Ni). While the gas-phase chemistry of the latter is well-described in terms of an *end-on* coordination of the type RCN-M^+, the dissociation products of the RCN/Cu^+ complexes point to a *side-on* complexation.

The reactivity of the first-row transition-metal ions Fe^+,[1] Co^+,[2] and Ni^+[3] to unbranched nitriles has been characterized by an *end-on* type of coordination where the metal initially coordinates to the lone-pair electrons of the nitrogen atom. A linear or near linear M–N–C unit results.[4] These species then undergo preferential C–H activation of the (terminal) methyl groups of nitriles containing four to eight carbon atoms,[1-3] generating in competition H_2 and C_2H_4 from the ω- and ($\omega - 1$)-positions. As the chain length is increased, activation of the internal C–H groups, i.e. the methylene C–H, becomes the dominant mode of reaction. The major differences between the metals studied thus far have been the different chain lengths necessary to allow internal C–H activation. In this report we describe the behavior of Cu^+ (a d^{10} atom), which is distinct from the preceding three transition-metal ions of the period. Instead of terminal C–H activation, Cu^+ appears to activate C–C and C–H bonds in the vicinity of the nitrile group, thus suggesting that *side-on* coordinated species serve as reactive intermediates.

The fact that Cu^+ has nearly the same reactivity as Fe^+ and Co^+, as reported recently,[5] toward C–H activation of simple alkenes is already surprising in light of the fact that Cu^+ has fully occupied d orbitals. Hence, its reactivity is expected to be more in line with that of Cr^+, a d^5 metal ion, which is unreactive with alkenes[5] but shows high reactivity with some alkynes.[6] As stated by Peake and Gross[5] further studies are warranted in order to unravel the unusual reactivity of Cu^+.

Table I. Partial Collisional Activation Spectra of Cu(nitrile)$^+$ Complexes[a]

	m/z			
nitrile	65[b]	92	105	118
$CH_3(CH_2)_2CN$	66	9	13	12
$CH_3(CH_2)_3CN$	58	12	15	15
$CH_3(CH_2)_4CN$	51	12	21	16
$CH_3(CH_2)_5CN$	44	11	22	23

[a] Data are given in % $\sum$ fragment ions = 100. Signals with intensities smaller 5% were omitted. [b] This signal corresponds to only $^{65}Cu^+$, i.e. detachment of the RCN ligand.

Table II. Effects of Deuterium Labeling on the Elemental Compositions of Ions A, B, and C

	ionic products		
precursor	A	B	C
$CH_3(CH_2)_3$-CD_2CN	$Cu(HCN)^+$, >99%	$Cu(D_2C_2N)^+$, >99%	$Cu(H_2DC_3N)^+$, ~70% $Cu(HD_2C_3N)^+$, ~30%
$CH_3(CH_2)_2$-CD_2CH_2CN	$Cu(HCN)^+$, ~70% $Cu(DCN)^+$, ~30%	$Cu(H_2C_2N)^+$, >99%	$Cu(HD_2C_3N)^+$, >99%
$CH_3CH_2CD_2$-$(CH_2)_2CN$	$Cu(HCN)^+$, ~70% $Cu(DCN)^+$, ~30%	$Cu(H_2C_2N)^+$, >99%	$Cu(H_3C_3N)^+$, >99%

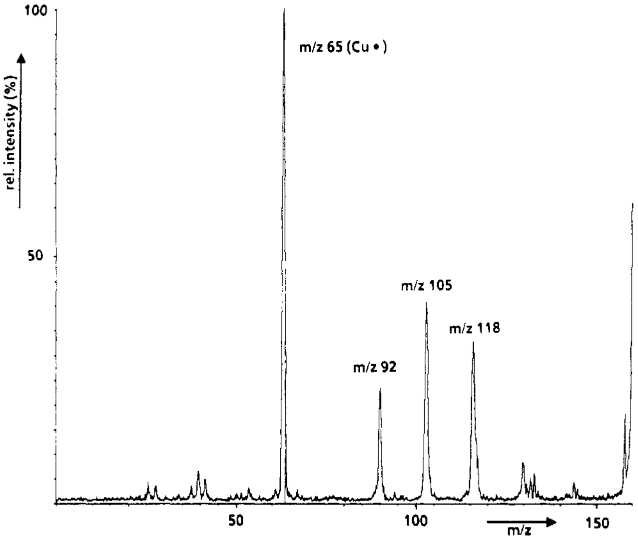

Figure 1. Collisional activation spectrum of $^{65}Cu(CH_3$-$(CH_2)_4CN)^+$.

Cu^+ was generated in a FAB[7] source of a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer of BEB configuration (B stands for magnetic and E for electric sector)[8] by bombarding $CuSO_4$, dissolved in water, with 8 keV of xenon atoms, using a procedure originally developed by Campana et al.[9] The cation was then re-

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[1] Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* 1987, *109*, 98.

[2] Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* 1987, *109*, 0000.

[3] Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes*, in press.

[4] In the present context we use the term "linear" very loosely, as we know little about the energetics and electronics of this coordination. No doubt, that depending on the internal energy of RCN/M^+ complexes deviation from linearity of the M–N–C–C unit must occur. There exist a few experimental studies that deal with the coordination of nitriles to metals. For references, see: (a) Wexler, R. M.; Muetterties, E. L. *J. Phys. Chem.* **1984**, *88*, 4037. (b) Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623. (d) Fewer yet are theoretical calculations dealing with this subject and the possibility of *side-on* coordination. One such investigation that, however, deals only with the HCN ligand and is based on concepts of qualitative MO theory may be found in: Howell, J. A. S.; Saillard, J. Y.; LeBenze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

[5] Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* 1987, *109*, 600 and references cited therein.

[6] Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* 1987, *6*, 0000 and references cited therein.

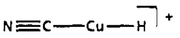
[7] FAB stands for fast atom bombardment. For leading references see: Barber, M.; Bordoli, R. S.; Elliott, G. J.; Sedgewick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *54*, 645A.

[8] Detailed description of the instrument and its operation are given in: (a) Weiske, T. Ph.D. Thesis, Technical University Berlin, D83, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665. (c) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368.

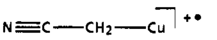
[9] (a) Freas, R. B.; Ross, M. M.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6195. (b) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6202. (c) Mestdagh, H.; Morin, N.; Rolando, C. *Tetrahedron Lett.* **1986**, 33.

acted with the nitriles (ca. 10^{-3} Torr),[10] and the resulting complex ($^{65}Cu^+$/nitrile) accelerated to 8 keV kinetic energy, mass selected by using BE, and collided with He (ca. 10^{-5} Torr) to induce fragmentation.[11] Spectra were recorded by scanning the second magnet. Organometallic complexes formed via FAB have been shown[3,12] to produce results identical with those for complexes formed through ion/molecule reactions of neutral organic substrates with transition-metal ions; the latter were generated upon electron-impact ionization of suitable organometallic precursors.

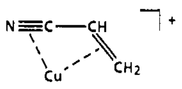
The reaction of Cu^+ with the linear nitriles from propyl to hexyl cyanide (Table I; Figure 1) yield three major products (in addition to Cu^+ (m/z 65) which is a simple ligand detachment reaction), corresponding to m/z 92, 105, and 118. Labeling the cyanide group with ^{13}C in hexyl cyanide produces a quantitative mass shift of one unit for all three products. Thus, the cyanide group remains coordinated to the metal throughout the reactions. Proposed and by no means proven[13] structures A–C are shown below. These assignments (which do not rule out isomers, as for example a structure $HCN{-}Cu^+$ as an alternative to A, as suggested by a reviewer) are consistent with the data obtained from the study of deuterium-labeled isotopomers (Table II).



A (m/z 92)



B (m/z 105)



C (m/z 118)

Labeling the α-positions with deuterium produces a shift of two mass units for B and one for C. No shift in A is observed. Some 30% of C, however, have incorporated two deuterium atoms. Deuterium labeling of the β-positions produces a one deuterium shift for some of A (ca. 30%), although the rest remains unchanged. No mass shift is observed for B, and a shift of two mass units is observed for C. Labeling the γ-positions again produces a shift of one mass unit for ca. 30% of A, while the rest remains unchanged. No mass shifts are observed for either B or C.

The labeling results reveal complex mechanisms *totally distinct* from those earlier proposed for Fe^+, Co^+, and Ni^+.[1-3] For example, the H atom of ion A does not come from the α-position but originates at least from the β- and γ-positions (>60%) and perhaps from C–H bonds even further away from the functional group. Ion B is produced via insertion of the Cu^+ ion into the $C(\alpha)–C(\beta)$ bond. The α-methylene group is fully retained in the ionic fragment B. Ion C may be formed by allylic C–H activation of the α-positions, followed by β-alkyl transfer and reductive elimination. The alternative sequence is also reasonable with initial C–C cleavage of the $C(\beta)–C(\gamma)$ bond followed by a hydrogen atom shift. However, the former pathway may be more favorable due to the initial activation of the allylic C–H position. Another mechanism is "dissociative attachment" whereby Cu^+ associates with a functional group (usually a heteroatom) and causes an organic molecule to rearrange and/or cleave. This mechanism has been proposed for the reactions of Cu^+ with ketones and esters,[14] alkyl chlorides,[15] and alcohols.[16,17] However, as stated by Gross and Peake[5] "dissociative attachment is thought to be a trait of alkali-metal ions".[18,19] We thus reacted Na^+ and Li^+, which bonds more strongly to heteroatoms, with pentyl cyanide and observed essentially no reactions. The only product was due to the loss of the ligand to regenerate Na^+ and Li^+, respectively.

Finally, it should be mentioned that *end-on* coordination of Cu^+ with RCN should also occur from simple electrostatic considerations. This mode is, for example, operative in the protonation and alkylation of nitriles that take place exclusively at the lone pair of the nitrogen.[20] However, this thermochemically favorable coordination most probably generates *unreactive* RCN/Cu^+ complexes. The species, which upon collisional activation[21] give rise to the products A, B, and C, are more likely to have a *side-on* coordination. If the reactive species would possess an *end-on* structure, we should observe products identical with those generated from RCN/M^+ (M = Fe, Co, Ni).

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[10] It should be mentioned that the detailed mechanism by which the RCN/Cu^+ complexes are formed from sputtered Cu^+ (or species of complex compositions) is unknown. The pressure in the ion source, however, is high enough to probably "cool" the complex by multiple collisions. Furthermore, the RCN/Cu^+ complex is big enough so that its lifetime is lengthened by dispersing the internal energy, gained in the complex formation, to the many vibrational modes.

[11] For leading references on this methodology see: (a) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (b) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum: New York, 1978.

[12] (a) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, R1. (b) Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.*, in press.

[13] Proposed structures are fictitious in nearly all cases studied in mass spectrometry; they are based on plausible considerations using as much direct and indirect "evidence" as available from experiments and model considerations. Strictly speaking, without detailed spectroscopic studies and state of the art high level ab initio MO calculations, both of which cannot be applied in the present case due to size of the molecules in question, none of the structures are proven. Nevertheless, the heuristic merits of such structural representations are indeniable in chemistry, as long as speculations remain within acceptable limits.

[14] Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

[15] Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794.

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[19] Hodges, R. V.; Beauchamp, J. L. *Anal. Chem.* **1976**, *48*, 825.

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[21] In order to study the effects of internal energy, deposited in the collision event in the RCN/Cu^+ complexes, we have performed some initial experiments at lower kinetic energies. It turned out that the production of ions A, B, and C from RCN/Cu^+ is not any longer observed when the kinetic energy of RCN/Cu^+ is less than 4 keV. Similarly, no fragment ions are observed under collision-free conditions.

Regioselective Insertion of Acrylonitrile into the Pt–N Bond of Hydrido(phenylamido)bis(triethylphosphine)platinum(II). A Model Step for Olefin Amination

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Summary: The new hydridoamido complex *trans*-$PtH(NHPh)(PEt_3)_2$ (I) inserts acrylonitrile to form *trans*-$PtH[CH(CN)(CH_2NHPh)](PEt_3)_2$, which reductively eliminates 3-anilinopropionitrile.

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