Activation of the CN Ligand in the Gas Phase: Reaction of Cyanoiron Cations with Allyl Chloride

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Summary: Gas-phase cationic complexes $Fe(CN)L_x^+$, obtained from reaction of $Fe(CO)_n^+$ with ICN, react with allyl chloride by two successive ligand coupling reactions, involving formation of a N−C bond leading to an isonitrile complex followed by formation of a C−C bond.

The gas-phase chemistry of cationic transition metal complexes is very rich and very dependent on the nature and number of ligands on the metal center.[1,2] Study of the reactivity of $Fe(CO)_n^+$ ions with allyl chloride has shown the occurrence of ligand coupling in the resulting metal complex $FeC_6H_{10}Cl_2^+$.[3] In order to study the influence of ligand nature on this type of reactivity, the cyano ligand appeared interesting for comparison with the carbonyl ligand. We report here that the reaction between $FeI_xC_yN_y^+$ complexes (arising from reaction of $Fe(CO)_n^+$ with cyanogen iodide) and allyl chloride results in a different type of gas-phase coupling involving the CN ligand.

Reactions of bare transition metal cations of the first row with cyanogen iodide produce $M(CN)^+$ cations.[4] In order to obtain and characterize cyanoiron cations bearing more than one ligand, iron carbonyl cations $Fe(CO)_n^+$ were reacted with cyanogen iodide. The experiments were performed on the MS/MS/MS multiquadrupole mass spectrometer described elsewhere.[5] Briefly, it is composed of the following parts: EI/CI source, first quadrupole analyzer, first RF-only collision cell, second analyzer, second RF-only collision cell, third analyzer, and detector. Under normal reaction conditions, the kinetic energy of the incoming ions followed a distribution centered around 1 eV and ca. 1 eV wide in the laboratory frame.[6]

Iron carbonyl cations $Fe(CO)_n^+$ (n = 0−5) were obtained from electron impact on $Fe(CO)_5$. Reaction of these mass-selected cations with cyanogen iodide in the first collision cell afforded various $Fe(CO)_nI_x(CN)_y^+$ complexes (n = 0−3, x = 0−2, y = 0−3), the most representative of which is $FeIC_2N_2^+$, the major product from $Fe(CO)^+$ and $Fe(CO)_2^+$. The ions $FeI_2C_3N_3^+$ (major product from $Fe(CO)_3^+$ and $Fe(CO)_4^+$), $FeICN^+$, $Fe(CO)ICN^+$, FeI_2CN^+, $FeI_2C_2N_2^+$, ... were also obtained.

When submitted to CAD in the second collision cell (5−25 eV; Xe as collision gas), $FeIC_2N_2^+$ led mainly to $FeCN^+$, corresponding to ICN loss, along with a minor amount of Fe^+ (increasing with collision energy) and traces of I^+. Therefore, this ion can be viewed as a two-ligand complex $Fe(CN)(ICN)^+$.[7] Detection of I^+ suggests that the ICN ligand is not bound by the I atom but by the CN group, likely by the N atom and similarly to nitrile ligands;[8] we have no indication concerning the binding mode of the CN ligand.

Mass-selected cyano iron cations were reacted with allyl chloride in the second collision cell. The monoligated $FeCN^+$ ion behaved in a similar way as Fe^+,[3] leading only to $C_3H_5^+$ (and further reaction products with allyl chloride) by chloride abstraction:

$$FeCN^+ + C_3H_5Cl \rightarrow C_3H_5^+ + FeClCN$$

No $FeC_3H_5Cl^+$ ion was detected, showing that $FeCN^+$ did not undergo ligand substitution, contrary to the less strongly bound $FeCO^+$.[3]

The major reaction pathway of $Fe(CN)(ICN)^+$ ions with allyl chloride can be summarized in the following scheme:

$$Fe(CN)(ICN)^+ + C_3H_5Cl \rightarrow FeClC_4H_5N^+\ (m/z\ 158{-}160) + ICN$$

$$FeClC_4H_5N^+ + C_3H_5Cl \rightarrow C_7H_{10}N^+\ (m/z\ 108) + FeCl_2$$

This scheme was established from the variation of product abundances with allyl chloride pressure; this method also allowed us to check that all or almost all of the incoming ions were able to react with the same efficiency, therefore excluding the involvement of excited

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(1) Review: Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121−1177 and references cited therein.

(2) (a) Stöckigt, D.; Sen, S.; Schwarz, H. *Chem. Ber.* **1993**, *126*, 2553−2557. (b) Tjelta, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 5531−5533. (c) Armentrout, P. B. *Acc. Chem. Res.* **1995**, *28*, 430−436.

(3) Mestdagh, H.; Rolando, C. *J. Am. Chem. Soc.* **1989**, *111*, 3476−3478.

(4) Sablier, M.; Capron, L.; Mestdagh, H.; Rolando, C. *Tetrahedron Lett.* **1994**, *35*, 2895−2898.

(5) Beaugrand, C.; Devant, G.; Jaouen, D.; Mestdagh, H.; Morin, N.; Rolando, C. *Adv. Mass Spectrom.* **1989**, *11A*, 256.

(6) The decelerating potential voltage applied to the collision cell was normally adjusted to its maximum value allowing satisfying ion recovery. In order to estimate the kinetic energy distribution of the reactant ions, voltage was progressively increased starting from this value and the resulting ion intensity decrease was followed; the energy distribution was obtained by derivation. Increase of 2 V resulted in the loss of more than 90% of the ions.

(7) Comparison of the CAD spectrum of $FeCN(ICN)^+$ with those of other ICN-containing Fe^+ complexes is in agreement with the proposed structure: ions $FeI(ICN)^+$ (obtained from $Fe(CO)_2^+$ and ICN) and $FeCl(ICN)^+$ (obtained from $Fe(ICN)^+$ and allyl chloride) lead respectively to FeI^+, with only a trace of $FeCN^+$, and to $FeCl^+$, with no detectable FeI^+ or $FeCN^+$. In these three complexes ICN loss is the nearly exclusive fragmentation pathway, suggesting the presence of a molecular ICN ligand rather than an inserted structure. In the case of $FeIC_2N_2^+$, an inserted high-valent species such as $FeI(CN)_2^+$ would have been expected to give at least a small amount of FeI^+ along with $FeCN^+$.

(8) See for example: (a) Czekay, G.; Eller, K.; Schroeder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1277−1278. (b) Stöckigt, D.; Sen, S.; Schwarz, H. *Organometallics* **1994**, *13*, 1465−1469.

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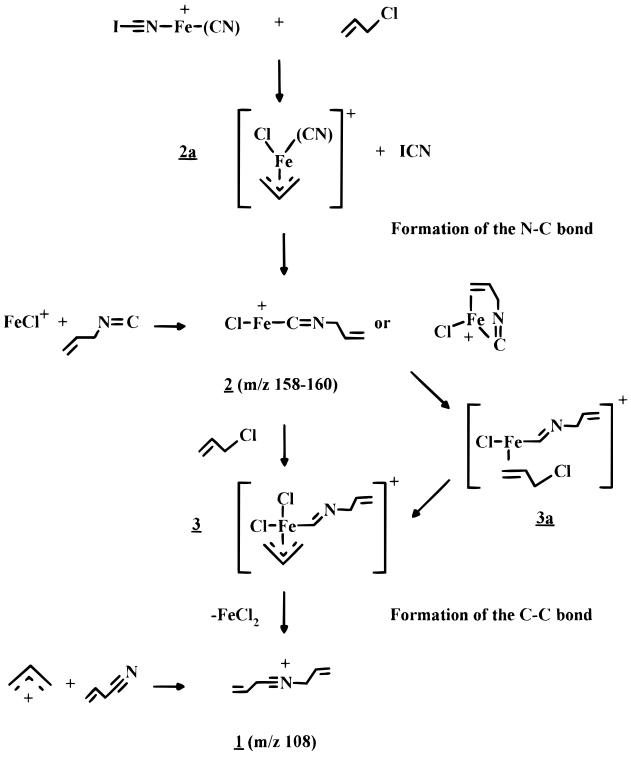
reactant ions.[9] The same successive ion products were also obtained in significant quantities from reaction of $Fe(CN)(ICN)_2^+$ or $Fe(ICN)_2^+$ with allyl chloride.[10,11]

In order to check that $C_7H_{10}N^+$ arose from $FeCl\text{-}C_4H_5N^+$, the corresponding reaction was effected separately: $Fe(CN)(ICN)^+$ ions, generated from a mixture of $Fe(CO)_5$ and ICN, were reacted with allyl chloride in the first collision cell;[12] reaction of the resulting $FeClC_4H_5N^+$ ions with allyl chloride in the second collision cell gave only $C_7H_{10}N^+$ and a minor amount of $C_3H_5^+$. The final product ion $C_7H_{10}N^+$ results from the coupling of two C_3H_5 and one CN unit, therefore requiring the formation of two new bonds. Its CAD spectrum consisted of $C_3H_5^+$ exclusively, and its reaction with CD_3CN led to $C_5H_5D_3N^+$ (replacement of C_3H_5CN by CD_3CN) and $C_9H_{10}D_3N_2^+$ (addition of CD_3CN). Both spectra were identical to the corresponding spectra of $C_7H_{10}N^+$ resulting from reaction of the $C_3H_5^+$ ion (generated in source from allyl chloride) with allyl cyanide $CH_2{=}CHCH_2CN$. According to these results, structure **1** can be assigned to the $C_7H_{10}N^+$ ion.

In order to establish the structure of the intermediate $FeClC_4H_5N^+$, its reactivity and CAD spectra were compared with those of isobaric complexes obtained in different ways. Reaction of $FeCl^+$ (generated from a mixture of $Fe(CO)_5$ and CH_2Cl_2) with allyl cyanide, propenyl cyanide, or allyl isocyanide in the first collision cell led respectively to two isomeric nitrile complexes $(CH_2{=}CHCH_2CN)FeCl^+$ and $(CH_3CH{=}CHCN)FeCl^+$ or to the isonitrile complex $(CH_2{=}CHCH_2NC)FeCl^+$. Of these three isomeric ions, only the isocyanide complex gave the $C_7H_{10}N^+$ ion when reacted with allyl chloride. In addition, its CAD spectrum was identical with that of our intermediate, consisting of $C_3H_5^+$ (FeClCN loss; 85−88%) along with small amounts of $FeCl^+$ (C_4H_5N loss; 7−10%) and $FeClHCN^+$ (C_3H_4 loss; 4−9%). The CAD spectra of the allyl and propenyl cyanide complexes consisted respectively of $C_3H_5^+$ (59%) + $FeCl^+$ (41%) and of $FeCl^+$ (100%).

Scheme 1



These results indicate that the reaction of $FeCN(ICN)^+$ with allyl chloride and the reaction of $FeCl^+$ with allyl isocyanide give identical $FeClC_4H_5N^+$ ions, to which structure **2** can be assigned. Scheme 1 summarizes the likely reaction sequence involved in the observed activation of the CN ligand. For the stable form of the $FeClC_4H_5N^+$ complex, structure **2** containing the molecular isonitrile ligand was preferred over inserted structure **2a** which might seem more consistent with the CAD spectrum, since it accounts for the ligand substitution reactivity and corresponds to the formation of the new C−N and C−C bonds in successive steps. Structure **2a**, analogous to the known stable complex $(C_3H_5)Fe(CN)^+$,[13] can be viewed as a higher energy intermediate on the fragmentation pathway of **2**, as well as on its formation route from $FeCN(ICN)^+$. This is consistent with the known properties of gas-phase cationic isonitrile iron complexes: iron does not spontaneously insert into the C−N bond, but upon collisional activation or metastable ion formation iron complexes undergo a variety of fragmentation pathways including N−C bond cleavage.[14]

It is interesting to notice that both steps of the mechanism depicted in Scheme 1 constitute the gas-phase analogue of well-known organometallic reactions in solution. The first step corresponds to alkylation of cyano complexes giving isocyanides complexes;[15] examples leading to cationic iron complexes are known.[16]

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[9] For each of the reactant ions studied, the pressure P of allyl chloride was varied from zero to ca. 10^{-4} Torr. At the highest pressure 90−95% of the reactant ions (depending on the reaction studied) were converted to products. In all cases the decrease of the relative intensity of reactant ions was well fitted by a e^{-kP} function on the whole pressure range. The corresponding apparent rate constants were of the same order as those of efficient ion−molecule reactions like ligand substitution on $FeCO^+$. When $FeClC_4H_5N^+$ ion was produced, the increase of the sum of m/z 158, 160, and 108 ions followed a $b(1 - e^{-kP})$ law (b being the branching ratio for $FeClC_4H_5N^+$ formation), and the 108/(158 + 160) intensity ratio was proportional to pressure at low pressure, as expected from the proposed reaction scheme. For $FeCN(ICN)^+$ ion the primary products and corresponding branching ratios determined in this way were as follows: $FeClC_4H_5N^+$, 55%; $C_3H_5^+$, 34%; $FeCl(ICN)^+$, 11%.

[10] Concerning the other ions containing the ICN ligand, these ions were obtained in low amount (6%) from $Fe(CO)(ICN)_2^+$, in trace amounts from $Fe(CO)(ICN)^+$ and $Fe(CO)_2(ICN)^+$, and not at all from $Fe(ICN)^+$, $FeI(ICN)^+$, or $FeCl(ICN)^+$.

[11] For the ions containing the ICN ligand, activation of the CN group requires preliminary cleavage of the I−C bond, which appears more or less facile depending on the other ligands on the metal ion, i.e. easier with ICN than with CO, Cl, or I. The electron-withdrawing character of the latter ligands is actually expected to increase the strength of the I−C bond by conferring to it some double-bond character (through a $I^+{=}C{=}N{-}Fe$ resonance structure). This is reflected in the CAD spectra of the complexes: beside ICN loss $Fe(ICN)_2^+$ is able to lose an iodine atom upon activation, a fragmentation pathway which was not observed with other ICN complexes.

[12] The result of this reaction was the same as when run in the second collision cell, confirming that $FeCN(ICN)^+$ ions behave identically whether they result from an ion−molecule reaction in the source or in a collision cell. Since the source conditions were close to chemical ionization, source-issued ions were actually not likely to have large internal energies.

[13] (a) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* **1989**, *8*, 2439−2446. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621−627. (c) Eller, K.; Karrass, S.; Schwarz, H. *Organometallics* **1992**, *11*, 1637−1646.

[14] (a) Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068−3071. (b) Eller, K.; Schwarz, H. *Organometallics* **1989**, *8*, 1820−1822. (c) Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 201−208.

[15] Review: Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209−310.

[16] Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660−664.

The second step is insertion of isocyanide into a metal–carbon bond;[15] in solution the resulting ligand remains bound to the metal, forming an acylimino complex as the final product; alkyl isocyanide complexes of iron[17] or ruthenium[18] undergo this reaction. In the case of the gas-phase insertion reaction, the possible transient alkyl isocyanide complex **3** would correspond to highly oxidized iron(IV) as the acylimino complex resulting from formation of the C–C bond. Therefore the complex evolves by detachment of the positively charged ligand **1**, leaving neutral iron(II) chloride.

The preceding results show that cationic cyanoiron complexes react with allyl chloride through a double coupling reaction involving first N–C bond formation and then C–C bond formation. The analogy between the first step and a known solution reaction suggests that in the starting complex $Fe(CN)(ICN)^+$ the CN ligand is bound in the same way as in the condensed phase, i.e. by the carbon atom. This binding mode may be different from that of $Fe(CN)^+$, since $Fe(CN)^+$ seems incapable of the coupling reaction, and theoretical studies of other $M(CN)^+$ complexes show that $(M-N-C)^+$ is slightly more stable than $(M-C-N)^+$.[19] Whether for structural or reaction dynamic reasons, the presence of one additional ligand on $Fe(CN)^+$ is sufficient to induce solution-like coupling reactions.

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(17) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem*. **1974**, *13*, 2145–2150.

(18) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem*. **1978**, *157*, C27–C29.

(19) Bouslama, L.; Daoudi, A.; Mestdagh, H.; Rolando, C.; Suard, M. *J. Mol. Struct. (Theochem)* **1995**, *330*, 187–190.