Room-Temperature Alkyne – Nitrile Metathesis and Unambiguous Proof for the Existence of a High-Valent Iron-Nitrido Dication in the Gas Phase

Short Communication

by **John P. Boyd***, **Maria Schlangen***, **Andreas Grohmann**, and **Helmut Schwarz**

Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, DE-10623 Berlin
(fax: + 49-30-31421102; e-mail: lycaeum@web.de; Maria.Schlangen@mail.chem.tu-berlin.de)

Dedicated to Professor *Richard R. Schrock*

An unprecedented alkyne – nitrile metathesis takes place when the high-valent iron-nitrido dication $[Fe(L)N]^{2+}$, with L = 2,6-bis(2-methyl-1,3-diaminopropan-2-yl)pyridine, is reacted with alkynes in the gas phase under thermal conditions. While the detailed role of the alkyne substrate with respect to relative rates, regioselectivities, and branching ratios remains to be elucidated, the very existence of this novel metathesis reaction provides additional experimental evidence of a genuine, long-lived, formal iron(V)-nitrido dication.

Introduction. – The past decade has witnessed the extraordinary impact of alkene metathesis on polymer chemistry and organic synthesis [1]; in contrast, the related metathesis of alkynes is still in its infancy [2]. Whilst the nature of the catalytically active species remained elusive for quite a while, *Katz*'s original proposal [3a] that metal carbynes initiate a sequence of formal [2 + 2] cycloaddition and cycloreversion steps, proceeding through metallacyclobutadiene intermediates, is now accepted as a general mechanism based on elegant experiments [3b] and detailed computational studies [3c – 3f]. Even much less is known about the formally related alkyne – nitrile [4] and N-atom – nitrile [5] cross-metathesis processes employing metal nitrides, alkynes, and nitriles (*Scheme 1*).

In this *Short Communication*, we report the first example for a room-temperature alkyne – nitrile gas-phase metathesis reaction[1]. Recently, we described the synthesis of the azido – iron(III) complexes $[Fe(L)(N_3)]X_2$, where X is either Br or PF_6, and L corresponds to the tetrapodal pentadentate N ligand 2,6-bis(2-methyl-1,3-diaminopropan-2-yl)pyridine [7]. We demonstrated that, by means of electrospray ionization (ESI) mass spectrometry, the dication $[Fe(L)(N_3)]^{2+}$ (**1**) can be transferred into the gas phase as an intact entity which, upon collisional activation (CA), undergoes an oxidative expulsion of molecular N_2 to afford the high-valent, dicationic nitrido-iron species $[Fe(L)N]^{2+}$ (**2**) as an intermediate. Extensive labeling experiments and computational studies revealed a number of unusual features of **2**, *e.g.*, intramolecular, suicidal insertion of the nitrido atom in C–H, N–H, and C–C bonds of the chelating

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[1])　For examples of gas-phase alkene metathesis, see [6].

Scheme 1. a) *Alkyne* (X, Y = CR′), *Nitrile – Alkyne* (X = N, Y = CR′); b) *Nitrile – Nitrile* (X, Y = N)
Metathesis Reactions
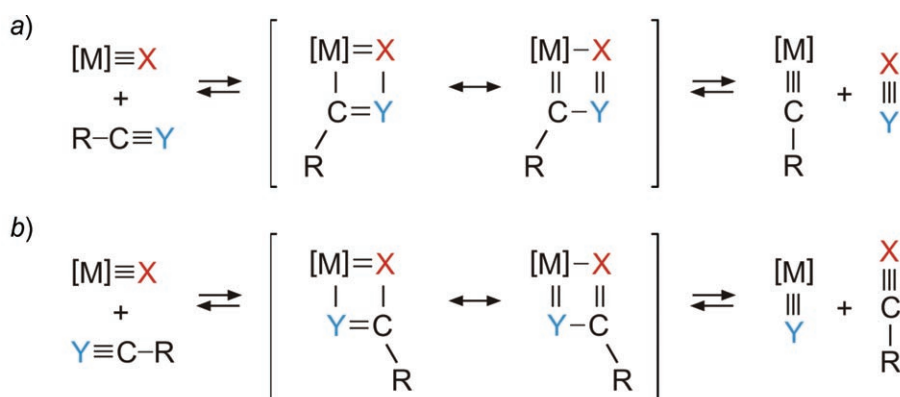
ligand L, or transfer of NH_2^+ and NH units, or a 'bare' N-atom in thermal ion – molecule reactions to activated olefins [7]. In the two latter reactions, it is the nitrido atom that is exclusively involved (*Scheme 2*) [7][2][3][4]).

Scheme 2
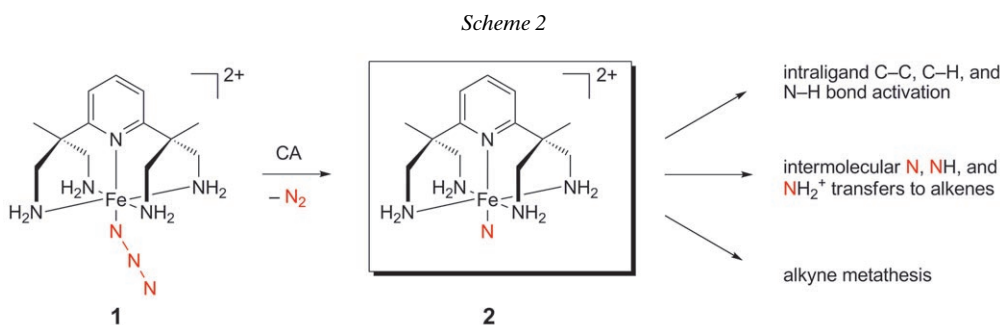
Experimental. – The experiments were carried out using a commercial *VG BIO-Q* mass spectrometer as described in detail in [11]. Briefly, the instrument consists of an ESI source combined with a tandem mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole). In the present experiments, millimolar solutions of $[Fe(L)(N_3)]Br_2$ dissolved in MeOH were introduced through a fused-silica capillary into the ESI source with a syringe pump (*ca.* 2 μl/min). N_2 was used as a nebulizing and drying gas at a source temp. of *ca.* 80°. Maximum yields of the desired dication $[Fe(L)(N_3)]^{2+}$ (**1**) and its fragment ion **2** due to loss of molecular N_2 from **1** were achieved by adjusting the cone voltage between 20 and 40 V. Ion-reactivity studies of mass-selected $[Fe(L)N]^{2+}$ (**2**) with commercially available alkynes

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2) For related gas-phase studies of the $[Fe(cylamacetato)N]^+$ mono-cation, see [8a], and of Pt^{II} complexes, see [8b].

3) For selected articles on functionalized N-atom transfer and metal-mediated C−N bond formations in solution, see [9].

4) For examples of metal-mediated gas-phase NR transfer processes, see [10].

Table. *Relative Reaction Efficiencies (k_{rel}) and Branching Ratios ([%]) for the Reactions of Mass-Selected [Fe(L)N]²⁺ with Alkynes R¹–C≡C–R²*

| R¹–C≡C–R² | | k_{rel}[a] | Adduct formation | Losses of neutral | | | | N-Atom transfer to alkyne[b] |
R¹	R²			R¹–C≡N	R²–C≡N	CH₂NH[c]	NH₃[d]	
H	CH₂OH	57[e]	2	–	68	–	30	
H	Pr	4[e]	28	–	72	–	–	–
H	ᵗBu	23[e]	65	8	25	[f]	–	2
Me	Et	10	70	14	14	2	–	–
Et	Et	69	58	34[g]		6	–	2
H	Ph	100[e]	6	16	15	[f]	–	63

[a]) k_{rel} is expressed in [%] and given relative to the reaction of [Fe(L)¹⁵N]²⁺ with HC≡CPh. [b]) We note that in the reaction of **2** with, *e.g.*, benzene, no N-atom transfer occurs. Here, the only process observed corresponds to adduct formation with $k_{rel} = 21\%$. [c]) This structurally not characterized neutral molecule is formed upon dissociative uptake of the alkyne by [Fe(L)N]²⁺. Labeling experiments demonstrate that neutral CH₂NH originates from the chelating ligand L. [d]) The N-atom of NH₃ stems exclusively from the nitrido group of **2** as evidenced by the reaction with [Fe(L)¹⁵N]²⁺. [e]) The reactions were actually performed with [Fe(L)¹⁵N]²⁺ to ensure the observation of R²C¹⁵N/[Fe(L)(CH)]²⁺ which, due to limited mass resolution, is not possible to monitor when [Fe(L)N]²⁺ is employed. [f]) Expulsion of CH₂NH cannot be monitored due to limited mass resolution from loss of HC¹⁵N; however, this process amounts to *ca.* 11% when [Fe(L)N]²⁺ is reacted with either HC≡CᵗBu or HC≡CPh. [g]) Due to the symmetrical nature of this alkyne, R¹CN, and R²CN are identical.
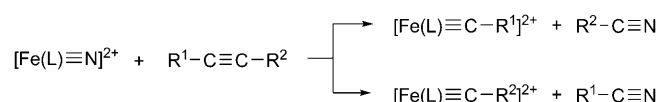
(*Table*) were performed in the hexapole at r.t., at an interaction energy nominally set to $E_{lab} = 0$ eV and at pressures in the order of 10^{-4} mbar; this is considered to correspond to nearly single-collision conditions [12].

Results. – When the mass-selected dication **2** (or, for mechanistic purposes, its ¹⁵N-nitrido and (ND₂)₄-labeled analogues) is reacted with alkynes under thermal conditions, a number of products is formed (*Table*). In addition to ubiquitous adduct formation, for some of the alkyne substrates we observe the eliminations of neutral CH₂NH and NH₃, as well as structure-indicative, specific N-atom transfer to the alkyne. However, most important is an unprecedented alkyne – nitrile metathesis that occurs for all substrates studied, except C_2H_2 which is inert under ambient conditions as are the substituted phenylacetylenes *p*-RC₆H₄C≡CH (R = MeO and CF₃).

In terms of relative reactivity, phenylacetylene reacts fastest ($k_{rel} = 100\%$) and pent-1-yne is the most sluggish alkyne ($k_{rel} = 4\%$). When the branching ratios and the relative reaction rates are combined, the alkyne – nitrile channel is the most productive for propargyl alcohol (38.8%) and phenylacetylene (31.1%), respectively, and lowest for pent-2-yne and pent-1-yne, respectively (2.8 and 2.9%); the sterically congested substrate HC≡CC(Me)₃ exhibits an intermediate alkyne – nitrile metathesis potential (6.7%). Obviously, there does not seem to exist a clear-cut relationship between the structure of the alkyne substrate (terminal *vs.* internal C≡C bond, steric demand of the alkyl group) and the propensity for a metathesis reaction, except that, for substituted phenylacetylenes *p*-RC₆H₄C≡CH, both electron-rich (R = MeO) and electron-poor (R = CF₃) substrates do not react with **2** at the detection limit in contrast to the parent compound R = H. This finding may be indicative for a change of the rate-determining

step [13] for Ph-substituted alkynes in the course of the alkyne – nitrile metathesis. As to the branching ratios in the formations of R^1CN *vs.* R^2CN from unsymmetrical alkynes (*Scheme 3*), for terminal alkyl-substituted substrates $HC\equiv CR$ the generation of $[Fe(L)CH]^{2+}/RCN$ is clearly favored if not occurring exclusively as is the case for $R = CH_2OH$ and Pr. However, in the reactions of $MeC\equiv CEt$ and of $HC\equiv CPh$, no regioselectivity is operative in the alkyne – nitrile metathesis.

Scheme 3

$$[Fe(L)\equiv N]^{2+} \;+\; R^1-C\equiv C-R^2 \longrightarrow \begin{cases} [Fe(L)\equiv C-R^1]^{2+} \;+\; R^2-C\equiv N \\ [Fe(L)\equiv C-R^2]^{2+} \;+\; R^1-C\equiv N \end{cases}$$

Finally, labeling experiments performed with $[Fe(L)^{15}N]^{2+}$ demonstrate for all substrates a clean and quantitative incorporation of ^{15}N into the newly formed nitriles. Exploratory attempts to bring about a thermal N-atom exchange according to *Scheme 1,b* by reacting $[Fe(L)^{15}N]^{2+}$ with nitriles such as PhCN or MeCN have not been conclusive due to limited mass resolution; however, up to three nitrile molecules were added to the dication.

While mechanistic details of this novel alkyne – nitrile metathesis by a high-valent nitrido-iron dication remain to be elucidated, and the role of the alkyne substrates on relative rates, branching ratios, and regioselectivities needs to be clarified, the present findings seem to be unprecedented. In addition, the specific exchange reaction reported here provides unambigous experimental evidence for the existence of a genuine, long-lived, formal iron(V)-nitrido dication.

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