"Tuning" CH/CC Bond-Activation Processes of Branched Amines by Choosing the Appropriate Gas-Phase Transition-Metal Ion

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The mechanisms of the deceptively similar gas-phase chemistry of amine complexes $RC(CH_3)_2CH_2NH_2/M^+$ (R = H, CH_3; M = Fe,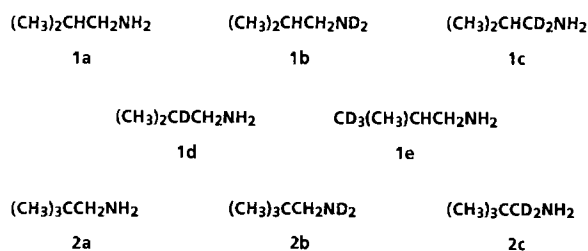 Co, Ni) are uncovered by the use of deuterium-labeled compounds. It is demonstrated that the details of CH/CC bond-activation reactions are strongly metal-ion-dependent, as is the product distribution itself.

Recent studies of transition-metal ion complexes of aliphatic amines did not only require a revision and modification[1] of the traditional concept[2] for the activation of CH/CC bonds in organometallic systems in the gas phase[3], but evidence could also be provided[4] that *direct activation* of a CC bond by bare metal ions (a reaction which has no parallel in condensed phase chemistry) can be achieved without prior CH bond activation. In this paper we describe experiments which permit a more detailed view about the mechanisms of the deceptively similar gas-phase chemistry of transition-metal ion/amine complexes $RC(CH_3)_2CH_2NH_2/M^+$ (R = H, CH_3; M = Fe, Co, Ni)[5]. In addition, results will be presented demonstrating that a "tuning" of the mechanisms that are operative, as well as the product distribution that results from CH/CC bond activation of the amines studies (Scheme 1) may be achieved by varying the transition-metal ion M^+.

The metastable ion (MI) mass spectra of the transition-metal ion complexes $1 - M^+$ (M = Fe, Co, Ni) are given in Scheme 2[6]. Except for the hydride transfer, all three metal ions generate the same products: molecular hydrogen, methane, and C_3H_6 (presumably propene).

Scheme 1

$(CH_3)_2CHCH_2NH_2$ $(CH_3)_2CHCH_2ND_2$ $(CH_3)_2CHCD_2NH_2$

    1a   1b   1c

$(CH_3)_2CDCH_2NH_2$ $CD_3(CH_3)CHCH_2NH_2$

       1d   1e

$(CH_3)_3CCH_2NH_2$ $(CH_3)_3CCH_2ND_2$ $(CH_3)_3CCD_2NH_2$

    2a   2b   2c

Scheme 2

$(CH_3)_2CHCH_2NH_2/M^+$

$1-M^+$

M = Fe, Co, Ni

| Δm	neutral molecule	% abundance M = Fe	M = Co	M = Ni
2	H_2	18	26	16
16	CH_4	74	59	2
42	C_3H_6	8	12	78
60/61	MH		3	4

Table 1. Label distribution for the generation of molecular hydrogen, methane, propene, and metal hydride from isotopomers of $1 - M^{+\ a)}$

	$1b-M^+$ Fe	Co	Ni	$1c-M^+$ Fe	Co	Ni	$1d-M^+$ Fe	Co	Ni	$1e-M^+$ Fe	Co	Ni
H_2	100	100	56	100	100	59			79	63	61	54
HD			44			41	100	100	21	37	39	46
CH_4	100	100	100	100	100	100	100	100	100			
CH_3D										57	38	47
CHD_3										43	62	53
C_3H_6	100	100	100	17	100	100				31		
C_3H_5D							100	100	100			
$C_3H_4D_2$				83						5	33	38
$C_3H_3D_3$										64	67	62
MH		100	100					100	100		100	100
MD				100	100							

a) Data are given in % of the sum of neutral products, for each neutral normalized to 100%.

1) *Generation of Molecular Hydrogen*. From the study of the labeled substrates **1b**−**1e** it becomes obvious that both M^+ = Fe^+ and M^+ = Co^+ generate molecular hydrogen in a highly specific fashion involving the ω/ω − 1 positions of the alkyl chain. The label distribution (Table 1) is in keeping with the previously established[3a] concept of "remote functionalization"[7] and can be described in terms of Scheme 3: CH bond activation (**1**−M^+ → **3**) is followed by β-H transfer (**3**→**4**) and reductive elimination of H_2. For the Ni^+ complexes, the dehydrogenation seems to be preceded by extensive hydrogen scrambling processes.

Scheme 3
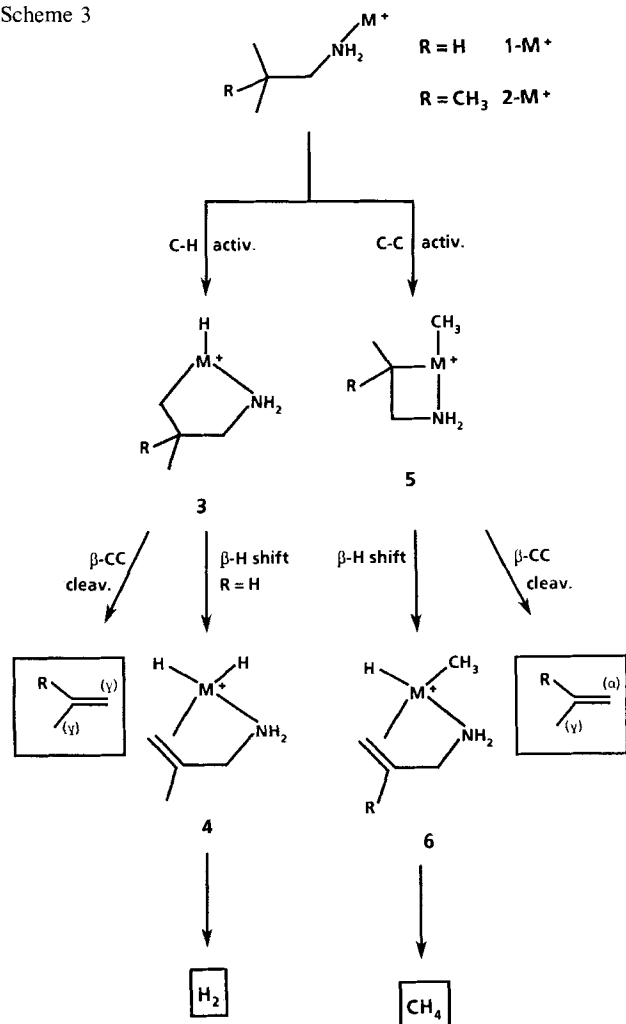
2) *Formation of Methane*. This process is highly specific for all three metal ions and can be described as a formal 1,2-elimination involving an intact methyl group and a hydrogen atom originating from the other γ-CH_3 group. The reaction commences with an insertion of the ("anchored") metal ion into a CC bond[1] (**1**−M^+ →**5**), followed by β-H transfer (**5**→**6**). Alternatively, the reversed sequence of steps, i.e. initial CH activation (**1**−M^+ →**3**) with a consecutive β-CH_3 shift[8], could also generate the same intermediate **6** from which reductive methane elimination occurs. While the present data do not permit a distinction, the labeling results, however, reveal differences between the metal ions as far as the branching ratio CH_3D/CD_3H is concerned: For Fe^+, loss of the former seems to be favoured, while the other two metal ions behave oppositely for reasons that are unknown so far[9].

3) *Elimination of Propene*. Quite surprisingly, the formation of this neutral is metal-ion-dependent. For M^+ = Fe^+ the labeling data uncover the operation of *two* completely different processes; one (which contributes to ca. 17%) involves intermediate **3**, which upon β-CC cleavage gives rise to the formation of C_3H_6, containing both γ-carbon atoms of the substrate. β-CC cleavage is also possible for the other metallacycle **5**, which is formed by initial CC activation. Propene, generated by this route, has incorporated the α-C and one γ-C atom, respectively. Given the branching ratio for CH vs. CC bond activation for unlabeled **1**−Fe^+, the migration of CH_3 is favoured over CD_3; however, in the present case no quantitative isotope effects can be evaluated from **1e**−Fe^+ due to the existence of a second reaction channel for **3** as well as for **5**. For Co^+ and Ni^+, propene is exclusively generated via intermediate **3**. In line with the results from the dehydrogenation, insertion into a CH bond is favoured over CD activation. As Ni^+ showed unspecific H_2 loss, only the Co^+ case can be compared, and the good agreement in the labeling distributions further substantiates the common intermediate **3**.

4) *Hydride Transfer to Generate Neutral MH*. This reaction is not observed for M = Fe. As noted earlier[1] for other amines, the data in Table 1 demonstrate the specificity of the reaction for M = Co, Ni where the hydride is exclusively provided by the α-CH_2 group to generate an immonium-type ion $RCH=NH_2^+$. It is tempting (although not proven) to interpret the different behaviour of Fe^+ versus Co^+/Ni^+ in terms of the Lewis acid character of the three transition-metal ions[10].

The gas-phase chemistry of the complexes of amine **2**, with its *tert*-butyl group, are also strongly dependent of the metal ion M^+, both in terms of the product distribution observed for metastable ions (Scheme 4) and of the labeling results (Table 2).

Scheme 4

	Δm	neutral molecule	% abundance M = Fe	M = Co	M = Ni
	2	H_2			7
$(CH_3)_3CCH_2NH_2/M^+$	16	CH_4	93	98	26
2-M⁺					
M = Fe, Co, Ni	56	C_4H_8	7	1	64
	60/61	MH		1	3

Table 2. Label distribution for the generation of molecular hydrogen, methane, isobutene, and metal hydride from isotopomers of **2**−M^+ [a]

	2b−M⁺			2c−M⁺		
	Fe	Co	Ni	Fe	Co	Ni
H_2			73			61
HD			27			39
CH_4	100	100	100	100	100	100
C_4H_8	100	100	100	50	100	100
$C_4H_6D_2$				50		
MH		100	100			
MD					100	100

[a] See footnote to Table 1.

Molecular hydrogen is only generated for the Ni^+ complex of **2**, and the labeling data suggest (as for **1**−Ni^+) quite extensive exchange processes. In contrast, methane is formed for all three metalion complexes in a specific fashion, most likely analogous to the lower homologue **1**, via **5**→**6**. Similarly, the specificity noted for the hydride transfer from **1** to generate neutral CoH and NiH is also observed for the reactions of **2**. The most differing behaviour is found for the generation of C_4H_8, presumably isobutene. For Co^+ and Ni^+ this neutral molecule *exclusively* originates from the *tert*-butyl group; in perfect analogy to the propene formation, only **3** is involved. For the Fe^+ complex, again, two processes are operative (each ca. 50%) as already found for **1**: Insertion into CH or CC bonds generates the respective metallacycles **3** and **5**, which decompose by β-CC cleavage to form butene containing 2 γ-C or 1 α-C and 1 γ-C.

The present data clearly demonstrate the dramatic effects transition-metal ions exert in deceptively similar gas-phase processes. Not only the product distribution can be strongly affected by choice of different metal ions (Schemes 2 and 4), with Ni^+ showing preferences greatly distinct from Fe^+ and Co^+; in addition, mechanisms can also be altered as can be seen, for example, in the different results for Fe^+ and Co^+ which on the other hand show very similar product distributions. The influence of the substrate itself is also noteworthy; for **1** (R = H) the product distribution is much more versatile than for **2** (R = CH_3). As stated earlier[3a], proper labeling studies constitute a necessary condition for uncovering mechanistic details of the intriguing processes of organometallic systems in the gas phase[3].

CAS Registry Numbers

1−Fe^+: 124857-40-5 / **1**−Co^+: 124857-41-6 / **1**−Ni^+: 124857-42-7 / **2**−Fe^+: 124857-43-8 / **2**−Co^+: 124857-44-9 / **2**−Ni^+: 124857-45-0

[1] [1a] S. Karraß, K. Eller, C. Schulze, H. Schwarz, *Angew. Chem.* **101** (1989) 634; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 607. − [1b] S. Karraß, T. Prüsse, K. Eller, H. Schwarz, *J. Am. Chem. Soc.*, in the press.

[2] [2a] J. Allison, D. P. Ridge, *J. Am. Chem. Soc.* **101** (1979) 4998. − [2b] S. Babinec, J. Allison, *ibid.* **106** (1984) 7718.

[3] For recent reviews on this topic, see: [3a] H. Schwarz, *Acc. Chem. Res.* **22** (1989) 282. − [3b] P. B. Armentrout, J. L. Beauchamp, *ibid.* **22** (1989) 315. − [3c] D. H. Russell (Ed.), *Gas Phase Inorganic Chemistry*, Plenum, New York 1989.

[4] [4a] S. Karraß, H. Schwarz, *Helv. Chim. Acta* **72** (1989) 633. − [4b] S. Karraß, H. Schwarz, *Organometallics*, in the press. − [4c] For other examples of CC bond activation *without* CH bond activation by bare transition-metal ions M^+, see: N. Steinrück, O. Dange, D. Stöckigt, H. Schwarz, *Angew. Chem.*, in the press; *Angew. Chem. Int. Ed. Engl.*, in the press.

[5] The experimental set-up has been described in earlier papers (ref.[1,3a,4]). Metal ions M^+ are either generated by 100-eV electron-impact ionization of $Fe(CO)_5$ or by bombarding $CoCl_2$ or $NiCl_2$ with 8-keV xenon atoms, using a procedure originally developed by Freas and Campana [R. B. Freas, J. E. Campana, *J. Am. Chem. Soc.* **107** (1985) 6202]. The sputtered metal ions (or organometallic species of unknown composition) were then treated in the ion source of a commercially available VG instruments (ZAB-HF-3F) mass spectrometer with the organic substrates. The resulting complexes are accelerated to 8-keV kinetic energy and mass-selected by using $B(1)E$; the unimolecular reactions [metastable ion (MI) spectra] occurring in the field-free region between E and $B(2)$ were recorded by scanning $B(2)$. Signal-averaging techniques were used to increase the signal-to-noise ratio. All compounds were synthesized and purified by standard laboratory procedures and characterized by spectroscopic means.

[6] For Fe^+, in addition to the products listed in the Scheme, small signals (<1%) for the generation of NH_3 and C_4H_8 as well as a ligand detachment signal (Fe^+) are observed. The former two signals are most likely formed via ion/dipole intermediates as evidenced by the labeling distribution from **1b**−**1e**. For a discussion of a similar case where the ion/dipole mechanism is operative, see: K. Eller, H. Schwarz, *Organometallics* **8** (1989) 1820.

[7] R. Breslow, *Acc. Chem. Res.* **13** (1980) 170.

[8] The operation of an authentic β-CH_3CH_2 shift is a controversially discussed topic. For many references and further discussion, see ref.[3,4b].

[9] For other examples, demonstrating that isotope effects are often metal-ion-dependent, see: C. Schulze, H. Schwarz, *Angew. Chem.*, in the press; *Angew. Chem. Int. Ed. Engl.*, in the press; and references cited therein.

[10] For a detailed discussion on this particular property of M^+, see: K. Eller, H. Schwarz, *Chimia*, in the press; and references cited therein.

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