Cationic Gas-Phase Species

DOI: 10.1002/anie.200603266

Pronounced Ligand Effects and the Role of Formal Oxidation States in the Nickel-Mediated Thermal Activation of Methane**

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Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

Transition-metal complexes are crucial in the selective activation of C–H bonds and the functionalization of saturated hydrocarbons, in particular, of methane. Although economically competitive and attractive large-scale processes have yet to be developed, rather detailed insight has been obtained into the particular role of the electronic structures of transition-metal complexes in the elementary steps involved in these reactions.[1] Gas-phase reactions of mass-selected transition-metal fragments monitored by advanced mass-spectrometric techniques in conjunction with theoretical studies have greatly helped in uncovering mechanistic aspects underlying metal-mediated bond activation.[2] Notable in the present context is the Shilov system, that is, the platinum(II)-mediated activation of hydrocarbons under ambient conditions;[3] gas-phase experiments have provided insights into its intrinsic features. For example, in the thermal dehydrogenation of methane by atomic Pt^+ [Eq. (1)],[4] relativistic effects are of great importance.[5]

$$Pt^+ + CH_4 \rightarrow [Pt(CH_2)]^+ + H_2 \qquad (1)$$

Carbene–platinum complexes are also formed under thermal conditions in the reaction of methane with small platinum clusters in different charge states, namely, $Pt_n^{0/-/+}$.[6] Likewise, platinum complexes with covalently bound ligands, such as gaseous $[Pt(CH_2)]^+$, $[PtO]^+$, $[Pt(O)_2]^+$, $[PtL]^+$ (L = H, Cl, Br, CHO), and $[PtCl_2]^+$, react thermally with methane under single-collision conditions.[4b,f,7,8] Although the nature and number of ligands certainly have some influence on the methane activation, the overall reactivity of the platinum systems seems to be controlled mainly by relativistic effects.[5b] With regard to the much debated role of the oxidation state of platinum in the Shilov system, it is notable that the formal Pt^{IV} species $[PtCl_3]^+$ does not react with methane in the gas phase.[8]

Perhaps the most striking ligand effects are observed in the gas-phase reactions of 3d transition metals.[9] Thus, thermalized ground-state 3d monoatomic cations do not activate methane,[2a,d,f,9,10] but some of the corresponding binary metal oxides exhibit remarkable reactivity;[2e,11] for example, Mn^+ is the least reactive 3d transition-metal cation toward alkanes, whereas $[MnO]^+$ is the most reactive one.[12,13] An extraordinary ligand effect was also reported for diatomic $[MH]^+$ ions (M = Fe, Co, Ni) [Eq. (2)]:[14] Whereas the naked

$$[MH]^+ + CH_4 \rightarrow [M(CH_3)]^+ + H_2 \qquad (2)$$

metal ions M^+ do not bring about thermal C–H bond cleavage, $[NiH]^+$ activates methane at temperatures as low as 80 K, $[CoH]^+$ reacts at room temperature, and for $[FeH]^+$ temperatures above 600 K are required for the H/CH_3 ligand exchange, which is exothermic for all three metal–hydrides.[15] Computational studies revealed that the different activation parameters reflect the differences in the energy separations between the $3d^{n-1}4s$ and the $3d^n$ states for Fe^+, Co^+, and Ni^+; the crossings of the potential-energy surfaces of the high- and low-spin states are higher in energy with increasing separation of the high- and low-spin states of the cations. The transition from one potential surface to the other takes place during the course of the reaction at both the entrance and the exit channels[15] ("two-state reactivity" concept).[2h,16]

Herein, we extend these studies on ligand effects and describe the reactivity of a series of cationic Ni^{II} and Ni^{III} complexes. We performed our room-temperature experiments with a quadrupole-based mass spectrometer equipped with an electrospray ionization (ESI) source (for details, see the Experimental Section). From solutions of the Ni^{II} halides NiF_2, $NiCl_2$, $NiBr_2$, and NiI_2 dissolved in CH_3OH/H_2O mixtures, among others, a series of bare and solvated $[NiL]^+$ ions (L = halogen, H, CHO, OCH_3, etc.) could be prepared and their gas-phase reactivity studied by the ESI methods.

In line with earlier findings,[14,15] $[NiH]^+$ generated by ESI reacts efficiently with methane [Eq. (3)], and the same holds true when additional "inert" ligands such as CO and H_2O are coordinated to the $\{NiH\}^+$ core [Eqs. (4) and (5)].[29] The presence of these ligands is associated with a slight decrease of the relative rate constants, relative to that for Equation (3). The kinetic isotope effects (KIEs), derived from various isotope variants (see note added in proof), suggest that C–H bond breaking contributes to the rate-limiting step of the overall process.[17] Not unexpectedly, a mixture of $[Ni(CH_3)]^+$

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[**] Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is acknowledged. We are grateful to a reviewer for valuable comments and suggestions.

and CD_4 leads to degenerate H/D exchange [Eq. (6)] with a distribution of $x = 3$ (55%), $x = 2$ (15%), and $x = 1$ (30%).

$$[NiH]^+ + CH_4 \xrightarrow{k_{rel}=100} [Ni(CH_3)]^+ + H_2 \quad (3)$$

$$[Ni(H)CO]^+ + CH_4 \xrightarrow{k_{rel}=97} [Ni(CH_3)CO]^+ + H_2 \quad (4)$$

$$[Ni(H)H_2O]^+ + CH_4 \xrightarrow{k_{rel}=75} [Ni(CH_3)H_2O]^+ + H_2 \quad (5)$$

$$[Ni(CH_3)]^+ + CD_4 \xrightarrow{k_{rel}=40} [Ni(CH_{3-x}D_x)]^+ + [CH_xD_{4-x}] \quad (6)$$

Thermal activation of methane [Eq. (7); L = OH, OCH_3, F, Cl, Br, I] has not been observed under our conditions for

$$[Ni(L)]^+ + CH_4 \not\rightarrow [Ni(CH_3)]^+ + HL \quad (7)$$

several $[NiL]^+$ cations with higher or lower binding energies than $[NiCH_3]^+$ (bond-dissociation energy = 40.6 kcal mol^{-1}).[18] As the reactions are predicted to be exothermic for some complexes (e.g., L = OH, OCH_3, and F),[18,19] the absence of activation points to the existence of kinetic barriers.

An unexpected and unprecedented reactivity toward methane has been encountered for the system $[Ni,H_2,O]^+$. High-level electronic-structure calculations predict the existence of several structural isomers, namely, $[Ni(H_2O)]^+$, $[Ni(O)(H_2)]^+$, and $[Ni(H)(OH)]^+$, two of which are of interest in the present context.[20] The global minimum of the system corresponds to a C_{2v}-symmetric $^2A_1$ state of the $[Ni(OH_2)]^+$ complex; the structurally analogous $^4A_2$ state (C_{2v}) is 41.7 kcal mol^{-1} higher in energy, and the formal Ni^{III} insertion complex $[Ni(H)(OH)]^+$ ($^4A''$) is even less stable by additional 12.8 kcal mol^{-1}. Whereas the quartet state of $[Ni(H)(OH)]^+$ is separated by a barrier of 17.6 kcal mol^{-1} from the quartet-state $[Ni(H_2O)]^+$ complex, on the doublet surface, the $^2A''$ insertion species $[Ni(H)(OH)]^+$ undergoes spontaneous isomerization to $^2A_1$ $[Ni(H_2O)]^+$ as a result of the negligibly small barrier of less than 0.2 kcal mol^{-1}.[20] Experimental confirmation of these predictions has not yet been reported. However, the collision-induced dissociation (CID) spectra shown in Figures 1 and 2 reveal that two structurally different, non-interconvertible isomers with the composition $[Ni,H_2,O]$ must indeed exist in the gas phase. Whereas the CID spectrum in Figure 1 is compatible with the presence of a $[Ni(H_2O)]^+$ complex (**1**), the spectrum in Figure 2 is in keeping with the insertion product $[Ni(H)(OH)]^+$ (**2**).[21] The structural assignments of **1** and **2** are further supported by ion/molecule reactions of the $[Ni,H_2,O]^+$ isomers with D_2O and D_2. In the reaction of D_2O with $[Ni(H_2O)]^+$, generated at a cone voltage of 60 V, complete ligand exchange is preferentially (78%) observed, whereas the isomer $[Ni(H)(OH)]^+$, generated at 40 V, gives rise exclusively to $[Ni(D)(OH)]^+$ and $[Ni(H)(OD)]^+$ upon reaction with D_2 and D_2O, respectively. Although we cannot determine the actual spin states of the two isomers, in conjunction with Ugalde's theoretical work,[20] it is obvious that, depending on the cone voltage and the composition of the solution, ESI of a solution of $[NiL_2]$/CH_3OH/H_2O (L = F, Cl, Br, I) produces two structurally distinct $[Ni,H_2,O]^+$ species.[22]

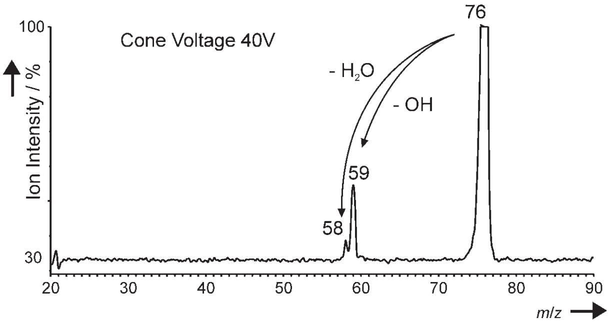

Figure 2. CID spectrum of the Ni^{III} complex cation $[Ni(H)(OH)]^+$ at $E_{lab} = 10$ eV.

In line with expectations, activation of the C–H bond is not observed in the reaction of the Ni^I aqua complex with methane (Figure 3). In contrast, the Ni^{III} isomer **2** undergoes H/CH_3 ligand exchange (Figure 4) with a relative rate constant greater than or equal to 45 (relative to the system $[Ni(H)]^+$/CH_4). The hydroxy group does not participate in this reaction and remains intact, as reaction of $[Ni(H)(OD)]^+$ with CH_4 [Eq. (8a)] liberates exclusively H_2. In contrast, the reaction with other isotopologues show that partial exchange of the hydrido ligand with the incoming hydrocarbon occurs prior to or during the formation of the nickel–carbon bond. For example, HD and D_2 are produced from $[Ni(H)(OH)]^+$/CD_4 [Eq. (8b)], HD and H_2 from $[Ni(D)(OH)]^+$/CH_4 [Eq. (8c)], and H_2, HD, and D_2 from $[Ni(H)(OH)]^+$/CH_2D_2 [Eq. (8d)]. A modeling study[23] of the labeling distributions in the products of these three reactions pairs reveals that direct

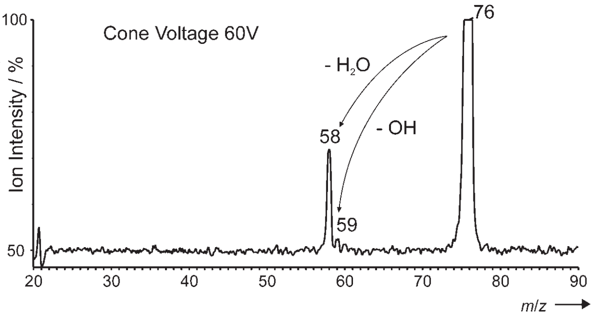

Figure 1. CID spectrum of the Ni^I complex cation $[Ni(H_2O)]^+$ at $E_{lab} = 10$ eV.

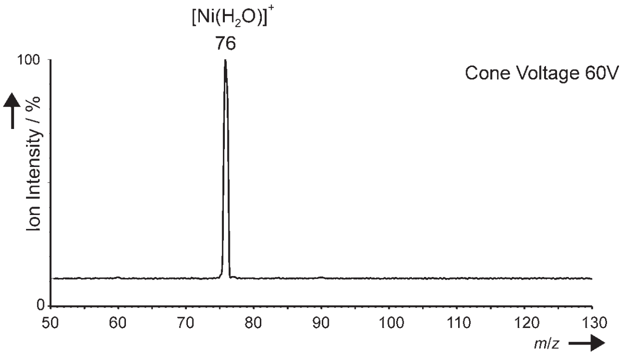

Figure 3. Mass-selected $[Ni(H_2O)]^+$ allowed to react with methane at $E_{lab} = 0$ eV: no reaction.

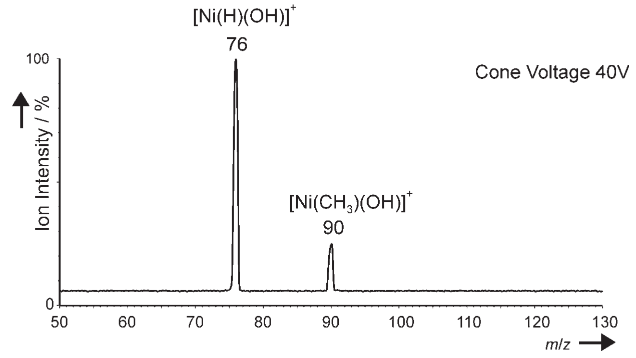

Figure 4. Mass-selected $[Ni(H)(OH)]^+$ allowed to react with methane at $E_{lab} = 0$ eV: C–H bond activation.

$$[Ni(H)(OH)]^+ + CH_4 \longrightarrow [Ni(CH_3)(OH)]^+ + H_2 \qquad (8)$$

$$[Ni(H)(OD)]^+ + CH_4 \xrightarrow{100\,\%} [Ni(CH_3)(OD)]^+ + H_2 \qquad (8a)$$

$$[Ni(H)(OH)]^+ + CD_4 \left\{ \begin{array}{l} \xrightarrow{69\%} [Ni(CD_3)(OH)]^+ + HD \\ \xrightarrow{31\%} [Ni(CD_2H)(OH)]^+ + D_2 \end{array} \right. \qquad (8b)$$

$$[Ni(D)(OH)]^+ + CH_4 \left\{ \begin{array}{l} \xrightarrow{65\%} [Ni(CH_3)(OH)]^+ + HD \\ \xrightarrow{35\%} [Ni(CH_2D)(OH)]^+ + H_2 \end{array} \right. \qquad (8c)$$

$$[Ni(H)(OH)]^+ + CH_2D_2 \left\{ \begin{array}{l} \xrightarrow{52\%} [Ni(CHD_2)(OH)]^+ + H_2 \\ \xrightarrow{43\%} [Ni(CH_2D)(OH)]^+ + HD \\ \xrightarrow{5\%} [Ni(CH_3)(OH)]^+ + D_2 \end{array} \right. \qquad (8d)$$

hydrogen/methyl ligand exchange amounts to 46%, while 54% of the H and D atoms undergo scrambling prior to loss of molecular hydrogen. For the former the kinetic isotope effect is 1.9, and for the latter KIE = 1.4, thus suggesting that breaking of the nickel–hydrogen and carbon–hydrogen bonds are involved in the rate-limiting step.

Finally, the thermal activation of methane by both $[Ni(H)(OH)]^+$ [Eq. (8)] and the diatomic cations $[MH]^+$ (M = Fe, Co, Ni) [Eq. (2)] prompted us to extend our studies to the complexes $[Fe(H)(OH)]^+$ and $[Co(H)(OH)]^+$. Both these ions can be generated—and distinguished from their structural isomers $[M(H_2O)]^+$—under ESI conditions; however, thermal reaction with methane according to Equation (9) (M = Fe, Co) does not take place at any measurable

$$[M(H)(OH)]^+ + CH_4 \not\rightarrow [M(CH_3)(OH)]^+ + H_2 \qquad (9)$$

rate. Exploratory B3LYP/TZVP calculations[24] predict[25,26] the ligand exchanges in Equations (8) and (9) to be exothermic, and, thus, a kinetic barrier could be the reason that this process is not observed for the iron and cobalt systems.

Experimental Section

The experiments were carried out by using a VG BIO-Q mass spectrometer with QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization source as described in detail previously.[27] In brief, the nickel ions were produced by ESI as follows: $[NiL]^+$ (L = F, Cl, Br, I) from a solution of NiL_2 in pure methanol, $[NiOH]^+$ from NiI_2 in H_2O, and the remaining $[NiL]^+$ complexes investigated (L = H_2O, OCH_3, HCO) from a solution of NiI_2 in a mixture of CH_3OH and H_2O (1:3). Labeled solvents (CD_3OD, $^{13}CH_3OH$, and D_2O) were used where necessary to avoid isobaric overlap. The cone voltage of the ESI source is a crucial parameter, which determines the amount of collisional activation of the ions evolving from solution in the differential pumping system of the ESI source and thus controls the nature of cluster ions formed.[22] For the methane-activation study, the ions containing ^{58}Ni were mass selected by means of Q1 and were exposed to methane in the hexapole at room temperature and pressures of approximately 10^{-4} mbar, which is considered to correspond to nearly single-collision conditions. The ionic products were detected by using Q2. Ion-reactivity studies with methane as well as the ion–molecule reactions of the $[Ni,H_2,O]^+$ isomers with D_2 and D_2O were performed at an interaction energy in the hexapole (E_{lab}) nominally set to 0 eV.[28] For the collision-induced-dissociation experiments (Figures 1 und 2), the collision energies amount to $E_{lab} = 10$ eV, and xenon was used as the collision gas. All experiments were performed with ^{58}Ni as well as ^{60}Ni. As identical results were observed, artifacts due to isobaric interferences can be ruled out.

Received: August 10, 2006
Revised: October 10, 2006

Keywords: C–H activation · gas-phase investigations · ligand effects · mass spectrometry · nickel

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[21] CID examinations of the complex $[^{58}Ni(D)(OH)]^+$, generated from $NiI_2/CD_3OH/H_2O$, reveal the specific eliminations of $D^\bullet$ (*m*/*z* 77→*m*/*z* 75) and $OH^\bullet$ (*m*/*z* 77→*m*/*z* 60). A signal corresponding to the cleavage of the Ni–H bond of **2** is, most likely, also present in Figure 2; however, owing to the asymmetric broadening of the parent ion and the limited mass resolution of the instrument, the signal at *m*/*z* 75 cannot be resolved from the precursor ion at *m*/*z* 76.

[22] Although the exact origin of these two isomers remains to be elucidated, we note that ESI of $NiI_2/CH_3OD/D_2O$ gives rise to $[Ni(H)(OD)]^+$ and $[Ni(D_2O)]^+$. Further, a parent-ion scan demonstrates that $[Ni(H_2O)]^+$ (**1**) is produced from $[Ni(H_2O)(CH_3OH)]^+$ (*m*/*z* 108); in contrast, isomeric $[Ni(H)(OH)]^+$ (**2**) originates from $[Ni(CH_2OH)(OH)]^+$ (*m*/*z* 106) in a rather complex sequence of events in which the intermediate $[Ni,C,H_2,O_2]^+$ (*m*/*z* 104) plays a key role. On the basis of exploratory labeling experiments, we assign the Ni^{III} ion $[Ni(HCO)(OH)]^+$ to this species. As expected, a CID experiment of this complex leads to loss of $OH^\bullet$, CO, and HCO (in the ratio 5:16:1). Further experiments suggest that Ni^{III} ions are generated in solution rather than in the gas phase. Thus, at lowest cone voltage (10 V), we detect the complex $[Ni(CH_2OH)(OH)(CH_3OH)_3]^+$, from which, upon increasing the cone voltage, methanol ligands are evaporated sequentially (*m*/*z* 202→*m*/*z* 170→*m*/*z* 138→*m*/*z* 106) until the "bare" Ni^{III} complex $[Ni(CH_2OH)(OH)]^+$ is formed. The rather independent pathways for the production of the two isomers **1** and **2** may explain the counterintuitive observation of the preferential formation of the high-energy isomer $[Ni(H)(OH)]^+$ (**2**) at lower cone voltages. Finally, the actual isomer composition is affected by both the cone voltage and (to a smaller extent) by the CH_3OH/H_2O mixture. At low cone voltage (ca. 30 V), the two isomers $[Ni(H)(OH)]^+$ (**2**) and $[Ni(H_2O)]^+$ (**1**) are formed in a ratio of greater than 9:1, this ratio drops to around 1:1 at 50 V, and above 60 V mostly $[Ni(H_2O)]^+$ is formed ($\mathbf{2}/\mathbf{1} \leq 1{:}8$).

[23] For technical details of the modeling studies, see: a) C. Trage, D. Schröder, H. Schwarz, *Organometallics* **2003**, *22*, 693; b) M. Schlangen, D. Schröder, H. Schwarz, *Helv. Chim. Acta* **2005**, *88*, 1405.

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[29] Note added in proof (January 4, 2007): Detailed modeling of the isotope distributions in reactions (3)–(5) for various isotope variants of the reactant couples reveals a competition between direct ligand switch and hydrogen-atom scrambling, each accompanied by kinetic isotope effects. The following data were obtained: (3) ligand exchange 87% (KIE = 1.8), scrambling 13% (KIE = 1.0); (4) 47% (1.5), 53% (1.1); (5) 45% (2.0), 55% (1.8).