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Inner-sphere electron transfer in metal-cation chemistry

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Abstract

Bond activation of organic molecules by metal cations is usually rationalized either in terms of the chemistry of Lewis acids or via oxidative addition of metal fragments to R–X bonds, that is, $R-X+M^+ \rightarrow R-M^+-X \rightarrow$ products. In most of these mechanisms, the positive charge is assumed to be located on the metal center. Here, we propose an alternative mechanism, to which we refer as inner-sphere electron transfer (ET). Thus, provided that certain conditions are fulfilled, the insertion species $R-M^+-X$ may isomerize via ET to $[R^+ \cdots MX]$ structures with the positive charge located mostly at the organic residue R. If $R-M^+-X$ and $[R^+ \cdots MX]$ are not just resonance structures but distinct minima on the related potential-energy surfaces, there also exists a transition structure between the two, that is, an ET-TS. Here, the role of inner sphere ET in organometallic gas-phase reactions and the possible existence of ET-TSs are discussed for a series of examples investigated both computationally and experimentally. (Int J Mass Spectrom 200 (2000) 163–173) © 2000 Elsevier Science B.V.

Keywords: Electron transfer; Metal ions; Potential-energy surfaces; Reaction mechanisms; Transition metals

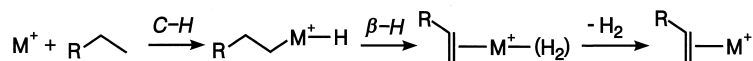
1. Introduction

Initiated by the seminal work of Müller in the early 1970s [1–4], the focus of gas-phase ion chemistry studies was shifted to that of organometallics. Since then, a huge body of experimental and theoretical information has been collected. This ranges from accurate thermochemical data for di- and polyatomic transition-metal compounds all the way down to profound insight into basic (elementary) organometallic reactions such as β -hydrogen transfer, metal-mediated cycloaddition reactions, and so forth [5]. New concepts have been developed for the activation

of nonreactive substrates such as methane [6] and selective bond activations in hydrocarbon side chains [7]. In another spin-off, helpful insight into inorganic synthesis has been provided [8]. In recent years, particular attention has been paid to the details of oxidation processes mediated by transition-metal ions in the gas phase [9]; some aspects of this otherwise esoteric gas-phase chemistry may even have implications for the understanding of enzymatic processes such as the mechanism of the hydroxylation of alkanes by cytochrome P-450 [10].

While the body of information about the gas-phase ion chemistry of transition metals is in fact enormous, it is usually assumed that the charge remains localized at the metal throughout the entire reaction pathway [1–11]. As far as monocationic species are concerned,

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Scheme 1.

this assumption is fairly justified by the relatively low ionization energies of many transition-metal compounds in various oxidation states compared to most organic and inorganic substrates. For example, the dehydrogenation of alkanes by bare transition metals is best described as an oxidative addition of the metal to a C–H bond followed by hydrogen transfer from the β position to deliberate molecular hydrogen and a cationic metal-alkene complex (Scheme 1). In this theoretically supported mechanistic scenario, the positive charge remains localized on the transition metal in all intermediates and transition structures [12–15].

Exceptions to the charge localization on the metal are, of course, found in those reactions where charge transfer is obvious. For example, because of the large ionization energy (IE) of atomic gold, electron transfer (ET) is frequent in the reactions of Au^+ with substrates having IEs similar or lower than $IE(Au)=9.23$ eV [16]; that is, charge transfer to yield the corresponding molecular ions occurs for arenes [17–19] such as benzene ($IE=9.25$ eV), toluene ($IE=8.82$ eV), and ethylbenzene ($IE=8.77$ eV). Similarly, some ions of high-valent transition-metal compounds with electronegative ligands, for example, CrF_n^+ ($n=3, 4$) [20], MoO_3^+ [21], and OsO_4^+ [22] react via electron transfer with most organic substrates. All these processes can be described as long-range, outer-sphere ET simply determined by the thermochemical properties of the separated reactants. Another variant is the harpoon-type mechanism operative in halide abstraction from haloalkanes by neutral alkali atoms, alkaline earth cations, and so on [23].

In this contribution, we would like to discuss some cases examined collaboratively in which ET is not obvious, yet some experimental and theoretical evidence suggests a hidden occurrence of ET along the reaction coordinates from reactants to products. The products of these particular reactions are, again, positively charged metal complexes, that is, with formal retention of the charge on the metal. Yet,

processes that we term structured- or inner-sphere ET may play a decisive mechanistic role and, particularly, determine the product distribution. By definition, however, mass spectrometric studies alone cannot provide direct evidence for the occurrence of inner-sphere ET. Instead, more indirect observations may hint toward participation of ET such as energetic and/or kinetic arguments, and of isotopic labeling experiments in particular. In this article, we aim to propose inner-sphere ET as a new mechanistic scenario in organometallic ion chemistry, which in turn, very much resembles some ideas of classical organic ion chemistry such as the concept of fluxional ion-dipole complexes [24]. For example, oxidation of ethene to acetaldehyde, promoted by the VO_2^+ cation, proceeds via $O_2V-CH_2CH_2^+$; this intermediate corresponds to a primary alkyl cation and, as such, undergoes rapid Wagner-Meerwein rearrangement to the secondary cation $O_2V-CH(CH_3)^+$ en route to the products [25].

2. Conceptual consideration

Before describing some reactions in which inner-sphere ET could play a role, some general aspects are outlined. Consider a complex $[AB]^+$ as a resonance hybrid of two forms, $[A^+ \cdots B]$ and $[A \cdots B^+]$. The bonding situation in $[AB]^+$ can be rationalized using the mixing diagram in Fig. 1 [26]. The wavefunction (Ψ) and stabilization energy (SE) caused by mixing is inversely proportional to the energy gap (ΔE) separating the two configurations and directly proportional to the square of the matrix element between them. While ΔE depends primarily on the relative IEs of A and B [27,28], it may be seriously affected by the electrostatic ion-dipole and ion-induced dipole interactions within each configuration. The matrix element is proportional to the overlap of the two orbitals, one on A and one on B, which participate in the electron

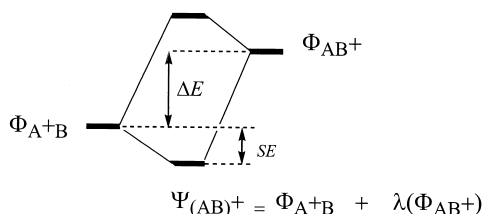


Fig. 1. Mixing diagram of the two configurations $[A^+ \cdots B]$ and $[A \cdots B^+]$ that contribute to the wavefunction of the $[AB]^+$ complex; λ is the mixing coefficient of the configurations.

shift from A to B^+ and vice versa. Maximization of this overlap determines in turn the relative orientation of A and B within the complex $[AB]^+$.

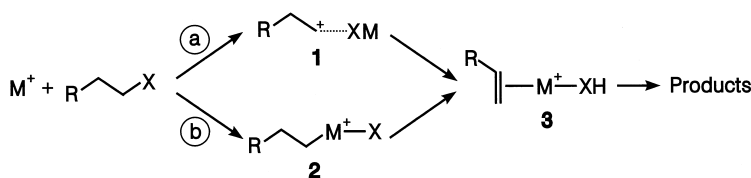
In some cases to be specified later, $[AB]^+$ is a saddle point that connects two minima that are best described by the localized configurations $[A^+ \cdots B]$ and $[A \cdots B^+]$. Such a transition structure (TS), which is bonded by the mixing of the configurations will be referred to hereafter as a structured ET-TS or inner-sphere ET-TS [29,30]. In contrast, if the configurations in Fig. 1 are merely mesomeric forms of a stable $[AB]^+$ complex, we shall not use the ET terminology to refer to this species. Nor will we refer by this terminology to situations where configurations such as those in Fig. 1 mix into the TS, which otherwise has another dominant character [26]. Let us now consider this model in the context of organometallic gas-phase ion chemistry.

In general, the IEs of metal compounds increase with the formal oxidation state of the metal. A good example is the series of chromium fluorides, for example, $IE(\text{Cr})=6.8$, $IE(\text{CrF})=8.4$, $IE(\text{CrF}_2)=10.1$, $IE(\text{CrF}_3)=11.5$, $IE(\text{CrF}_4)=12.3$, and $IE(\text{CrF}_5)>12.5$ eV [20]. Hence, ET from a substrate to a cationized metal compound becomes more likely the larger the metal's formal valency. This rule of thumb holds true not only for reactants and products but also for potential intermediates of ion–molecule reactions such as bond-insertion intermediates formed via oxidative addition. Moreover, the nature of the ligands plays a decisive role because they determine the electrophilicity of the metal center via their electron-withdrawing or -donating character. For example, the IEs of the neutral Fe^{I} compounds FeX to the formal

Fe^{II} species FeX^+ range from 8.11, 8.08, and 7.82 eV for the electronegative ligands $X=\text{F}$, Cl , and Br [31,32], respectively, to only 7.2 and 6.9 eV for $X=\text{H}$ and CH_3 [16]. Similarly, coordinative ligands can drastically change the redox behaviors of metal compounds caused by stabilization of the ionic species; for example, the decreasing IEs in the series $IE(\text{Fe}^+)=16.2$, $IE(\text{Fe}(\text{H}_2\text{O})^+)=14.3$, and $IE(\text{Fe}(\text{H}_2\text{O})_2^+)=12.6$ eV reflect the pronounced role of solvation in the corresponding dicationic species [33].

A second factor to be considered is the stabilization energy of the ion–dipole complexes possibly formed on interaction of metal cations with neutral substrates. The $\text{Au}(\text{benzene})^+$ cation [17,18] may serve as an extreme case of Fig. 1 because the binding partners atomic gold and benzene have almost identical IEs (9.23 and 9.25 eV, respectively [16]). Accordingly, the $[\text{Au}^+ \cdots \text{C}_6\text{H}_6]$ and $[\text{Au} \cdots \text{C}_6\text{H}_6^+]$ configurations may be expected to identically contribute to the wavefunction. However, electronic structure calculations indicate that $\text{Au}(\text{benzene})^+$ is best described as a Au^+ cation interacting with the π -system of benzene (in an η^2 mode [34]), rather than the reverse, that is, $\text{C}_6\text{H}_6^{+\cdot}$ cation radical interacting with neutral gold. As discussed above for Fig. 1, this preference for charge localization at the metal center can originate in differences of ion–dipole interactions in the two forms. In $[\text{Au}^+ \cdots \text{C}_6\text{H}_6]$, a localized cation interacts with a neutral having a large polarizability ($\alpha(\text{C}_6\text{H}_6)=10.5 \text{ \AA}^3$), whereas the alternative $[\text{Au} \cdots \text{C}_6\text{H}_6^+]$ configuration would involve the interaction of delocalized arene cation with the less polarizable gold atom ($\alpha(\text{Au})=5.8 \text{ \AA}^3$). Of course, the real bonding situation is some resonance hybrid of both configurations (see below), and the η^2 - instead of η^6 -coordination may be regarded as an indication for the contribution of both resonance structures.

Involvement of inner-sphere ET in mechanistic schemes is meaningful only if it has distinct consequences on some observables. Thus, whenever $[A^+ \cdots B]$ and $[A \cdots B^+]$ are not only mesomeric contributions but generate two distinct minima, there also exists a transition structure connecting them. As such a barrier is essentially caused by electron transfer, it is denoted as an ET-TS [29,35,36]; a somewhat



Scheme 2.

related concept is that of bond-stretch isomerism [37–39]. Obviously, a fair balance of IE(A) and IE(B) is a prerequisite for this scenario. Considering that no discrete minima for $[A^+ \cdots B]$ and $[A \cdots B^+]$ are to be expected otherwise, another prerequisite for the existence of an ET-TS is at least one of the components show pronounced structural differences between the neutral and ionic forms. To a first approximation, the differences of vertical and adiabatic ionization energies of the separate constituents can be regarded as a measure of these geometric changes [40]. While these differences ($\Delta IE_{v/a}$) are small for many neutral transition-metal fragments because of the ability to accommodate variable oxidation states, major reorganization energies can occur for small organic radicals, for example, $\Delta IE_{v/a} = 0.7$ eV for the aminomethyl radical [41], $\Delta IE_{v/a} = 0.8$ eV for phenyl [42], and even $\Delta IE_{v/a} = 1.5$ eV for the acetyl fragment [43]. Hence, oxidative addition of a metal cation M^+ to an R–X bond may result in the formation of an insertion intermediate for which the two structures $R-M^+-X$ and $[R^+ \cdots MX]$ represent distinct structural isomers separated by an ET-TS. Having made these considerations, it further becomes obvious that only a single structure exists in the case of the $Au(\text{benzene})^+$ cation discussed above, as $\Delta IE_{v/a}$ of gold atom is zero by definition and that of benzene is small [41].

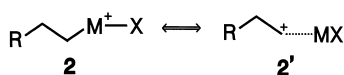
After having made these conceptual remarks, let us return to the possible role of inner sphere ET in mechanistic scenarios. The key hypothesis is that the structures $[A^+ \cdots B]$ and $[A \cdots B^+]$ exist as genuine minima and are connected by an ET-TS. Instead, the ET-TS disappears when $[A^+ \cdots B]$ and $[A \cdots B^+]$ represent mesomeric structures of a common resonance configuration. Thus, the idea of inner sphere ET coincides with the classical double versus single

minimum problem with the resulting mechanistic implications in each case. Existence or nonexistence of an ET-TS may therefore be manifested in kinetic parameters such as rate constants, product branching ratios, and isotope distributions in particular. However, the observables can only probe the ET-TS indirectly, for example, as a dependence of a property from the IEs of the components. Unfortunately, many contemporary theoretical methods encounter severe difficulties when accurate description of the balance between $[A^+ \cdots B]$ and $[A \cdots B^+]$ as well as complete geometry optimization of both structures are requested.

3. Dehydrohalogenation of alkyl halides: A potential candidate for inner-sphere ET?

Prototypical examples for the involvement of carbocationic species in metal-ion chemistry are the reactions of M^+ ions with alkyl halides. Experimentally, dehydrohalogenation is observed in most cases to yield the corresponding alkene complexes; depending on the strengths of the M^+ –alkene and M^+ –XH interactions; also, $M(\text{XH})^+$ products are observed [44,45].

Two types of mechanistic scenarios are generally involved. The first involves a harpoon-type halide capture (route [a] in Scheme 2) by the metal cation to yield intermediate **1**, which consists of a carbocation bound to a neutral metal halide; this is also referred to as ion/dipole mechanism [11]. The other variant is an oxidative addition of the metal to the R–X bond (route [b] in Scheme 2) to yield the insertion species **2**. Proton transfer from the carbocation to MX in **1** and transfer of a hydrogen atom from the β -position in **2**



Scheme 3.

can then afford the bisligated species **3**, which serves as a precursor for HX and alkene losses. Depending on the nature of the metal as well as the substrate R–X, either one or both routes are accessed [46]. For example, alkali cations or d^0 and d^{10} transition-metals ions cannot undergo oxidative addition to R–X bonds such that only route (a) is feasible, while Allison and Ridge have provided good evidence for the involvement of insertion intermediates such as **2** in the case of several transition metals [44].

The putative inner sphere ET variant suggested in this article is the conversion of the insertion species **2** into its charge-inverted form **2'** (Scheme 3). Note that structure **2'** differs from **1**, as in the former, the carbocation is coordinated to the metal and not the halogen—a junction rather unlikely for alkaline metals, for example.

Deliberately, the connection of structures **2** and **2'** in Scheme 3 does not fix whether or not these entities are mesomeric or isomeric structures; only in the latter case there also exists an inner-sphere ET-TS. However, one may consider the involvement of structure **2'** as a superfluous complication of the mechanistic scenario as long as no decisive and experimentally observable consequences of the proposed inner-sphere ET mechanisms can be proposed.

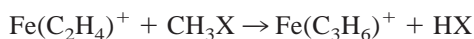
Finally, let us distinguish the three routes discussed for the dehydrohalogenation of alkyl halides in terms of the number of electrons involved in the associated redox processes [47]. The ion/dipole mechanism in route [a] resembles the typical chemistry of Lewis acids and as such does not involve any change in valencies, that is, no electron transfer. Oxidative addition and reductive elimination in route [b] are associated with changes in the formal oxidation states by ± 2 , that is, double electron transfers. The ET-TS variant proposed above involves valency changes by ± 1 , that is, single electron transfers.

4. Case studies

We have reported several organometallic reactions of gaseous ions in which inner-sphere ET might play a role [25,48–51]. Among these, let us select few specific examples to outline the implications of the possible existence of ET isomers and a mutual ET-TS.

4.1. Homologization of $M(\text{alkene})^+$ complexes

Inspired by previous studies of the gas-phase reactions of metal complexes with alkyl halides [52,53], we have examined in some detail C–C bond couplings in the reactions of some $M(\text{alkene})^+$ complexes [54]. In these processes, the metals mediate homologizations of olefines by alkyl halides; for example, an ethene ligand can be converted into propene on treatment with CH_3X , reaction (1):



The reaction proceeds via insertion of the metal into the C–X bond followed by carbometallation of the double bond and subsequent reductive elimination of HX. In the present context, two specific aspects of the experimental results are worth being discussed in more detail.

In the reactions of CH_3X with $\text{Fe}(\text{C}_2\text{D}_4)^+$, significant H/D equilibration is observed, and the ratios of HX/DX losses very much depend on the nature of X (Table 1). While the data of the halides follow a common trend, that is, increasing amounts of H/D equilibration with decreasing reaction exothermicities, X=OH does not fit this correlation, and it has been stated that “a presently unknown effect must be responsible for the increased tendencies for H/D exchange” for X=OH [54]. Instead, a reasonable correlation exists between the HX/DX ratios and IE(FeX), thus suggesting the occurrence of inner-sphere ET in the intermediates formed along the reaction paths. Thus, the HX/DX ratios decline exponentially (Fig. 2): The smaller the IE the larger the HX/DX ratios. At IE(FeX) of ~ 7.8 eV, a value of ~ 1.4 is approached, which is assigned to the kinetic

Table 1

Weighted ratios of HX/DX losses in the reactions of $\text{Fe}(\text{C}_2\text{D}_4)^+$ with CH_3X and the related reaction exothermicities ($\Delta_r\text{H}$) as well as ionization energies of the corresponding FeX species; experimental data are taken from ref. [54].

X	HX/DX ^a	$\Delta_r\text{H}$ (kcal/mol) ^b	IE (FeX) (eV) ^b
F	0.40	-17	8.11
Cl	0.41	-13	8.08
Br	1.03	-11	7.82
I	1.37	-8	7.8
OH ^c	0.67	-20	7.9

^a The experimentally measured ratios reported previously are normalized for the HX/DX ratio of 0.75, if three H and four D atoms were statistically equilibrated.

^b Derived from data in references [5,16,31,32].

^c The hydroxyl group does not participate in H/D equilibration; see references [54,55].

isotope effect (KIE) associated with HX and DX losses after complete H/D equilibration. Quite interestingly, this KIE coincides with the independently measured $\text{H}_2\text{O}/\text{HDO}$ ratio of 1.36 ± 0.05 in the dehydration of labeled 2-propanol/ Fe^+ complexes after H/D equilibration [55]. Involvement of an ET-TS connecting structures $\text{C}_3\text{H}_7\text{-M}^+\text{-X}$ and $[\text{C}_3\text{H}_7^+\cdots\text{MX}]$ can provide a mechanistic rationale for these observations, that is, the lower the IEs the more extensive H/D equilibration occurs.

The second aspect concerns the regioselectivity in alkene homologization. MS/MS studies reveal that the reaction of the propene complex $\text{Fe}(\text{C}_3\text{H}_6)^+$ with

CH_3X exclusively affords linear butene, rather than iso-butene, complexed to the metal ion (Scheme 4). Mechanistically, this result implies that the metal adds to the more substituted carbon atom in the gas-phase variant while carbometallation of olefins in the condensed phase gives terminal metal alkyls in most cases except palladium [56]. While various arguments could be put forward to explain this result, an obvious one involves stabilization of structure **4** via the corresponding carbocationic structure **4'**, whereas such a structure is much less likely for **5**, as a primary carbocation would be formed in **5'**.

While these two pieces of evidence suggest the contribution of inner sphere ET in reaction (1), they can only provide indirect evidence and do not prove (or disprove) whether the structures $\text{R-M}^+\text{-X}$ and $[\text{R}^+\cdots\text{MX}]$ are resonance contributors or discrete minima.

4.2. Reaction of FeO^+ with cyclohexane

Various metal cations are capable of multiply dehydrogenating cyclohexane to yield the corresponding cyclohexene, cyclohexadiene, and even benzene complexes [11,57]. Examination of [*all-cis*-1,2,3,4,5,6- D_6]-cyclohexane [57–59] provides a delicate probe for the mechanistic course of multiple C–H bond activation of the substrate. For example, early transition metals such as Ti^+ act like

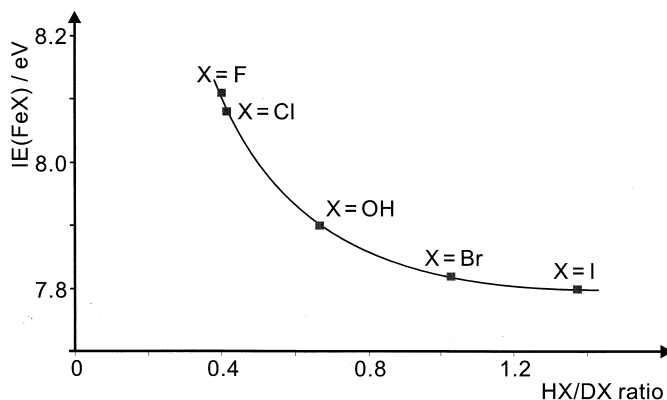
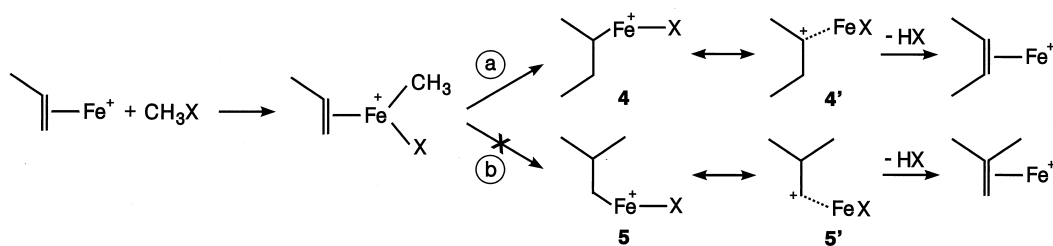


Fig. 2. Ionization energies of FeX species versus statistically weighted HX/DX ratios in the reactions of $\text{Fe}(\text{C}_2\text{D}_4)^+$ cations with CH_3X (X=F, Cl, Br, I, OH); data adopted from references [31,32,54].



Scheme 4.

a razor and cut off all hydrogens (deuteriums) from the initial site of docking to yield $M(\text{C}_6\text{H}_6)^+$ and $M(\text{C}_6\text{D}_6)^+$, respectively, but no mixed isotopomers. Late transition metals such as $\text{Fe}^+ - \text{Ni}^+$ are somewhat less effective and also yield mono- and diene complexes but still exhibit high degrees of stereospecificity. Minor processes leading to H/D equilibrations between both sides of the six-membered ring can be attributed to C–C bond activations in competing side reactions [57].

Not surprisingly, the reactive FeO^+ cation also promotes triple dehydrogenation of cyclohexane to yield $\text{Fe}(\text{C}_6\text{H}_6)^+$ [9,60]. In contrast to the bare metal cations, however, extensive H/D equilibration is observed with [*all-cis*-1,2,3,4,5,6- D_6]-cyclohexane (Fig. 3) [43]. Using conventional mechanistic schemes, this result is rather surprising because one would expect significantly lowered lifetimes of the reaction intermediates because of the large exothermicity of cyclohexane dehydrogenation by FeO^+ . Thus, the genera-

tion of $\text{Fe}(\text{cyclohexene})^+$ from cyclohexane and FeO^+ is 36 kcal/mol more exothermic than for bare Fe^+ , and the driving force is provided by formation of water as a neutral product. Moreover, involvement of initial C–C bond activation to account for H/D equilibration appears unlikely, as almost all reactions of FeO^+ with saturated hydrocarbons examined so far commence with C–H bond activation [9,61]. Conventional mechanisms, therefore, cannot account in a straightforward manner for the extensive H/D equilibration observed. Among other explanations, the involvement of a carbocationic intermediate [$c\text{-C}_6\text{H}_{11}^+ \cdots \text{FeOH}$] formed after initial C–H bond activation in the very first step provides a plausible rationale for the experimental findings because degenerate H/D equilibration in cyclohexyl cation is facile. In fact, for a $c\text{-C}_6\text{H}_{11}^+$ cation, Wagner-Meerwein rearrangements can afford rapid and complete loss of the stereochemical identity of the H and D atoms.

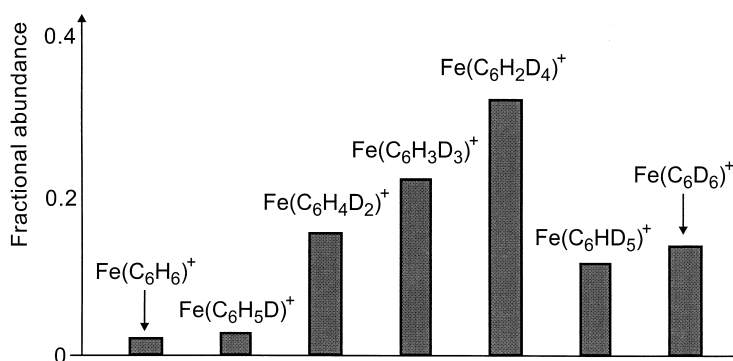


Fig. 3. Isotope distribution of $\text{Fe}(\text{benzene})^+$ formed in the reaction of [*all-cis*-1,2,3,4,5,6- D_6]-cyclohexane with FeO^+ cation [43]; the experimental data are expressed as fractional abundances ($I_i/\Sigma I_i$) and are corrected for natural ^{13}C contributions as well as incompleteness of the deuterium incorporation [57].

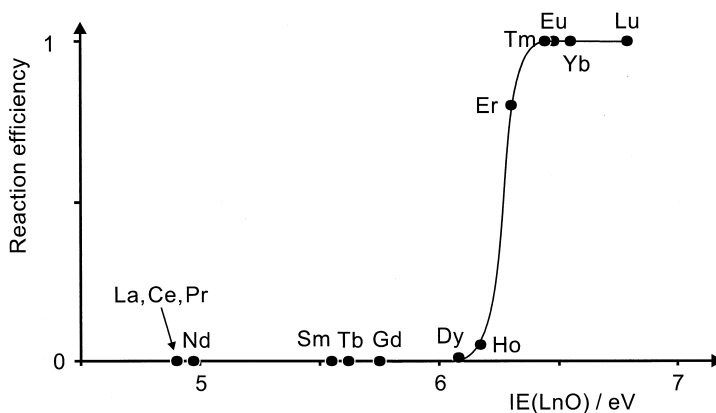


Fig. 4. Reaction efficiencies for LnO^+ cations with 1,3-butadiene versus ionization energies of the neutral lanthanide oxides LnO ; data adopted from reference [62].

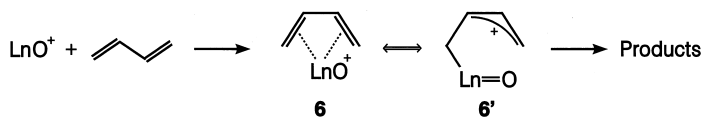
4.3. Activation of 1,3-butadiene LnO^+ cations

An impressive example for the participation of inner-sphere ET is provided by the reactions of lanthanide cations Ln^+ and their oxides LnO^+ with 1,3-butadiene [62]. Among the series of Ln^+ and LnO^+ cations, the influence of the oxo ligand is quite pronounced. Those lanthanides that do react with butadiene as bare metal cations are unreactive as oxides, while several unreactive Ln^+ cations become reactive on oxidation. Most interesting in the present context is the clear correlation between the reactivity of the LnO^+ toward butadiene and the respective IEs of the neutral metal oxides LnO (Fig. 4). For $\text{IE}(\text{LnO}) < 6$ eV, no reaction takes place at all, DyO^+ reacts very slowly ($\text{IE}(\text{DyO}) = 6.08$ eV), and the reactivity sharply increases to reach unit efficiency for thulium with $\text{IE}(\text{TmO}) = 6.44$ eV. Hence, an energy range of only 0.4 eV spans from zero to unit efficiency. This notable trend has been explained by an interplay of the diene complex **6** with the charge-permuted carbocationic intermediate **6'** in the rate-determining step (Scheme 5). As build-up of a posi-

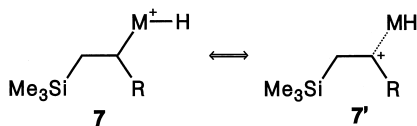
tive charge on carbon becomes more likely the larger $\text{IE}(\text{LnO})$ is, this scenario can provide a satisfactory explanation for the sharp sigmoid curve apparent in Fig. 4.

4.4. Bond activation of silyl derivatives by metal cations

In 1990, it was shown that terminal silyl substituents have pronounced effects on the regioselectivities of metal-ion mediated activations of remote C–H bonds in linear nitriles [63]. Thus, C–H bond activation of nonsubstituted alkane nitriles by transition-metal cations is characterized by moderate regioselectivities, as expected for the similar C–H bond strengths and accessibilities in reasonably long aliphatic chains [64]. On silylation at the terminus, however, bond activation of nitriles occurs by and large exclusively in the $\omega/(\omega-1)$ positions. While the high degree of regioselectivity is already quite remarkable, even more impressive are the diastereoselective bond activations occurring in metal-ion complexes of appropriately labeled (branched)



Scheme 5.



Scheme 6.

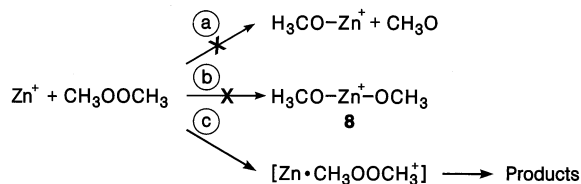
ω -silylnitriles [65]. Involvement of single electron transfer between structures **7** and **7'** (Scheme 6) has been invoked to account for the observed regio- and diastereoselectivities.

Note that the putative carbocation center in **7'** experiences further stabilization by the silyl substituent because of the well-known β -silicon effect.

4.5. O–O bond cleavage of dimethyl peroxide

The reactions of all transition-metal monocations (except Tc)¹ with dimethylperoxide have been examined systematically [66,67]. For most metals, oxidative addition across the peroxidic O–O bond predominates, leading to transient $M(\text{OCH}_3)_2^+$ complexes. Subsequently, either one methoxy group is lost or a formal disproportionation leads to metal-bound methanol and formaldehyde ligands that are eventually liberated from the complex. From a thermochemical point of view, ET could occur for all metals examined with $\text{IE}(\text{M}) \geq \text{IE}(\text{CH}_3\text{OOCH}_3) = 9.1$ eV, that is, Ir, Au, Zn, and Hg. However, outer-sphere ET that affords ionized dimethylperoxide is only observed for zinc and mercury with IEs of 9.4 and 10.4 eV, respectively. While for Hg^+ charge transfer occurs exclusively, the major product with Zn^+ corresponds to $\text{Zn}(\text{OCH}_3)^+$. Formation of the latter product ion appears straightforward, as it could be understood as a methoxy abstraction from the peroxide to yield a methoxy radical concomitant with the formal Zn^{II} compound $\text{Zn}(\text{OCH}_3)^+$ (route [a] in Scheme 7).

Again, isotopic labeling reveals that the seemingly simple loss of methoxy radical in the reaction of



Scheme 7.

dimethylperoxide with bare Zn^+ is much more complicated than anticipated. Thus, on reacting Zn^+ with CD_3OOCH_3 , a mixture of $\text{Zn}(\text{OCH}_3)_{2-n}\text{D}_n^+$ ions ($n=0-3$) is formed; that is, H/D equilibration between the methyl groups takes place. Obviously, an abstraction mechanism such as route [a] cannot account for this result. Similarly, it should be apparent that formation of a conventional insertion intermediate **8** via route [b] is strictly excluded in the case of zinc because it cannot accommodate the required Zn^{III} oxidation state in $\text{Zn}(\text{OCH}_3)_2^+$. Instead, inner-sphere ET (route [c]) can easily account for the experimental findings, as extensive H/D equilibration—concomitant with isomerization—is known to occur in ionized dimethylperoxide [68]. Resemblance of the chemistry of the free dimethylperoxide ion therefore suggests that $[\text{Zn}^+ \cdots \text{C}_2\text{H}_6\text{O}_2]$ and $[\text{Zn} \cdots \text{C}_2\text{H}_6\text{O}_2^+]$ are distinct intermediates involved in this particular case.

5. Conclusions

Several examples from gas-phase ion chemistry provide indirect evidence for the involvement of inner-sphere ET as a mechanistic concept in organometallic chemistry. While none of the examples discussed above strictly requires an ET-TS as the only rationalization of the experimental findings, the scenario offers a consistent explanation for otherwise cumbersome results. So far, these examples deal with monopositive ions, but similar considerations could well apply for multiply charged metal fragments as well as anionic species. The essence of the inner-sphere ET model is the assumed existence of the structures $[\text{A}^+ \cdots \text{B}]$ and $[\text{A} \cdots \text{B}^+]$ as discrete minima rather than resonance structures. This assumption results in the hypothetical existence of an

¹For practical reasons, the reaction of Os^+ was not included in reference [66]. Subsequent experimental studies showed prevailing disproportionation of transient $\text{Os}(\text{OCH}_3)_2^+$ and, as expected, complete absence of ET [67].

ET-TS and, hence, the possibility of inner-sphere ET contributing to the rate-determining steps in organometallic reactions in the gas phase. This bridges the classical description of metal-ion chemistry in terms of Lewis acids (or bases) without electron transfer with oxidative addition/reductive elimination processes with two-electron transfers and with reactions in which single-electron transfers take place. Nonetheless, all arguments put forward so far are indirect, and the search for more direct indications for the occurrence of inner-sphere ET in organometallic ions remains a formidable challenge for experiment and theory.

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