Insertion of Molecular Oxygen in Transition-Metal Hydride Bonds, Oxygen-Bond Activation, and Unimolecular Dissociation of Metal Hydroperoxide Intermediates

Short Communication

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Dedicated to Professor *Rudolf Zahradník* on the occasion of his 80th birthday

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Thermal activation of molecular oxygen is observed for the late-transition-metal cationic complexes $[M(H)(OH)]^+$ with M = Fe, Co, and Ni. Most of the reactions proceed *via* insertion in a metal−hydride bond followed by the dissociation of the resulting metal hydroperoxide intermediate(s) upon losses of O, OH, and H_2O. As indicated by labeling studies, the processes for the Ni complex are very specific such that the O-atoms of the neutrals expelled originate almost exclusively from the substrate O_2. In comparison to the $[M(H)(OH)]^+$ cations, the ion−molecule reactions of the metal hydride systems $[MH]^+$ (M = Fe, Co, Ni, Pd, and Pt) with dioxygen are rather inefficient, if they occur at all. However, for the solvated complexes $[M(H)(H_2O)]^+$ (M = Fe, Co, Ni), the reaction with O_2 involving O−O bond activation show higher reactivity depending on the transition metal: 60% for the Ni, 16% for the Co, and only 4% for the Fe complex relative to the $[Ni(H)(OH)]^+/O_2$ couple.
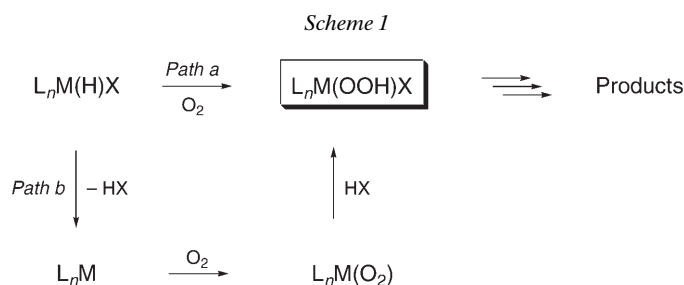

Introduction. – Molecular oxygen constitutes the quintessential terminal oxidant, because the reagent is available at virtually no cost and produces no environmentally hazardous by-products [1]. Practical and principal challenges associated with, *e.g.*, overoxidation of the starting material ('combustion') or with spin constraints in these typically spin-forbidden processes have been solved by Nature by developing powerful metalloenzymes (*e.g.*, oxidases) [2], and for *in vitro* experiments numerous efficient catalytic systems, often based on Pd complexes, are now available[1]).

As to the mechanism(s) of metal-mediated oxidations by molecular oxygen, several variants have been proposed [3], and of particular interest is the direct insertion of triplet oxygen into a (singlet) palladium(II) – hydride bond to generate a palladium(II) hydroperoxide species (*Scheme 1*; M = Pd, *Path a* [4]).

While formation of genuine palladium(II) hydroperoxides has been demonstrated experimentally to occur [5], it has been difficult to mechanistically unambiguously characterize how O_2 interacts with the Pd center, *e.g.*, *via Path a* or *via* reductive elimination of HX followed by O_2 and HX uptakes, *i.e.*, *Path b*[2]). Computational

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[1]) For a review, see [3] and references cited therein.
[2]) For a detailed discussion of mechanistic questions, see [6].

Scheme 1

$$L_n\text{M(H)X} \xrightarrow[\text{O}_2]{\textit{Path a}} \boxed{L_n\text{M(OOH)X}} \Longrightarrow \text{Products}$$

Path b $\downarrow$ – HX $\uparrow$ HX

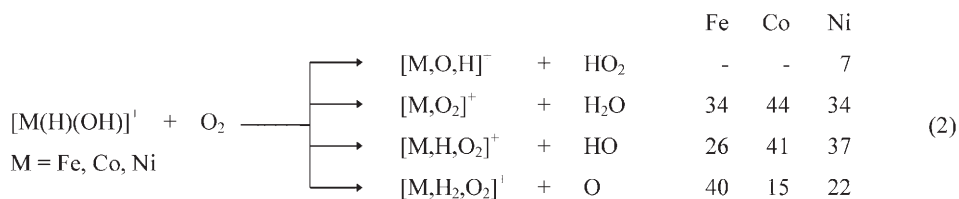$$L_n\text{M} \xrightarrow{\text{O}_2} L_n\text{M(O}_2\text{)}$$

studies suggest that, depending on the nature of the ligand L and the counterion X, in addition to *Scheme 1* quite a few mechanistic alternatives are conceivable, and the investigations of structurally more simple model complexes were recommended [7]. Further, for the oxidation of other late transition metal hydrides different mechanisms, *e.g.*, radical chain autoxidation, seem to exist, and examples which have been looked at include hydride complexes of Rh, Pt, Co, and Ir [8]; however, neither the lighter congener of Pd and Pt, *i.e.*, nickel hydride derivatives nor Fe-based compounds have been examined.

In the context of gas-phase oxygen-activation studies aimed at uncovering intrinsic mechanistic features of this important class of processes, numerous ionic systems have been investigated [9], and, with regard to the above described mechanistic puzzles of metal hydride/O_2 couples, we have decided to explore the thermal reactions of molecular oxygen with structurally rather simple transition metal hydride cations $[\text{M(H)(OH)}]^+$ in the gas phase. These formally M^{III} cations were chosen for the quite extraordinary reactivity some of them had exhibited, *e.g.*, $[\text{Ni(H)(OH)}]^+$ brings about efficient thermal activation of methane (*Eqn. 1*). In contrast, although thermochemically feasible, the analogous Fe^{III} and Co^{III} hydrides do not react according to *Eqn. 1* [10].

$$[\text{Ni(H)(OH)}]^+ + \text{CH}_4 \rightarrow [\text{Ni(CH}_3\text{)(OH)}]^+ + \text{H}_2 \tag{1}$$
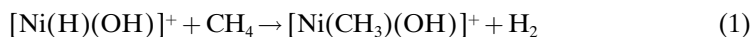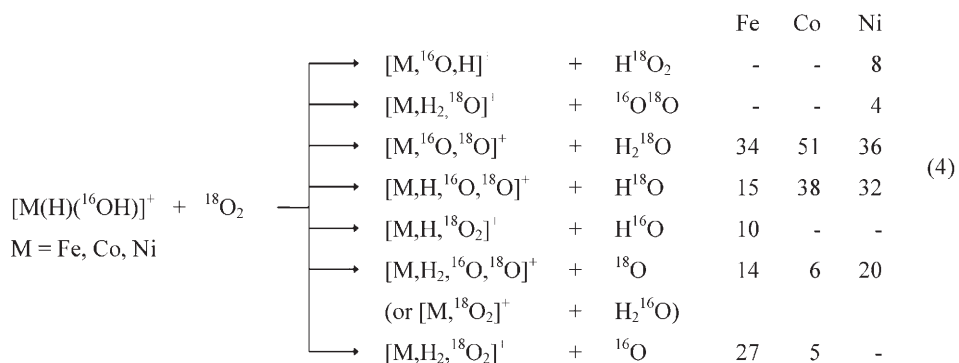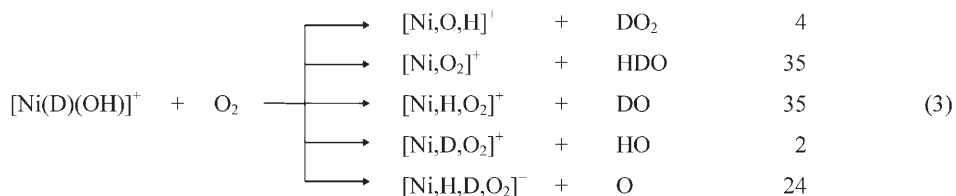
Results and Discussion. – Here, we describe the thermal ion–molecule reactions of O_2 with three basic systems, *i.e.*, the transition metal(III) hydride complexes $[\text{M(H)(OH)}]^+$, diatomic metal hydrides $[\text{MH}]^+$, and their mono-hydrated analogues $[\text{M(H)(H}_2\text{O)}]^+$. The gas-phase oxidation experiments were performed at room temperature with a quadrupole-based mass spectrometer, equipped with an electrospray ionization (ESI) source; under near single-collision conditions, the mass-selected complexes were reacted with molecular oxygen (for details, see *Exper. Part*).

The [M(H)(OH)]⁺/O₂ Couples. $[\text{Ni(H)(OH)}]^+$ was found to react efficiently ($k_{\text{rel}} = 22\%$ relative to the $[\text{NiH}]^+/\text{CH}_4$ system which reacts at near collision rate) according to *Eqn. 2*. Branching ratios for the various reaction channels are given in % throughout.

$$[M(H)(OH)]^{\cdot} + O_2 \longrightarrow$$

M = Fe, Co, Ni

|		Fe	Co	Ni
$[M,O,H]^-$ + HO_2		–	–	7
$[M,O_2]^+$ + H_2O		34	44	34
$[M,H,O_2]^+$ + HO		26	41	37
$[M,H_2,O_2]^{\cdot}$ + O		40	15	22

(2)

While the actual structures of the ionic products generated remain by and large unknown in these types of mass-spectrometric experiments, details of the course of the reactions – which form the focus of this study – can be extracted from appropriate labeling experiments (*Eqns. 3* and *4*).

$$[Ni(D)(OH)]^+ + O_2 \longrightarrow$$

$[Ni,O,H]^{\cdot}$ + DO_2		4
$[Ni,O_2]^+$ + HDO		35
$[Ni,H,O_2]^+$ + DO		35
$[Ni,D,O_2]^+$ + HO		2
$[Ni,H,D,O_2]^-$ + O		24

(3)

$$[M(H)(^{16}OH)]^+ + {}^{18}O_2 \longrightarrow$$

M = Fe, Co, Ni

		Fe	Co	Ni
$[M,{}^{16}O,H]^{\cdot}$ + $H^{18}O_2$		–	–	8
$[M,H_2,{}^{18}O]^{\cdot}$ + ${}^{16}O^{18}O$		–	–	4
$[M,{}^{16}O,{}^{18}O]^+$ + $H_2{}^{18}O$		34	51	36
$[M,H,{}^{16}O,{}^{18}O]^+$ + $H^{18}O$		15	38	32
$[M,H,{}^{18}O_2]^{\cdot}$ + $H^{16}O$		10	–	–
$[M,H_2,{}^{16}O,{}^{18}O]^+$ + ${}^{18}O$		14	6	20
(or $[M,{}^{18}O_2]^+$ + $H_2{}^{16}O$)				
$[M,H_2,{}^{18}O_2]^{\cdot}$ + ${}^{16}O$		27	5	–

(4)

An inspection of the labeling data reveals an extraordinarily high selectivity. For example, in the formation of HO_2, the OH group of $[Ni(H)(OH]^+$ is not involved at all, and the production of H_2O follows a path in which the O-atom is exclusively provided by molecular oxygen. Similarly, the liberated OH· radical contains the H-atom and its O-atom originates from O_2; obviously, the OH ligand of the Ni complex remains intact. Finally, the O-atom eliminated from the encounter complex of the ion–molecule reaction also stems specifically from molecular oxygen. Thus, O−O bond activation is crucial in the course of these reactions.

While HO_2 could be formed by direct H-atom abstraction (*Scheme 2*; **1** → **4**), the other product channels require the initial activation of the Ni−H bond giving rise to hydroperoxide intermediate(s). Although we cannot decide whether **3** is formed *via*
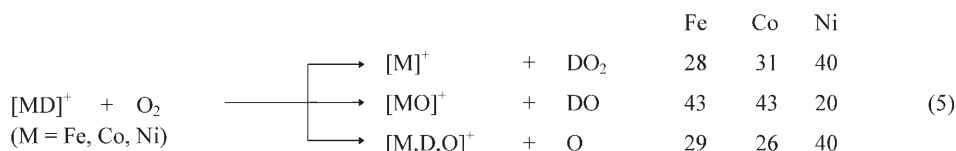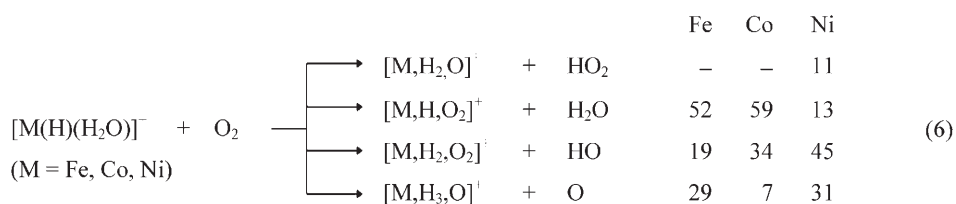
Scheme 2
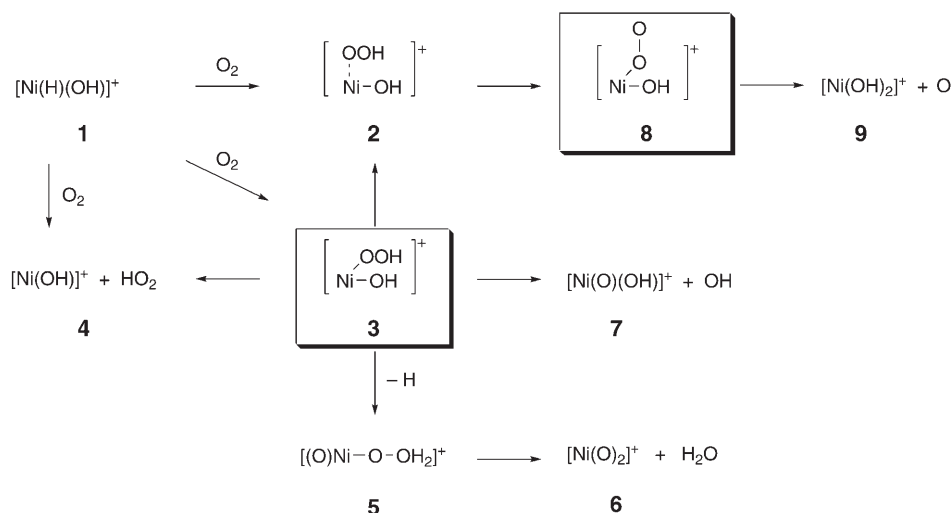
direct insertion (*i.e.*, **1** → **3**) of triplet O_2 into the Ni−H bond of the quartet state [11], or if insertion is preceded by the generation of a loosely bound complex **2**, which then has the option to collapse to **3** and/or **8**, there cannot possibly exist any doubt that both peroxide derivatives **3** and **8** act as central intermediates en route to the dissociations according to *Eqns. 2–4*. Given the nature of the experiment, *i.e.*, single-collision conditions, any chain reactions or reductive elimination of H_2O from the Ni center preceding the O−O bond activation, according to *Path b* in *Scheme 1*, can be excluded as conceivable mechanistic variants.

In the reactions of O_2 with the metal(III) hydride complexes $[M(H)(OH)]^+$ (M = Fe and Co; *Eqn. 2*), except for the formation of HO_2, all other processes reported for $[Ni(H)(OH)]^+$ occur with comparable branching ratios and only slightly diminished efficiencies; the latter amount to 48% (for M = Fe) and 54% (for M = Co) relative to the $[Ni(H)(OH)]^+/O_2$ couple. Although the experiments of $[M(H)(^{16}OH)]^+$ with $^{18}O_2$ (*Eqn. 4*) demonstrate that activation of the O−O bond occurs, as indicated by the formations of $H_2^{18}O$ and $H^{18}O$, respectively, the competitive productions of ^{16}O and ^{18}O from the Fe and Co couples indicate a more complex reaction scenario. Further, the expulsion of $H^{16}O$ from $[Fe(H)(^{16}OH)]^+/^{18}O_2$ points to a ligand replacement of the OH group in competition with a combined insertion of O_2 in the Fe−H and activation of the O−O bond in analogy to *Scheme 2*.

The [MH]$^+$/O$_2$ and [M(H)(H$_2$O)]$^+$/O$_2$ Systems. The diatomic M^{II} hydrides $[MH]^+$ bring about only sluggish ion–molecule reactions with dioxygen, with $k_{rel} < 1\%$ (relative to $[Ni(H)(OH)]^+/O_2$). Two of the products formed in *Eqn. 5* demonstrate O−O bond activation, most likely proceeding through an insertion of O_2 in the metal−D bond.

$$
\begin{array}{cccc}
 & \text{Fe} & \text{Co} & \text{Ni} \\
\end{array}
$$

$$
[MD]^+ \; + \; O_2 \quad \longrightarrow
\begin{cases}
[M]^+ & + & DO_2 & 28 & 31 & 40 \\
[MO]^+ & + & DO & 43 & 43 & 20 \\
[M,D,O]^+ & + & O & 29 & 26 & 40 \\
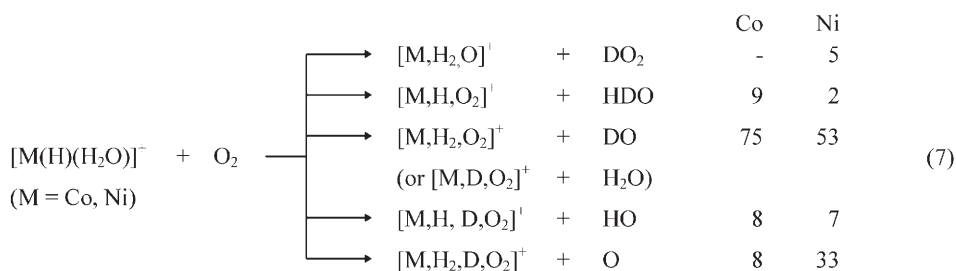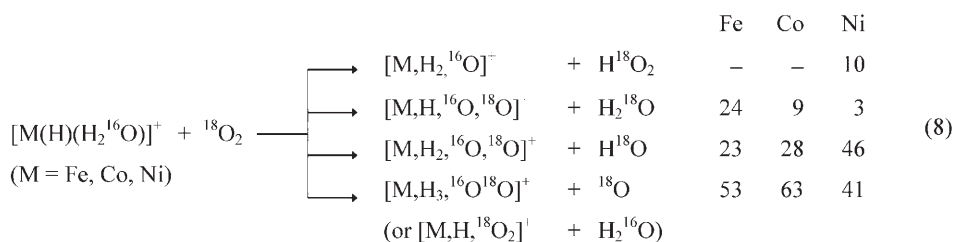\end{cases} \qquad (5)
$$

(M = Fe, Co, Ni)

The conclusion, however, that transition metal hydrides carrying a formal oxidation state II are, in general, of low reactivity towards molecular oxygen is not warranted. For example, in the thermal reactions of O_2 with the solvated M^{II} hydride complexes $[M(H)(H_2O)]^+$ (M = Fe, Co, Ni), O−O bond activation accounts for > 90% of the total reaction, and insertion of O_2 in the M−H bond is operative (*Eqn. 6*). As to the efficiencies of the reactions (relative to the $[Ni(H)(OH)]^+/O_2$ couple), there is quite some variation with 60% for the Ni, 16% for the Co, and only 4% for the Fe complex of $[M(H)(H_2O)]^+$.

$$
\begin{array}{cccc}
 & \text{Fe} & \text{Co} & \text{Ni} \\
\end{array}
$$

$$
[M(H)(H_2O)]^- \; + \; O_2 \quad \longrightarrow
\begin{cases}
[M,H_2O]^- & + & HO_2 & - & - & 11 \\
[M,H,O_2]^+ & + & H_2O & 52 & 59 & 13 \\
[M,H_2,O_2]^- & + & HO & 19 & 34 & 45 \\
[M,H_3,O]^- & + & O & 29 & 7 & 31 \\
\end{cases} \qquad (6)
$$

(M = Fe, Co, Ni)

Labeling experiments were conducted for a few selected systems (*Eqns. 7* and *8*). While we observe little atom scrambling for the $[Ni(H)(H_2O)]^+/O_2$ couple, the majority of the processes are highly specific. This holds true also for the productions of HO and atomic oxygen from the Fe and Co complexes, as indicated by the specific formations of $H^{18}O$ and ^{18}O in the reactions of the metal hydrides with $^{18}O_2$ and the absence of signals due to the losses of $H^{16}O$ and ^{16}O (*Eqn. 8*).

However, for the Fe and Co complexes some remarkable differences exist. For example, although the H_2O-loss channel cannot be analyzed quantitatively due to an overlap of the isobaric $H_2^{16}O/^{18}O$ and H_2O/DO molecules, respectively, a comparison of the data given in *Eqns. 6–8* indicates that, for these two systems, much of the H_2O eliminated results from displacement of the already present H_2O ligand by the incoming O_2 molecule.

$$
\begin{array}{ccc}
 & \text{Co} & \text{Ni} \\
\end{array}
$$

$$
[M(H)(H_2O)]^- \; + \; O_2 \quad \longrightarrow
\begin{cases}
[M,H_2O]^- & + & DO_2 & - & 5 \\
[M,H,O_2]^- & + & HDO & 9 & 2 \\
[M,H_2,O_2]^+ & + & DO & 75 & 53 \\
(\text{or } [M,D,O_2]^+ & + & H_2O) & & \\
[M,H,D,O_2]^- & + & HO & 8 & 7 \\
[M,H_2,D,O_2]^+ & + & O & 8 & 33 \\
\end{cases} \qquad (7)
$$

(M = Co, Ni)

	Fe	Co	Ni
$[M,H_2,^{16}O]^+ \quad + \quad H^{18}O_2$	–	–	10
$[M,H,^{16}O,^{18}O]^+ \quad + \quad H_2^{18}O$	24	9	3
$[M,H_2,^{16}O,^{18}O]^+ \quad + \quad H^{18}O$	23	28	46
$[M,H_3,^{16}O^{18}O]^+ \quad + \quad ^{18}O$	53	63	41

$$[M(H)(H_2^{16}O)]^+ \ + \ ^{18}O_2 \longrightarrow \qquad\qquad\qquad\qquad\qquad\qquad (8)$$

$$(M = Fe, Co, Ni)$$

$$(or\ [M,H,^{18}O_2]^+ \quad + \quad H_2^{16}O)$$

Finally, in view of the formal relationship of the group-10 metal hydride complexes [12], we have also tried to generate $[Pd(H)(OH)]^+$ and $[Pt(H)(OH)]^+$ by ESI. However, while all attempts failed to generate these isomers, we succeeded in producing diatomic $[PdH]^+$ and $[PtH]^+$ and reacting them with O_2 (*Eqn. 9*). In a moderately efficient process ($k_{rel} = 8\%$ relative to the $[Ni(H)(OH)]^+/O_2$ system), $[PdH]^+$ brings about H-atom abstraction; $[PtH]^+$ does not react with O_2 under thermal conditions.

$$[MH]^+ + O_2 \rightarrow M^+ + HO_2 \qquad\qquad\qquad (9)$$

$$(M = Pd, Pt)$$
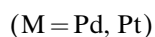
In summary, thermal activation of molecular oxygen, *via* genuine insertion in a metal–hydride bond and dissociation of the resulting metal hydroperoxide intermediate(s) are facile gas-phase processes for the late transition metal cation complexes $[M(H)(OH)]^+$, with M = Fe, Co, Ni. In contrast, for the diatomic $[MH]^+$ species, with M = Fe, Co, Ni, Pd, and Pt, the analogous reactions are rather inefficient, if they occur at all. However, the addition of an 'inert' H_2O ligand to a metal(II) hydride, as in $[M(H)(H_2O)]^+$ (M = Fe, Co, Ni), recovers much of the reactivity. Clearly, high-level computational studies are indicated to uncover the electronic structure origin(s) of these rather remarkable ion–molecule oxidation processes, to shed light on the energetic and dynamic features including the crucial role of spin changes[3][4]), and to address the relationship of the gas-phase experiments to analogous reactions in the condensed phase [3–7], in the hope that these combined efforts will help to elucidate the microscopic details of these important transformations.

Experimental Part

The experiments were performed with a *VG BIO-Q* mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an ESI source as desribed in [15]. In brief, the cationic Ni, Fe, and Co complexes $[M(H)(OH)]^+$ and $[M(H)(H_2O)]^+$, and their isotopologues were produced from millimolar solns. of metal halides in CH_3OH/H_2O (or CD_3OH/H_2O) according to the procedures reported earlier [10][16]. $[PdH]^+$ and $[PdD]^+$ were generated from $PdBr_2$ dissolved in CH_3OH and

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[3])   For a review, see [13].

[4])   That spin aspects can matter in the gas-phase reactions of O_2 with organometallic species is convincingly demonstrated by the observation that the otherwise extremely reactive $[M(CH_3)]^+$ (M = Mn, Fe, Co) and $[Mg(C_5H_5)]^+$ cations remain unoxidized by O_2 in the gas phase despite a very favorable thermochemistry (see [14]).

CD$_3$OH, resp. [10][16]. Due to the poor solubility of Pt halides in either CH$_3$OH or H$_2$O, a soln. of H$_2$PtCl$_6$ in CH$_3$OH was used, and the ions of interest generated as described earlier [17]. The complexes of interest were mass-selected by means of Q$_1$ and then exposed to react with oxygen admitted to the hexapole collision cell at r.t. and pressures of *ca.* 10^{-4} mbar; this is considered to correspond to nearly single-collision conditions. Ionic products were analyzed using Q$_2$.

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