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On the gas-phase decomposition of acyclic ethers mediated by “rollover” cyclometalated $[Pt(bipy{-}H)]^+$ (bipy = 2,2′-bipyridine): A mechanistic study

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ABSTRACT

The thermal ion/molecule reactions of diethyl, and ethyl methyl ether with cyclometalated $[Pt(bipy{-}H)]^+$ were probed in gas-phase experiments. For most of the reaction channels the initial step corresponds to a platinum-mediated transfer of an α-hydrogen atom from the ether to the (bipy−H)-ligand. This conclusion is based on a combination of extensive deuterium-labeling experiments and analogous reactions with the platinum methyl complexes $[Pt(CH_3)(bipy)]^+$, $[Pt(CD_3)(bipy)]^+$, $[Pt(CH_3)(phen)]^+$, and $[Pt(CD_3)(phen)]^+$. Furthermore, the labeling experiments with diethyl ether and ethanol isotopologues permit to derive a mechanistic scheme that is in keeping with the experimental observations. A comparison of these results with those obtained in the ion/molecule reactions of analogous thioethers reveals some distinct differences: while formal dehydrosulfurization dominates the gas-phase chemistry of $[Pt(bipy{-}H)]^+$ with organic sulfides the analogous process is practically absent for the respective ethers.

1. Introduction

In former studies it has been shown that cyclometalated $[Pt(bipy{-}H)]^+$ (**1**) can formally dehydrosulfurize a variety of thioethers in the gas-phase [1]; especially in the reaction with dimethyl sulfide efficient oxidative C–C bond coupling along with the formation of neutral ethene was observed [2]. In a recent study dealing with dimethyl ether as a substrate, it has been shown that the exchange of sulfur for oxygen has dramatic consequences with regard to the product distribution: no C–C bond formation is observed anymore for the oxygen compound whereas the formation of neutral formaldehyde constitutes the main reaction channel (see Scheme 1) [3]. These differences can be traced back to the weaker interaction of the platinum core with oxygen in comparison with that of sulfur and were explained in detail on the basis of DFT-calculated potential energy surfaces for the relevant reaction pathways. In general, pre-complexation of a substrate with the active center of a catalyst via the heteroatom of the incoming ligand promotes C–H bond activation reactions [4–7]. Therefore, comparative studies of structurally related ether/thioether compounds in the ion/molecule reactions (IMRs) with organometallic reagents may be quite instructive. As solution-phase experiments are, by definition, obscured by both solvent and aggregation effects as well as the influence of counter ions, ion/molecule experiments in the gas-phase are better suited to study the intrinsic features of such kind of processes.

Here, we report gas-phase studies of different platinum(II) complexes (Scheme 2), including cyclometalated $[Pt(bipy{-}H)]^+$ (**1**), generated by electrospray ionization (ESI) [8,9], with the ethers and alcohols shown in Scheme 3 (for a complete description of the results concerning the reactions of **1** with **4** and $[D_3]$-**4**, see [3]). Time-honored labeling experiments provide insight into the origin of the hydrogen atoms transferred and therefore into mechanistic details of the various reaction channels. Moreover, the role of the nature of the heteroatom of ethers versus thioethers is studied by an analysis of the product distributions in the ion/molecule processes.

2. Experimental details

The present experiments were performed with a *VG BIO-Q* mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an ESI source as described in detail previously [10,11]. In brief, millimolar methanolic solutions of dimeric $[Pt(CH_3)_2(\mu\text{-}(CH_3)_2S)]_2$ or $[Pt(CD_3)_2(\mu\text{-}(CH_3)_2S)]_2$ (prepared according to Ref. [12]) and the desired ligands, i.e. 2,2′-bipyridine (bipy) (and the fully deuterated analogue $[D_8]$-bipy) and 1,10-phenanthroline (phen), were introduced through a fused-silica capillary to the ESI source via a syringe pump (ca. 3 μL/min) in order to produce the ligated platinum(II) cations under inves-

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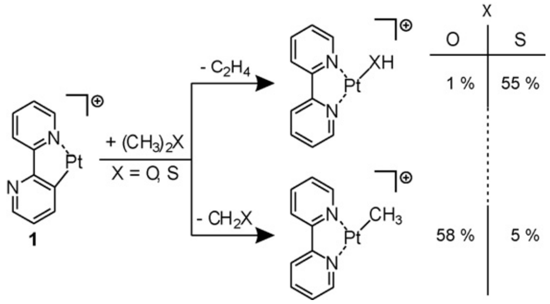

Scheme 1. Comparison of the main reaction channels in the reactions of "rollover" cyclometalated $[Pt(bipy-H)]^+$ (**1**) with $(CH_3)_2X$ (X = O, S) [3].

tigation (see Scheme 2). All heterocyclic ligands employed were purchased. Nitrogen was used as a nebulizing and drying gas at a source temperature of 80 °C. Maximal yields of the desired platinum complexes were achieved by adjusting the cone voltage (U_c) between 50 and 60 V; U_c determines the degree of collisional activation of the incident ions in the transfer from the ESI source to the mass spectrometer [13]. The identity of the ions was confirmed by comparison with the expected isotope patterns [14], collision-induced dissociation (CID) experiments, and labeling studies. The isotope pattern also assisted in the choice of the adequate precursor ion in order to avoid coincidental mass overlaps of isobaric species in the mass-selected ion beam [15]. The ion/molecule reactions of the platinum complexes with the organic substrates shown in Scheme 3 were probed at a collision energy (E_{lab}) set to nominally 0 eV, which in conjunction with the ca. 0.4 eV kinetic energy width of the parent ion at peak half-height [10] allows the investigation of quasi-thermal reactions, as demonstrated previously [16–20]. The rate constants extracted from measurements at different pressures are given relative to the reaction of $[Pt(bipy-H)]^+$ (**1**) with diethyl ether (**5**) ($k_{rel} = 100$); the reported rate constants as well as the branching ratios represent the average of different measurements performed at 3 different days. All unlabeled compounds and [1,1,1-D_3]-dimethyl ether were purchased. The labeled diethyl ethers shown in Scheme 3 were synthesized according to standard procedures from the labeled alcohols with the respective bromides in diglyme as a high-boiling solvent in order to enable efficient separation of the product by distillation from the solvent, and the ethers were afterwards purified via preparative gas chromatography. The labeled alcohols and bromides were produced by reduction of acetic acid or fully deuterated acetic acid with $Li[AlD_4]$ or $Li[AlH_4]$ in diethyl ether; after evaporation of the ether, careful hydrolysis with water or hydrobromic acid (48%) and slow distillation gave the alcohols or bromides, respectively.

3. Results and discussion

3.1. Dimethyl ether (4)

The details of the ion/molecule reactions of cyclometalated $[Pt(bipy-H)]^+$ (**1**) with dimethyl ether (**4**) ($k_{rel} = 64 \pm 11$) and [1,1,1-D_3]-dimethyl ether ([D_3]-**4**) were already discussed in Ref. [3]. However, the mechanism for the formation of neutral formaldehyde (58% of the branching ratio) in the reaction of **1** with **4** is briefly summarized in Scheme 4. The key step which is responsible for the pronounced H/D exchange between the two methyl groups preceding formaldehyde formation in the reaction with [D_3]-**4** is indicated by an asterisk.

Furthermore, we note that in the ion/molecule reactions of $[Pt(bipy)(CD_3)]^+$ ([D_3]-**2**) with **4**, after CHD_3 elimination, CH_2O is lost.[1] The $[Pt(bipy)(\mathbf{4}-H)]^+$ intermediate, which is common for the reactions of both **1** and [D_3]-**2** with **4**, is formed with different energy contents depending on its genesis. This becomes obvious when one compares the reaction enthalpies, calculated at the BP86 level of theory, for $[Pt(bipy-H)]^+$ (**1**) + $(CH_3)_2O$ (**4**) → $[Pt(bipy)(\mathbf{4}-H)]^+$ ($\Delta_R H = -223\ kJ\ mol^{-1}$) and $[Pt(CH_3)(bipy)]^+$ (**2**) + $(CH_3)_2O$ (**4**) → $[Pt(bipy)(\mathbf{4}-H)]^+ + CH_4$ ($\Delta_R H = -112\ kJ\ mol^{-1}$) [3]. The lower energy content of the intermediate, generated from **2**/**4** (or [D_3]-**2**/**4**) will certainly affect its further reactivity, and we will return to the implications further below. In fact, it is reasonable to argue that all subsequent degradation steps involve the bidentate bipyridine complex rather than a cyclometalated isomer because in the reactions of $[Pt(phen)(CD_3)]^+$ ([D_3]-**3**) with **4**, after loss of CHD_3, one observes the liberation of formaldehyde analogous to the IMR of the couple **1**/**4** although phen, on structural ground, is not able to form a cyclometalated complex in the reaction of [D_3]-**3** with **4**.

3.2. Diethyl ether (5)

The ion/molecule reaction of **1** with diethyl ether (**5**) ($k_{rel} = 100$; Fig. 1) is in terms of the product distribution not as selective as that of **1** with dimethyl ether; mass differences (Δm) that correspond to the formal eliminations of $[C_2H_6]$ (24%), $[C_2H_4O]$ (19%), $[C_2H_6O]$ (9%), $[C_3H_6O]$ (12%), and $[C_4H_8O]$ (30%) constitute the main reaction channels. Minor processes are adduct formation (1%), the losses of $[C_2H_8O]$ (1%) and $[C_4H_6O]$ (1%), and the generation of $[bipy+H]^+$ (3%). The elemental composition of the different neutral molecules eliminated was confirmed by the reaction of **1** with fully deuterated diethyl ether [D_{10}]-**5**. In comparison, in the IMR of **1** with the sulfur analogue $(C_2H_5)_2S$ the main reaction channel corresponds to the sequential losses of two ethene fragments (86%) (rather than to the oxidative coupling of two C_2H_5 fragments) [1]. An analogous process in the reaction of **1** with $(C_2H_5)_2O$ is below the detection limit. Again, this comparison demonstrates the crucial role that the heteroatom plays in seemingly related systems. However, the f_{exc} values (for a definition see Ref. [1]) in the reactions of [D_7]-**1** with **5** are in the range of 4–9% and point to a small H/D exchange behavior between **5** and the ([D_8]-bipy−D)-ligand; this is rather similar to that observed for the couple [D_7]-**1**/$(C_2H_5)_2S$ [1].

As to the molecular nature of the neutral products generated (see Fig. 1), on the basis of the data presented so far, it is not possible to distinguish between the loss of a single neutral entity and the operation of consecutive eliminations of neutral products from the association complex **1**/**5**. However, the IMR of **1** with ethanol (**7**) provides some clues to this question as the spectra for the IMRs of **1** with diethyl ether and ethanol show remarkable similarities (see Fig. 2). In fact, the spectrum shown in Fig. 2a can be interpreted in terms of a consecutive loss scenario such that ethene elimination from the adduct complex **1**/**5** generates a short-lived intermediate that formally contains $[C_2H_6O]$ and from which the same fragments are lost as from the adduct complex **1**/**7**. While this way of reasoning is sensible for the eliminations of $[C_2H_6]$ (C_2H_4/H_2), $[C_2H_6O]$ (C_2H_4/H_2O), $[C_3H_6O]$ (C_2H_4/CH_2O), and $[C_4H_8O]$ (C_2H_4/C_2H_4O), for neutral $[C_2H_4O]$, however, on energetic grounds the loss of acetaldehyde instead of ethene and an oxygen atom is clearly favored.[2] Plausible suggestions for all reaction channels, partially based on the results from the reaction of **1** with

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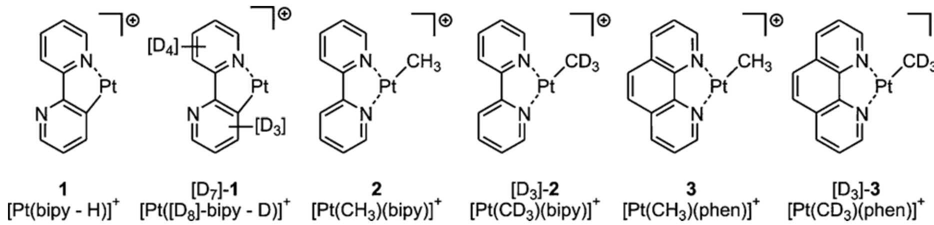
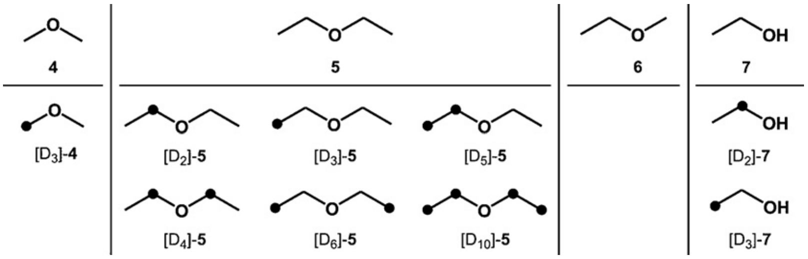
[1] The CD_3-labeled complex was used to avoid isobaric overlap of relevant signals.

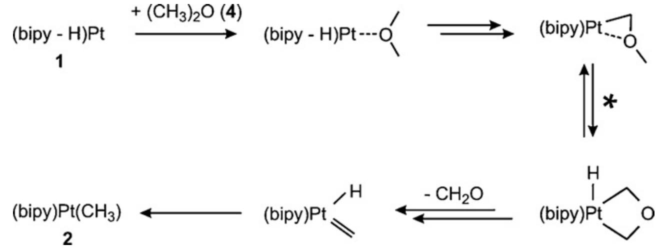
[2] The presence and unequivocal assignment of a signal with $\Delta m = 16$ in the spectrum of the IMR of **1** with ethanol cause a problem in that a clear assignment to CH_4 or O is not possible based on the labeling data as the relevant signals overlap in all cases. Moreover, this signal seems to originate from a rather efficient secondary reaction as the signal intensity is pressure dependent.



Scheme 2. Platinum(II) complexes employed in the IMRs with the ethers and alcohols shown in Scheme 3.



Scheme 3. Ethers and alcohols used for IMRs with the mass-selected platinum(II) complexes shown in Scheme 2. The black dots represent CD_2 and CD_3 units, respectively.



Scheme 4. Mechanism for the ion/molecule reaction $[Pt(bipy{-}H)]^+$ (**1**) + $(CH_3)_2O$ (**4**) → $[Pt(bipy)(CH_3)]^+$ (**2**) + CH_2O on the basis of DFT calculations as well as deuterium-labeling experiments [3]. The step marked with an asterisk is responsible for the H/D exchange process observed in the reaction with $[D_3]$-**4**. For the sake of clarity, the positive charge for all platinum-containing species is omitted.

4, are depicted in Scheme 5, and a justification for this mechanistic scenario is presented further below.

The preferential abstraction of an α-hydrogen atom from diethyl ether (**5**) in the first steps of the IMR of **1** with **5** is supported by the fact that also in the reaction of $[Pt(CH_3)(phen)]^+$ (**3**) with **5** methane is preferably lost under abstraction of a hydrogen atom from the α-position. This is proved by the reactions of $[Pt(CH_3)(phen)]^+$ (**3**) with the deuterated diethyl ethers. As shown in Table 1, this reaction is preceded by incomplete hydrogen atom exchange that takes place between the platinum-bound methyl group and the incoming ether prior to methane loss, e.g., eliminations of 21% CH_2D_2 versus 78% CH_3D in the case of $[D_{10}]$-**5**. On the other hand, a preference for the initial abstraction of an α-hydrogen atom [5] must exist to account for the loss of 63% CH_4 from $[D_6]$-**5**; if one hydrogen atom was abstracted randomly from either the α- or β-position one would expect from this precursor a ratio of CH_4:CH_3D = 40:60; similarly, the elimination of CH_3D from $[D_4]$-**5** is more pronounced than that of CH_4 opposite to what one would expect for an indiscriminately H/D abstraction; especially in the latter case the observed preference for the loss of CH_3D cannot be alone explained through the

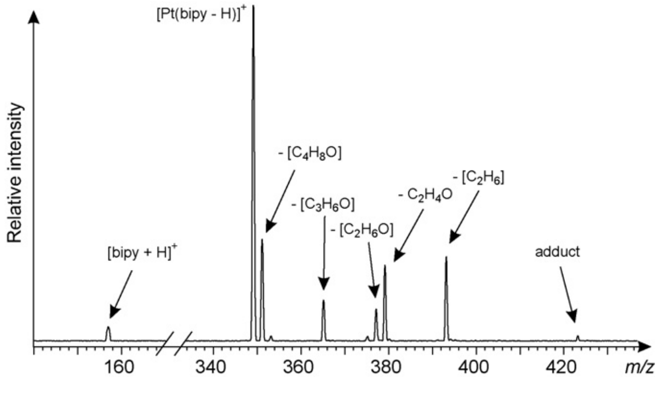


Fig. 1. Ion/molecule reaction of mass-selected $[Pt(bipy{-}H)]^+$ (**1**) with diethyl ether (**5**).

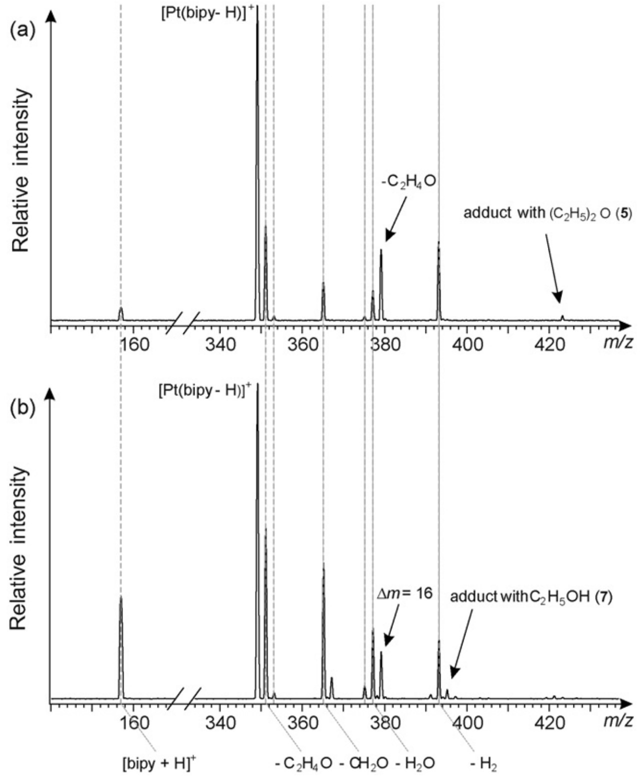
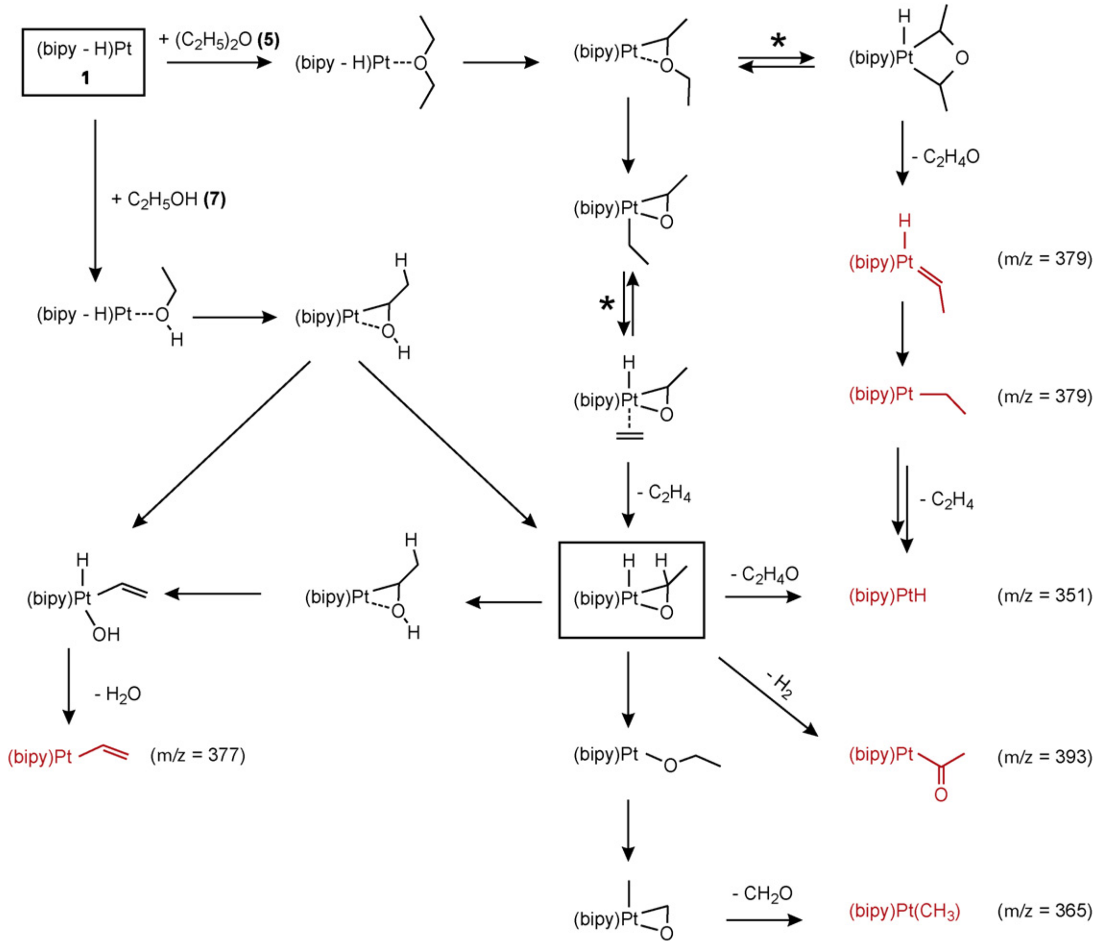


Fig. 2. Comparison of the IMRs of mass-selected $[Pt(bipy{-}H)]^+$ (**1**) with (a) diethyl ether and (b) ethanol. The assignments of the signals at the bottom are given in relation to an assumed ethene loss in the former case.



Scheme 5. Suggested decomposition network for the most important reaction channels in the ion/molecule reaction of mass-selected $[Pt(bipy-H)]^+$ (**1**) with diethyl ether (**5**) and ethanol (**7**). Red structures correspond to the species observed in the product-ion spectrum. The steps marked with an asterisk may be responsible for the hydrogen exchange processes which are observed for all reaction channels. For the sake of clarity, the positive charge for the platinum-containing species is omitted.

operation of a kinetic isotope effect which would normally favor the elimination of CH_4.

These results have some bearing also for the interpretation of the reaction of **1** with **5** due to the noted analogy in the IMRs of **1** and [D_3]-**2** with dimethyl ether that was already discussed above and for which a common intermediate was implied. In fact, as shown in Fig. 3, in the reactions of [D_3]-**2** and [D_3]-**3** with **5** signals are present which can be explained in a related way: CHD_3 loss from the adduct complexes gives rise to products from which all other relevant signals can be derived as secondary products. The close resemblance of fragments generated in the reaction of $[Pt(bipy-H)]^+$ (**1**) with $(C_2H_5)_2O$ is obvious. In particular, the losses of [C_2H_6], [C_2H_4O] and [C_2H_6O] have similar branching ratios. Differences, as the decreased intensity of products like CHD_3/[C_3H_6O] and CHD_3/[C_4H_8O], can be explained by the different energy contents of the intermediates initially formed reflecting the different genesis of the ions produced in the reactions with **1** or the methyl complexes as already illustrated above for the reactions of **1** and **2** with dimethyl ether. Furthermore, in the reactions of $[Pt(CH_3)(phen)]^+$ (**3**) with the labeled diethyl ethers the isotope patterns for the eliminations of [C_2H_6], [C_2H_4O] and [C_2H_6O] after methane loss closely resemble the ones obtained in the reactions with **1**. All these results are clear indications that the ion/molecule reactions of **1**, **2**, [D_3]-**2**, **3**, and [D_3]-**3** with different ethers can be accounted for in terms of a common intermediate which we assign to $[Pt(L)(ether-H)]^+$ (L = bipy, phen).

In order to obtain further insight into processes occurring after the initial hydrogen transfer (Scheme 5), we conducted an analysis of the labeling distributions for the ionic products derived from the reactions of **1** with deuterium labeled diethyl ethers and ethanols; especially the reactions of the latter may provide additional evidence for the hypothesis of a consecutive elimination scenario proceeding through ethene loss as the first step in

Table 1
Experimentally observed distributions (in %) for the loss of [$CH_{4-x}D_x$] (x = 1–4) in the ion/molecule reactions of $[Pt(CH_3)(phen)]^+$ (**3**) with the isotopologues of diethyl ether given in Scheme 3.[a]

Neutral fragments	[D_2]-**5**	[D_3]-**5**	[D_4]-**5**	[D_5]-**5**	[D_6]-**5**	[D_{10}]-**5**
CH_4	64	79	34	59	63	
CH_3D	25	16	53	35	29	78
CH_2D_2	(11)	1	4	6	6	21
CHD_3		(4)	2	0	2	1
CD_4			(7)	0	0	0

[a] The distributions are normalized to Σ = 100%. Numbers in parentheses are due to unidentified impurities in the spectrum.

Table 2
Experimentally observed distributions (in %) for the formation of $[C_2H_{6-x}D_x]$ (x = 0–6) in the ion/molecule reactions of [Pt(bipy−H)]$^+$ (**1**) with the isotopologues of diethyl ether given in Scheme 3.[a]

Neutral fragments lost	[D_2]-**5**	[D_3]-**5**	[D_4]-**5**	[D_5]-**5**	[D_6]-**5**
[C_2H_6]	6	**39**	1		
[C_2H_5D]	**29**	10	1	**22**	
[$C_2H_4D_2$]	**65**	10	18	19	12
[$C_2H_3D_3$]		**41**	**58**	3	**68**
[$C_2H_2D_4$]			22	16	16
[C_2HD_5]				**40**	1
[C_2D_6]					3

[a] The distributions are normalized to $\Sigma = 100\%$. Numbers printed in bold correspond to the main reaction channels.

Table 3
Experimentally observed distributions (in %) for the formation of $[C_2H_{4-x}D_xO]$ (x = 0–4) and of $[C_2H_{6-y}D_yO]$ (y = 0–6) in the ion/molecule reactions of [Pt(bipy−H)]$^+$ (**1**) with the isotopologues of diethyl ether given in Scheme 3.[a]

Neutral fragments		[D_2]-**5**	[D_3]-**5**	[D_4]-**5**	[D_5]-**5**	[D_6]-**5**
[C_2H_4O]		*20*[b]	*17*[b]	6[b]	*14*[b]	0[b]
[C_2H_3DO]		*23*[b]	11[b]	*29*[b]	11[b]	2[b]
[$C_2H_2D_2O$]	[C_2H_6O]	**28**[b,c]	15[b,c]	16[b,c]	6[b]	13[b]
[C_2HD_3O]	[C_2H_5DO]	7[c]	***36***[b,c]	9[b,c]	**18**[b,c]	*44*[b,c]
[C_2D_4O]	[$C_2H_4D_2O$]	**22**[c]	3[c]	**29**[b,c]	*25*[b,c]	8[b,c]
	[$C_2H_3D_3O$]		**18**[c]	6[c]	6[c]	9[c]
	[$C_2H_2D_4O$]			5[c]	4[c]	**21**[c]
	[C_2HD_5O]				**16**[c]	1[c]
	[C_2D_6O]					2[c]

[a] The distributions are normalized to $\Sigma = 100\%$. The meaning of the bold/italics code is explained in the text.
[b] Loss of $[C_2H_{4-x}D_xO]$ (x = 0–4).
[c] Loss of $[C_2H_{6-y}D_yO]$ (y = 0–6).

Table 4
Experimentally observed distributions (in %) for $[CH_{4-x}D_x]$ (x = 0–4) bound to the platinum core in the ion/molecule reactions of [Pt(bipy−H)]$^+$ (**1**) with the isotopologues of diethyl ether given in Scheme 3.[a]

Neutral fragments remaining	[D_2]-**5**	[D_3]-**5**	[D_4]-**5**	[D_5]-**5**	[D_6]-**5**
[CH_4]	**65**	**38**	25	**34**	4
[CH_3D]	*28*	12	**56**	*20*	1
[CH_2D_2]	7	9	17	4	14
[CHD_3]		**41**	2	*21*	**63**
[CD_4]			0	**21**	18

[a] The distributions are normalized to $\Sigma = 100\%$. Numbers printed in bold correspond to the main reaction channels as described in the text. Numbers printed in italics can be explained by an α,α′-hydrogen exchange process (compare Scheme 4).

the reaction with diethyl ether. The results in Tables 2–5 for the eliminations of [C_2H_6], [C_2H_4O], [C_2H_6O], [C_3H_6O], and [C_4H_8O] indicate, however, that extensive hydrogen atom exchange seems to precede the next elimination steps. The origin of this hydrogen exchange may be the consequence of a facile β-H-rearrangement step after the alkyl transfer shown in Scheme 5; actually, it is well-known that hydrogen exchange is both efficient and extensive in such platinum-hydride ethene adducts [21]. Moreover, hydrogen exchange processes between the α-carbon atoms of diethyl ether could also proceed through a mechanism similar to that found for the reaction of **1** with **4** (Scheme 4). Nevertheless, some qualitative trends can be extracted from the data, and these will be discussed next.

According to the labeling data shown in Table 2, the elimination of [C_2H_6] from **1**/**5** corresponds preferably to the loss of an ethyl chain together with one hydrogen atom that originates from the α-position of the other chain (see data presented in bold in Table 2); this becomes particularly obvious in the preferred [$C_2H_3D_3$] elimination in the reactions of **1** with both $(CH_3CD_2)_2O$ ([D_4]-**5**) and $(CD_3CH_2)_2O$ ([D_6]-**5**) and also in the reactions of **1** with [D_2]-**5** and [D_3]-**5**. Furthermore, the data derived from the reactions of **1** with [D_2]-**5** and [D_5]-**5** permit to estimate a primary kinetic isotope effect of around 2 (i.e., loss of 40% [C_2HD_5] versus 22% [C_2H_5D] in the case of [D_5]-**5** and 65% [$C_2H_4D_2$] versus 29% [C_2H_5D] in the case of [D_2]-**5**). For the couple **1**/[D_3]-**5** no such KIE is observed which indicates that only the α-positions of the ethyl chains are involved in the rate determining steps of [C_2H_6] formation. These observations are in keeping with the proposed consecutive losses of C_2H_4 and H_2 as illustrated in Scheme 5; however, the origin of the observed KIE cannot be unequivocally assigned. Moreover, and

Table 5
Experimentally observed and modelled distributions (in %) for $[H_{2-x}D_x]$ (x = 0–2) remaining in the platinum complex in the ion/molecule reactions of [Pt(bipy−H)]$^+$ (**1**) with the isotopologues of diethyl ether shown in Scheme 3.[a,b]

Neutral fragments remaining	[D_2]-**5**	[D_3]-**5**	[D_4]-**5**	[D_5]-**5**	[D_6]-**5**
H_2	52 (53)	68 (68)	19 (19)	32 (30)	39 (41)
HD	42 (42)	29 (30)	55 (55)	49 (50)	53 (51)
D_2	6 (5)	3 (2)	26 (26)	19 (20)	8 (8)

[a] The distributions are normalized to $\Sigma = 100\%$. Numbers given in parentheses refer to the modeled values.
[b] The model parameters are $f_{sel} = 0.55$, $f_{scr} = 0.45$, $f_{\alpha\alpha} = 0.24$, $f_{\alpha\alpha'} = 0.28$, $f_{\alpha\beta} = 0.28$, $f_{\alpha\beta'} = 0.20$, and $KIE_{scr} = 1.5$, $KIE_{\alpha\alpha} = 1.2$, $KIE_{\alpha\alpha'} = 1.3$, $KIE_{\alpha\beta} = 1.2$, $KIE_{\alpha\beta'} = 0.9$.

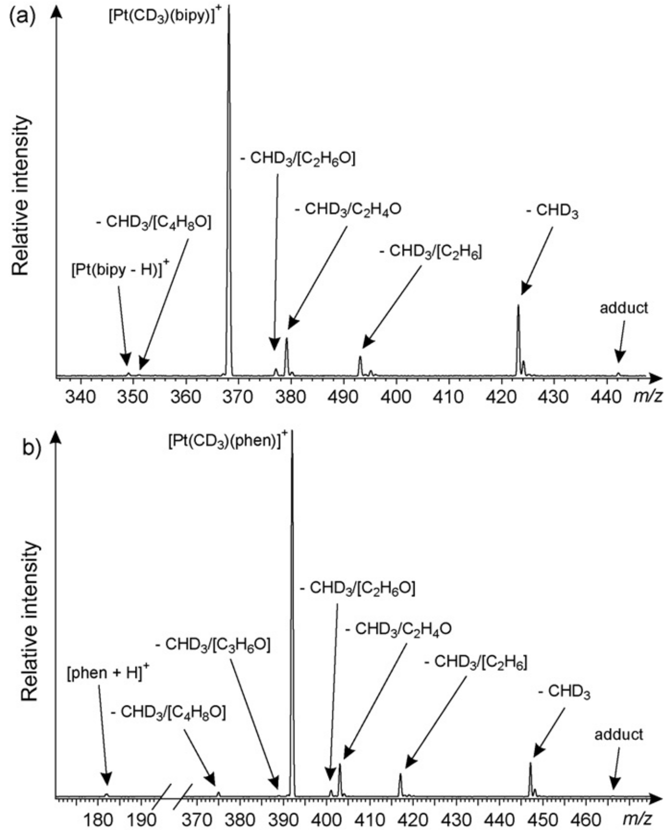


Fig. 3. Ion/molecule reactions of mass-selected (a) $[Pt(CD_3)(bipy)]^+$ ($[D_3]$-**2**) and (b) $[Pt(CD_3)(phen)]^+$ ($[D_3]$-**3**) with diethyl ether.

strictly speaking, the elimination of an intact ethane unit cannot be completely ruled out based on these results. However, in the reaction of **1** with ethyl methyl ether (**6**) no CH_4 is eliminated (see Fig. 4); the latter could have been generated from the methyl group together with an α-hydrogen atom of the ethyl group in analogy to the $[C_2H_6]$ formation from diethyl ether. This is an indication that in the reaction of **1** with **5** $[C_2H_6]$ does not correspond to ethane but rather to ethene and dihydrogen.

The mechanism proposed in Scheme 5 is also consistent with the results of the reactions of **1** with deuterium labeled ethanols when one assumes that the structure given in the center of Scheme 5 is formed from this couple via an initial α-hydrogen transfer. From the adduct complex **1**/**7** molecular hydrogen is mainly lost from the α-position of the ethyl chain together with the hydrogen atom from the hydroxyl group. The hydrogen atom eliminated from the OH-group in the reaction of **1** with **7** corresponds formally to the β-hydrogen atom transferred from the ethyl group to the platinum center in the reaction of **1** with **5**.

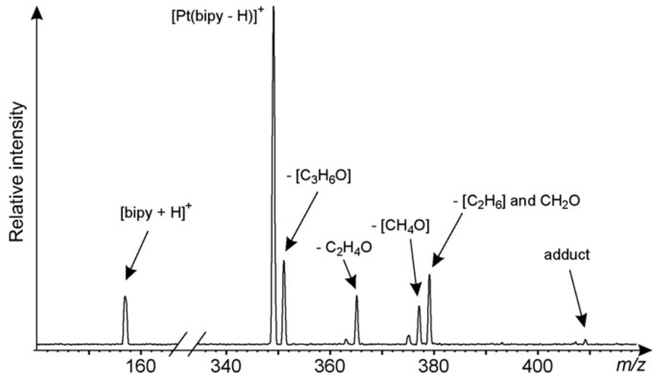


Fig. 4. Ion/molecule reaction of mass-selected $[Pt(bipy{-}H)]^+$ (**1**) with ethyl methyl ether (**6**).

The isotope patterns for the losses of $[C_2H_4O]$ and $[C_2H_6O]$ in the reaction of **1** with the deuterated diethyl ethers exhibit several overlapping signals (Table 3). Nevertheless, it is still possible also for these two channels to extract some informations concerning the mechanism. The numbers printed in italics in Table 3 refer to the formation of acetaldehyde being formed from an ethoxy group of diethyl ether except a hydrogen atom from its α-position. The data printed bold in Table 3 are assigned to the loss of $[C_2H_6O]$ consisting of an ethoxy group together with one β-hydrogen atom from the second ethyl chain. The date printed in both bold and italics corresponds to a signal resulting from both processes. The highlighted data represent indeed the most intensive signals in the spectra. We note that this assignment is consistent with the mechanisms proposed in Scheme 5 for the loss of acetaldehyde and a consecutive elimination of C_2H_4 and H_2O. Moreover, the assumption of a consecutive process in the latter case is again supported by the reactions of **1** with deuterium labeled ethanols: H_2O is indeed preferably eliminated in a formal 1,2-elimination mode. Nevertheless, one cannot exclude definitively that $[C_2H_6O]$ corresponds to intact ethanol. The existence of such an additional process is indicated by the fact that $[CH_4O]$ is eliminated in the IMR of **1** with ethyl methyl ether; here $[CH_4O]$ must correspond to methanol because a consecutive elimination of CH_2 and H_2O can be ruled out on energetic grounds.

The elimination of $[C_3H_6O]$ in the reaction of **1** with **5** formally implies that $[CH_4]$ remains in the platinum complex. From the data in Table 4 it becomes obvious that mostly one intact methyl group of one of the ethyl chains together with an α-hydrogen atom from the same or from the other chain is transferred to the organometallic part (compare especially the reactions of **1** with $(CH_3CD_2)_2O$ ($[D_4]$-**5**) and with $(CD_3CH_2)_2O$ ($[D_6]$-**5**)). There seems to be no clearcut preference from which ethyl group the α-hydrogen originates, although an abstraction from the same ethyl group seems to be slightly preferred (see **1** + $(C_2H_5)O(C_2D_5)$ ($[D_5]$-**5**)). This observation may result from an α,α′-hydrogen exchange as described above and already observed in the reaction of **1** with **4** (Scheme 4). Also for the elimination of $[C_3H_6O]$, experiments with deuterium labeled ethanols point to a sequence of C_2H_4 and CH_2O expulsion because also in the reaction of **1** with ethanol one notes that $[CH_4]$ remains in the platinum complex, and this unit is preferably formed from the methyl group together with an α-hydrogen atom.

Finally, a qualitative analysis for the $[C_4H_8O]$ loss channel in the reaction of **1** with **5** proved not to be that straightforward (see Table 5). For this very reason we have applied a kinetic model [22–30] to the data which includes the following assumptions: (*i*) a selective reaction channel (f_{sel}) and a channel which includes complete hydrogen scrambling (f_{scr}) between all hydrogen atoms of the incoming ether are mixed in a linear combination, (*ii*) the selective channel is subdivided into four separate channels $f_{\alpha\alpha}$, $f_{\alpha\alpha'}$, $f_{\alpha\beta}$, and $f_{\alpha\beta'}$ which describe the transfer of two hydrogen atoms from the respective positions of the diethyl ether to the platinum complex (interestingly it is not necessary to include the channels $f_{\beta\beta}$, and $f_{\beta\beta'}$), and (*iii*) each reaction channel is associated with its own kinetic isotope effect, i.e., KIE_{scr}, $KIE_{\alpha\alpha}$, $KIE_{\alpha\alpha'}$, $KIE_{\alpha\beta}$, and $KIE_{\alpha\beta'}$. The results of the modeling procedure are given in Table 5 together with the experimental data.

The selective channel amounts to ca. $f_{sel} = 55\%$ and the exchange channel to ca. $f_{scr} = 45\%$. The further subdivision of the selective channel does not result in any preference apart from the fact that one hydrogen atom is always transferred from the α-position of the ether to the platinum complex; this is further indicated by the fact that an inclusion of the channels $f_{\beta\beta}$, and $f_{\beta\beta'}$ is not necessary to improve the model. On the other hand, there is obviously not only one mechanistic scenario to explain the loss of [C_4H_8O] in the reaction of **1** with **5**; ethyl vinyl ether formed in a formal 1,2-elimination as well as the consecutive elimination of C_2H_4 together with C_2H_4O are conceivable mechanistic variants, and the latter has been included in Scheme 5. This is also indicated by the fact that in the course of the C_2H_4O loss in the reaction of **1** with ethanol the hydrogen atoms, transferred to the platinum complex, originate mainly from the α-position together with one β-H atom or the H atom from the hydroxy group, respectively.

3.3. *Ethyl methyl ether (**6**)*

In addition to the reactions of **1** with the symmetric ethers **4** and **5** also the ion/molecule reactions of **1** with ethyl methyl ether (**6**) were studied ($k_{rel} = 96 \pm 10$; Fig. 4). As no deuterated analogues were investigated for ethyl methyl ether, the assignment of the signals is based on the isotope patterns due to the ^{13}C content of the ionic products. The most important reaction channels correspond to the eliminations of [CH_4O] (13%), [C_2H_4O] (19%), and [C_3H_6O] (26%) as well as to the loss of a fragment with $\Delta m = 30$ (24%); the protonated ligand $[bipy+H]^+$ is formed with 11%. Minor reactions concern adduct formation (1%) and eliminations of H_2 (1%), C_2H_4 (<1%), [CH_6O] (3%) and [C_2H_6O] (1%). The fragment with $\Delta m = 30$ corresponds to a mixture of CH_2O and [C_2H_6] with the latter prevailing as derived from the corresponding ^{13}C-signal.

Also for the reaction of **1** with ethyl methyl ether, the results contrast sharply with the data obtained for the reaction of **1** with ethyl methyl sulfide where losses of C_2H_4 (33%), C_2H_4/H_2 (34%), and C_3H_6 (9%) correspond to the main channels [1].

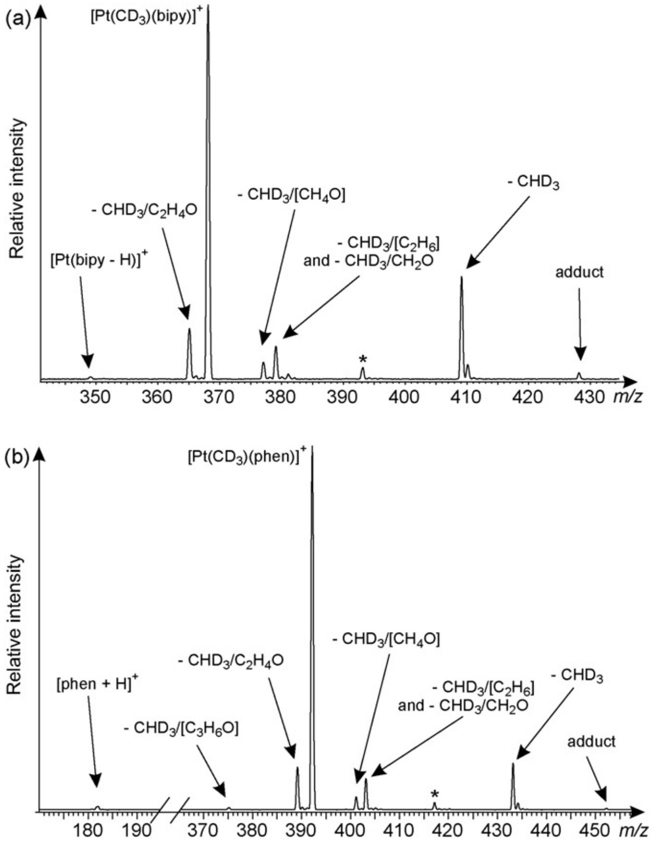


Fig. 5. Ion/molecule reactions of mass-selected (a) $[Pt(CD_3)(bipy)]^+$ ([D_3]-**2**) and (b) $[Pt(CD_3)(phen)]^+$ ([D_3]-**3**) with ethyl methyl ether. The signals indicated by an asterisk correspond to an unassigned loss of $\Delta m = 16$ with reference to the elimination of CHD_3.

The reaction of $[Pt(CD_3)(bipy)]^+$ ([D_3]-**2**) with ethyl methyl ether shows a similar trend as observed in the reaction of [D_3]-**2** with diethyl ether, and the same holds true for the analogous reactions of [D_3]-**3** (Fig. 5): after the elimination of CHD_3 one observes as major processes the losses of [C_2H_6] or CH_2O, [CH_4O], and [C_2H_4O] as in the reactions from the adduct of **3** with **6**. Once more, these findings support the above-mentioned conclusions.

4. Conclusion

We have studied the ion/molecule reactions of diethyl ether, and ethyl methyl ether with cyclometalated $[Pt(bipy-H)]^+$ (**1**) in the gas-phase. The reactions of these substrates with the platinum methyl cations $[Pt(CH_3)(bipy)]^+$, $[Pt(CD_3)(bipy)]^+$, $[Pt(CH_3)(phen)]^+$, and $[Pt(CD_3)(phen)]^+$ suggest that the initial step for all major reaction pathways corresponds to the transfer of one α-hydrogen atom to the (bipy−H)-ligand. Extensive labeling studies with deuterated diethyl ethers as well as the reactions of **1** with deuterated and undeuterated ethanol suggest a mechanistic picture for most of the reaction pathways. In particular, the comparison of the reactions of **1** with diethyl ether and ethanol strongly suggests the existence of consecutive losses of first ethene and then other fragments in many reaction channels for the couple **1**/**5**. In the reactions in which formaldehyde or acetaldehyde is lost, the initial hydrogen transfer is most probably followed by an α′-hydrogen transfer to the platinum core and a [2+2] cycloreversion process as found earlier in DFT calculations for the reaction of **1** with dimethyl ether to form neutral formaldehyde. A comparison of the reactions of the ethers with those of the analogous sulfur compounds is rather instructive and points to distinct differences in the reactions with $[Pt(bipy-H)]^+$; while formal dehydrosulfurization corresponds to the most pronounced process for organic sulfides this is not the case for the corresponding ethers. This different behavior can be traced back to the different interaction of platinum with oxygen and sulfur.

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