CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200902742

Ion–Molecule Reactions of “Rollover” Cyclometalated $[Pt(bipy-H)]^+$ ($bipy = 2,2'$-bipyridine) with Dimethyl Ether in Comparison with Dimethyl Sulfide: An Experimental/Computational Study

Burkhard Butschke, Shadan Ghassemi Tabrizi, and Helmut Schwarz*[a]

Dedicated to Hans Groß, Ernst Schmitz, Manfred Schulz on the occasion of November 9, 1989 and in memory of Heinrich Kriegsmann

Abstract: The ion–molecule reactions of dimethyl ether with cyclometalated $[Pt(bipy-H)]^+$ were investigated in gas-phase experiments, complemented by DFT methods, and compared with the previously reported ion–molecule reactions with its sulfur analogue. The initial step corresponds in both cases to a platinum-mediated transfer of a hydrogen atom from the ether to the (bipy−H) ligand, and three-membered oxygen- and sulfur-containing metallacycles serve as key intermediates. Oxidative C−C bond coupling (“dehydrosulfurization”), which dominates the gas-phase ion chemistry of the $[Pt(bipy-H)]^+$ ion with dimethyl sulfide, is practically absent for dimethyl ether. The competition in the formation of C_2H_4 and CH_2X ($X = O$, S) in the reactions of $[Pt(bipy-H)]^+$ with $(CH_3)_2X$ ($X = O$, S) as well as the extensive H/D exchange observed in the $[Pt(bipy-H)]^+/(CH_3)_2O$ system are explained in terms of the corresponding potential-energy surfaces.

Keywords: C−H activation • density functional calculations • ion–molecule reactions • mass spectrometry • platinum

Introduction

Cyclometalated transition metal compounds[1] have received much interest in different areas of chemistry, because of their photoluminescent and electronic properties,[2] as metallomesogens,[3] or as building blocks for supramolecular architectures.[4] Moreover, one encounters cyclometalated intermediates in different metal-mediated organic transformations such as the Heck reaction and Suzuki coupling,[5] and these compounds can also be employed for the synthesis of various heterocycles.[6] Their direct use as catalysts, however, has hardly been explored. For example, Periana and coworkers investigated the heterolytic C−H bond activation of methane and benzene with a cyclometalated Pt^{II} complex as well as catalytic methane hydroxylation using an Ir^{III} NNC pincer complex in acidic solution;[7,8] another study deals with transfer hydrogenation mediated by a cyclometalated Ir^{III} compound.[9] 2,2′-Bipyridine (bipy) and related heterocycles, which are versatile ligands in the coordination chemistry of transition metals,[10] are well suited for the formation of cyclometalated compounds. Moreover, it has been shown that cyclometalated $[Pt(bipy-H)]^+$ (**1**) can formally dehydrosulfurize a variety of thioethers in the gas phase;[11] especially in the reaction with dimethyl sulfide, efficient oxidative C−C bond coupling and concomitant formation of neutral ethene was observed.[12] In general, pre-complexation of a substrate with the active center of a catalyst through the heteroatom of the incoming ligand promotes C−H bond activation reactions,[13] and in gas-phase processes the nature of the substrate itself may also affect the reaction, in that the energy content of the adduct complex changes when the heteroatom is altered. For example, in the adduct formation of an ether with an ionic late transition metal complex, the energy gained is smaller than with the analogous thioether because the ion-induced dipole interaction is smaller for oxygen, as is its polarizability, when compared with the sulfur analogues. To probe the influence of the heteroatom on the outcome of the reaction, comparative studies of structurally related ether/thioether compounds in ion–molecule reactions (IMRs) with organometallic reagents

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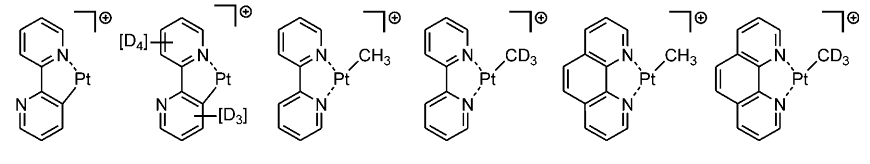
[a] Dipl.-Chem. B. Butschke, S. Ghassemi Tabrizi, Prof. Dr. H. Schwarz
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Tel.: (+49) 30-314-23483
Fax: (+49) 30-314-21102
E-mail: Helmut.Schwarz@mail.chem.tu-berlin.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902742.

could be interesting. As solution-phase experiments—by definition—are obscured by both solvent and aggregation effects as well as the influence of counterions, related ion–molecule experiments in the gas phase, due to their very nature, are well suited to study the intrinsic features of such processes.

Here, we report gas-phase studies on different Pt^{II} complexes (Scheme 1), including cyclometalated $[Pt(bipy{-}H)]^+$ (**1**), generated by electrospray ionization (ESI),[14] with dimethyl ether and [1,1,1-D_3]dimethyl ether. Labeling experiments provide insight into the origin of the hydrogen atoms transferred and therefore into mechanistic details of the various reaction channels. The role of the nature of the heteroatom of ethers versus thioethers was studied by analysis of the product distributions in the ion–molecule processes; quantum-chemical calculations were performed with the aim of gaining further understanding of mechanistic aspects of the reactions.



1 $[Pt(bipy - H)]^+$ **[D_7]1** $[Pt([D_8]bipy - D)]^+$ **2** $[Pt(CH_3)(bipy)]^+$ **[D_3]2** $[Pt(CD_3)(bipy)]^+$ **3** $[Pt(CH_3)(phen)]^+$ **[D_3]3** $[Pt(CD_3)(phen)]^+$

Scheme 1. Pt^{II} complexes employed in the studies.

Experimental and Computational Section

Experiments: 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.[15] In brief, millimolar solutions of dimeric $[\{Pt(CH_3)_2(\mu\text{-}Me_2S)\}_2]$ or $[\{Pt(CD_3)_2(\mu\text{-}Me_2S)\}_2]$ (prepared according to ref. [16]) and the desired ligands, that is, 2,2′-bipyridine (bipy) or its fully deuterated analogue ([D_8]bipy) and 1,10-phenanthroline (phen), in pure methanol were introduced through a fused-silica capillary to the ESI source by syringe pump (ca. 3 $\mu L\,min^{-1}$) to produce the ligated Pt^{II} ions under investigation (see Scheme 1). All heterocyclic ligands employed were purchased. Nitrogen was used as 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.[17] The identity of the ions was confirmed by comparison with the expected isotope patterns,[18] collision-induced dissociation (CID) experiments, and labeling studies. The isotope pattern also assisted in the choice of the adequate precursor ion to avoid coincidental mass overlaps of isobaric species in the mass-selected ion beam.[19] The ion–molecule reactions of the platinum complexes with the substrates 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[15a] allows the investigation of quasithermal reactions, as demonstrated previously.[20] Dimethyl ether (**4**) and [1,1,1-D_3]dimethyl ether ([D_3]**4**) were purchased. To confirm the correct labeling of [D_3]**4**, it was allowed to react with atomic Fe^+ (generated from a millimolar solution of $FeCl_2$ in methanol); we observed the formation of CH_3D, CH_2D_2, and CHD_3 in a ratio of 56:1:43 which confirms [D_3]**4** to be $(CH_3)O(CD_3)$.[21]

Computations: In the computational studies we employed the Gaussian 03 program package[22] using basis sets of approximately triple-ξ quality. For H, C, N, O, and S atoms these were the triple-ξ plus polarization basis sets (TZVP) of Ahlrichs and co-workers.[23] For platinum, the Stuttgart–Dresden scalar relativistic pseudopotential (ECP60MDF replacing 60 core electrons) was employed in conjunction with the corresponding (8s,7p,6d)/[6s,5p,3d] basis set describing the 6s5d valence shell of Pt.[24] In these computational studies we focused on four aspects of the reaction of $[Pt(bipy{-}H)]^+$ (**1**) with dimethyl ether (**4**): 1) does the initial bond-activation step after adduct formation correspond to insertion of the platinum center into a C–O or a C–H bond of the ether, 2) which reaction mechanism is responsible for the main reaction channel, 3) why is ethene loss, as observed in the reaction of **1** with dimethyl sulfide, not an option for dimethyl ether, and 4) what is the origin of the extensive hydrogen exchange between the methyl groups of dimethyl ether in the reactions of **1** with [D_3]**4**? The reaction pathways for the processes defined in Equations (1) and (2) (X = O, S) were calculated with the BP86[25] functional and the basis sets given above. All energies (given in $kJ\,mol^{-1}$) are corrected for (unscaled) zero-point vibrational energy contributions. Intrinsic reaction coordinate (IRC) calculations were performed to link transition structures with the respective intermediates.[26] The discussion of the computational findings is confined to the singlet state of the various platinum cations, because exploratory calculations revealed that the triplet states are generally much higher in energy for all species investigated and are therefore not likely to be involved in experiments conducted at ambient temperature.

$$[Pt(bipy{-}H)]^+ + (CH_3)_2X \rightarrow [Pt(bipy)(CH_3)]^+ + CH_2X \qquad (1)$$

$$[Pt(bipy{-}H)]^+ + (CH_3)_2X \rightarrow [Pt(bipy)(XH)]^+ + C_2H_4 \qquad (2)$$

Results and Discussions

Experimental results: The product-ion spectrum of the ion–molecule reaction (IMR) of cyclometalated $[Pt(bipy{-}H)]^+$ (**1**) with dimethyl ether (**4**) is shown in Figure 1. The main reaction channels correspond to loss of neutral CH_2O (58 %), most probably being formaldehyde, formation of

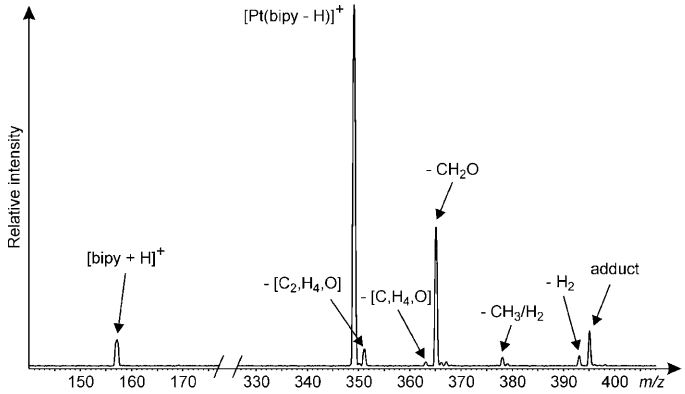


Figure 1. Ion–molecule reaction of mass-selected $[Pt(bipy{-}H)]^+$ (**1**) with dimethyl ether (**4**).

protonated bipy [bipy+H]$^+$ (14%), and elimination of [C_2,H_4,O] (8%). Adduct formation (9%), and the losses of H_2 (4%) and [C,H_4,O] (2%) are of only minor importance. The assignment of the signals to particular elemental compositions is based on the reaction of **1** with [1,1,1-D_3]dimethyl ether ([D_3]**4**) as well as on the ^{13}C isotope patterns of the ionic products. For example, elimination of a fragment with $\Delta m = 17$ (4%) is assigned to the combined losses of CH_3 and H_2 rather than to neutral OH because the reaction of **1** with [D_3]**4** gives rise to $\Delta m = 17$, 18, 19, and 20 in a ratio of 6:15:35:44; thus, the fragment with $\Delta m = 17$ must contain more than one hydrogen atom. We note that, among the products generated from the couple **1**/**4**, formation of neutral ethene is negligible (1%) in contrast to the reaction of **1** with $(CH_3)_2S$, for which this channel amounts to 55%. Loss of CH_2S, however, is of minor importance (5%) for **1**/$(CH_3)_2S$.[12] Obviously, the exchange of sulfur for oxygen has dramatic consequences with regard to the product distribution. We also carried out the reaction of **4** with the fully deuterated analogue of [Pt(bipy−H)]$^+$ (**1**), that is, [Pt([D_8]bipy−D)]$^+$ ([D_7]**1**). Similar to the IMRs with $(CH_3)_2S$,[12] partial exchange of hydrogen atoms between the incoming ether and the (bipy−H) ligand takes place. In terms of the f_{exc} value (defined in ref. [11]) hydrogen exchange in the adduct complex prior to the elimination of neutral molecules is much less pronounced for the oxygen compound than for dimethyl sulfide; for example, for the loss of CH_2X (X=O, S) the analysis leads to $f_{exc}(X{=}O) = 28\%$ versus $f_{exc}(X{=}S) = 66\%$; formation of protonated bipyridine [bipy+H]$^+$ is accompanied by $f_{exc}(X{=}O) = 19\%$ versus $f_{exc}(X{=}S) = 77\%$.

Further, the reactions of [Pt(CD_3)(L)]$^+$ (L=bipy, phen; [D_3]**2**, [D_3]**3**) with dimethyl ether also shed light on the initial steps of the reaction of **1** with these substrates. The use of the CD_3-labeled platinum complexes aids in separating isobaric ions; in addition, when phen is employed as ligand the reaction manifold is simplified on the grounds that this ligand, in contrast to bipy, is not able to undergo a ("rollover") cyclometalation process and therefore also can not engage in hydrogen/deuterium exchange processes with the incoming ether; this simplification is of importance in the interpretation of the data. As shown in Figure 2a for the complex [D_3]**2**, adduct formation with dimethyl ether (**4**) is followed by the loss of mainly CHD_3. This requires activation of a C−H bond of **4**, which has also been observed in solution experiments.[13c] More interesting than the mere C−H bond-activation process is the fact that in the gas phase elimination of CHD_3 is followed by liberation of CH_2O; as noted above, the latter reaction constitutes the main channel in the reaction of **1** with **4** (Figure 1). This observation suggests that both couples **1**/**4** and [D_3]**2**/**4** decompose via a common intermediate. The fact that the spectrum resulting from the reaction of [D_3]**3** with **4** (Figure 2b) resembles essentially that for the reaction of [D_3]**2** with **4** and that phen, in contrast to bipy, is not able to undergo a "rollover" cyclometalation point to an intermediate which we assign to [Pt(L)(**4**−H)]$^+$ with L=phen, bipy.

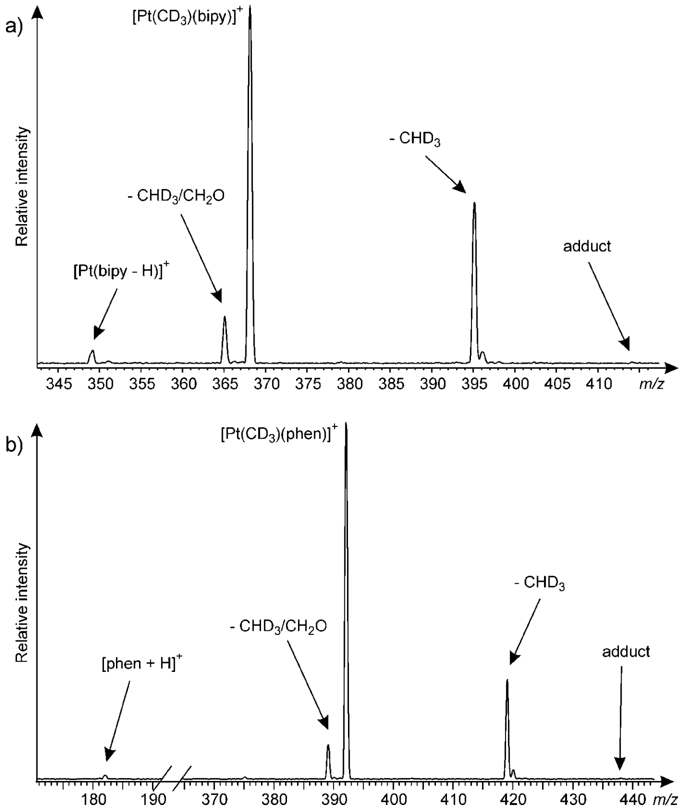


Figure 2. Ion–molecule reactions of mass-selected a) [Pt(CD_3)(bipy)]$^+$ ([D_3]**2**) and b) [Pt(CD_3)(phen)]$^+$ ([D_3]**3**) with dimethyl ether (**4**).

To gain further insight into mechanistic features of the reaction, we carried out the reaction of **1** and [D_7]**1** with [1,1,1-D_3]dimethyl ether ([D_3]**4**); one observes the formation of CH_2O, CHDO, and CD_2O in ratios of 21:54:25 and 20:54:26, respectively. These data indicate rather extensive hydrogen/deuterium exchange between the hydrogen atoms within the incoming (CH_3)O(CD_3) substrate prior to the production of formaldehyde. In the reactions of **2** and **3** with [D_3]**4** one observes losses of CH_4, CH_3D, and CH_2D_2 in a ratio of 55:42:3; reactions of [D_3]**2** and [D_3]**3** with [D_3]**4** give rise to elimination of CH_2D_2, CHD_3, and CD_4 in a ratio of 4:53:43. This indicates a kinetic isotope effect of about 1.3 for abstraction of a hydrogen atom from the methyl group of dimethyl ether without the occurrence of pronounced H/D exchange processes. Moreover, also in the reactions of **2**, **3**, [D_3]**2**, and [D_3]**3** with [D_3]**4** the loss of formaldehyde, following methane elimination, is accompanied by extensive hydrogen/deuterium exchange within the ether; on average, the methyl group is lost together with H/CH_2O, H/CHDO or D/CH_2O, H/CD_2O or D/CHDO, and D/CD_2O in a ratio of 7:46:41:5.

Computational results: To gain deeper insight into the mechanistic details of the reaction of [Pt(bipy−H)]$^+$ (**1**) with dimethyl ether, the pathways for production of CH_2O and C_2H_4 were computationally explored. After adduct formation the initial step either corresponds to a C−H or to a

C−O bond insertion. We succeeded in locating two transition structures $\mathbf{TS1_{C-O}}$ and $\mathbf{TS2_{C-O}}$ for C−O bond insertion, which lie −8 and −16 kJ mol^{-1}, respectively, below the entrance channel, as well as a transition structure $\mathbf{TS_{C-H}}$ (−13 kJ mol^{-1}) for the direct transfer of one hydrogen atom of dimethyl ether to the bipyridyl ligand (for the structures, see Supporting Information SI 1). If the experimentally confirmed hydrogen transfer actually proceeds via this energetically rather demanding $\mathbf{TS_{C-H}}$, and this step then necessarily constitutes the rate-limiting act, a sizable kinetic isotope effect is expected to occur in the reaction of **1** with $[D_3]$**4**. However, the extensive hydrogen-exchange processes observed in the reaction of **1** with $[D_3]$**4** make it difficult, if not impossible, to measure this effect; in fact, a kinetic isotope effect is not observed in the related IMRs of the couples **1**/$[D_3]$**4** and $[D_7]$**1**/$[D_3]$**4**, respectively. While we cannot definitively rule out the involvement of $\mathbf{TS_{C-H}}$ (Supporting Information SI 1), an extensive search of the PES (Figure 3) provided as an alternative a multistep sequence for the hydrogen transfer that is significantly lower in energy than $\mathbf{TS_{C-H}}$ and which accounts for the experimental findings. The resulting PES for the reactions given in Equations (1) and (2) (X=O) is depicted in Figure 3, and some important structures together with the relevant geometric details are given in Figure 4 (for a comprehensive presentation of all structures, see Supporting Information SI 2 and SI 3).

The first step after formation of the adduct complex **5** corresponds to an isomerization forming **6**; this intermediate is characterized by an agostic interaction of the platinum center with one of the C−H bonds of the ether, which is therefore elongated to 1.233 Å. Next, **6** is subject to a sequence of oxidative addition via **TS 6/7** and reductive elimination via **TS 7/8** which are followed by a minor structural reorganization (**TS 8/9**) to eventually result in the reconstruction of an intact bipyridine ligand in **9**; a rather energy-demanding "retro-rollover" process via **TS 9/10** gives rise to **10**. The latter serves as a common intermediate for the reactions of **1**, **2**, and $[D_3]$**2** with **4**. Species **10** is formed with different energy contents depending on its precursors. This becomes obvious when one compares the reaction enthalpies calculated at the BP86 level of theory for the reactions $[Pt(bipy-H)]^+$ (**1**) + $(CH_3)_2O$ (**4**) → $[Pt(bipy)(\mathbf{4}-H)]^+$ (**10**) ($\Delta_R H = -223$ kJ mol^{-1}) and $[Pt(CH_3)(bipy)]^+$ (**2**) + $(CH_3)_2O$ (**4**)→$[Pt(bipy)(\mathbf{4}-H)]^+$ (**10**) + CH_4 ($\Delta_R H = -112$ kJ mol^{-1}).[27] In fact, it is reasonable to argue that all further steps involve the bidentate bipyridine complex instead of a cyclometalated isomer, because 1) in the reactions of both $[D_3]$**2** and $[D_3]$**3** with **4**, after loss of CHD_3, one observes liberation of formaldehyde analogous to the IMR of the couple **1**/**4**, although phen can not form a cyclometalated complex in the reaction of $[D_3]$**3** with **4**, and 2) the energy gained through the regeneration of a bidentate ligand provides the driving force for the subsequent reactions, as indicated by previous DFT calculations.[12] Species **10** also serves as a branching point to explain the preferred formation of neutral formaldehyde and to account for the negligible loss of C_2H_4. With regard to the former process, **10** isomerizes via **TS 10/11** to give rise to **11**, which is stabilized by an

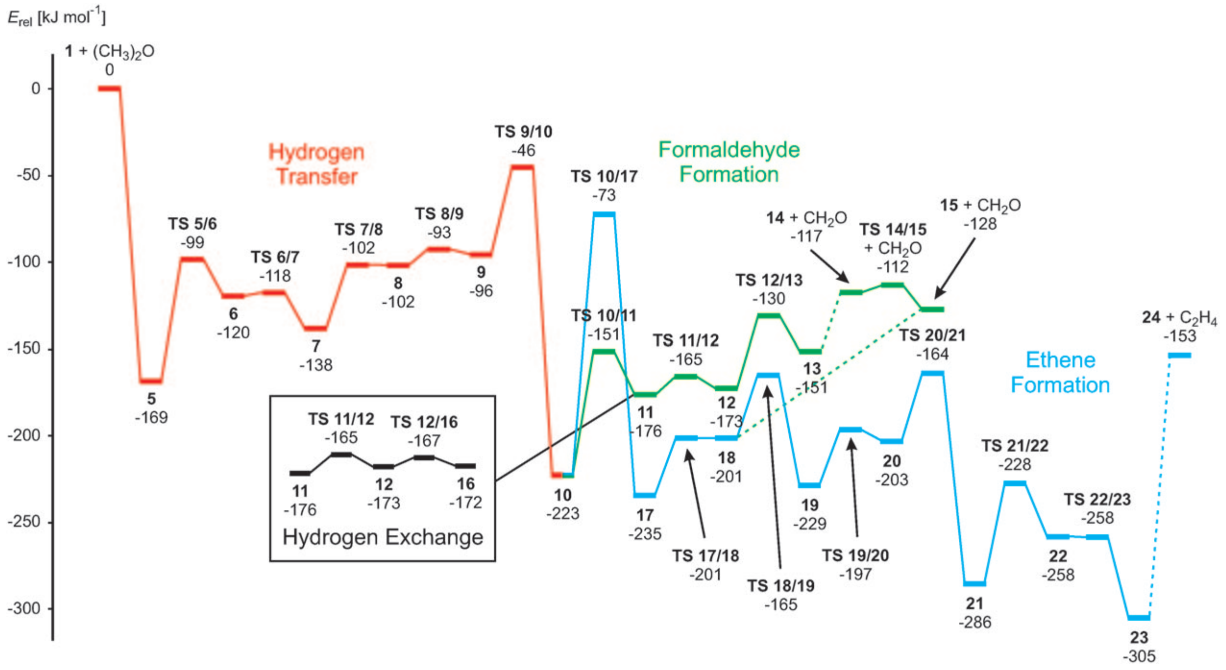


Figure 3. Simplified potential-energy surface for the ion–molecule reaction of $[Pt(bipy-H)]^+$ (**1**) with $(CH_3)_2O$ (**4**) to generate CH_2O and C_2H_4, as calculated at the BP86 level of theory. The red part corresponds to the initial transfer of a hydrogen atom from the ether to the bipyridyl ligand followed by a "retro-rollover" process to generate **10**. Intermediate **10** serves as branching point to generate CH_2O (major process; green part) and C_2H_4 (minor reaction; blue part). The half-reaction for the degenerate isomerization of **11** (depicted in black in the inset) accounts for the hydrogen exchange between the methyl groups of the ether that precedes formation of formaldehyde and **15**.

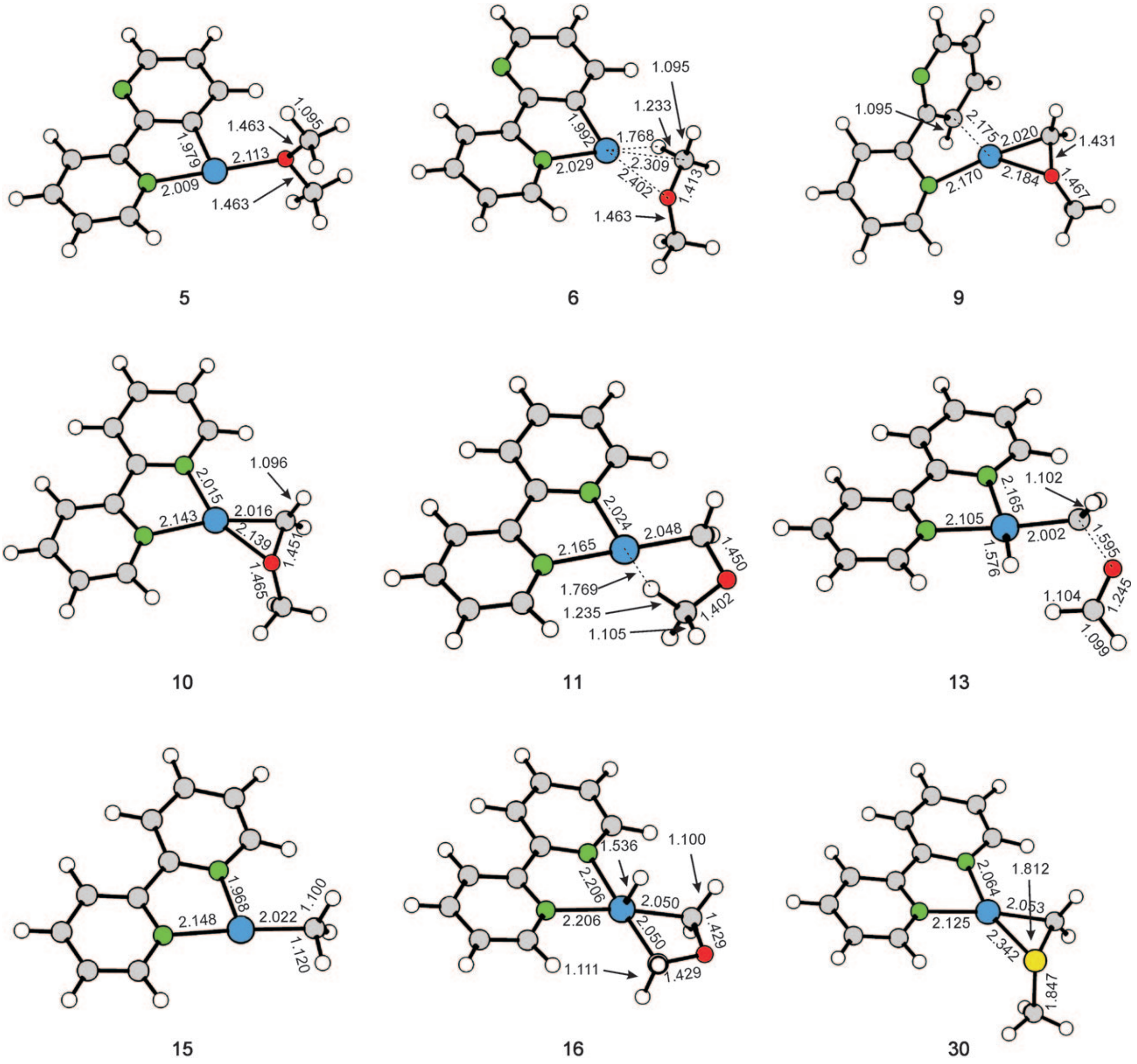


Figure 4. Geometry-optimized minimum structures of some of the species mentioned in Figures 3 and 5 together with relevant bond lengths (in Å) around the Pt core as calculated with the BP86 functional.

agostic interaction of the platinum center with a C−H bond of the methyl group (elongation of one C−H bond to 1.235 Å). Oxidative addition into this C−H bond leads to the formal Pt^{IV} hydride **12**, from which formaldehyde complex **13** can be formed via **TS 12/13** in a [2+2] cycloreversion reaction. From **13** neutral CH_2O is eliminated in a barrierless reaction to give Pt^{IV} hydrido carbene complex **14**, which may isomerize to the Pt^{II} methyl complex **15** via **TS 14/15**. In the experimentally observed H/D exchange preceding formation of CH_2O, **11** serves as the starting point. The inset in Figure 3 shows the half-reaction for the degenerate isomerization of **11**, in the course of which one hydrogen atom from the methyl group is transferred to the methylene group. To this end **11** isomerizes via **TS 11/12** and **TS 12/16** to give symmetric metallaoxocyclobutane intermediate **16**, a formal Pt^{IV} hydride complex, from which the platinum-bound hydrogen atom is easily transferred to either of the methylene groups by reversion of the above-mentioned steps. As these steps are energetically much below the exit channel for the loss of formaldehyde, a nearly statistical hydrogen-atom exchange is expected to occur in the reactions of **1** and $[D_7]$**1** with $[D_3]$**4**;[28] the hydrogen atoms of the (bipy−H) ligand are hardly involved in this process. The experimental observation of the same hydrogen exchange accompanying formaldehyde loss after methane elimination in the reactions of the methyl complexes **2**, **3**, $[D_3]$**2**, and $[D_3]$**3** with $[D_3]$**4** illustrates that **10** and **11** are indeed the key intermediates for both formaldehyde loss and hydrogen exchange within the ether. As to the negligible formation of ethene, the PES depicted in Figure 3 can explain this result. Starting from **10**, formation of C_2H_4 requires transfer of the methyl group to the platinum center (**10**→**17**) followed by a sequence of rather complex rearrangements which eventually lead to formation of [Pt(bipy)(OH)(C_2H_4)]$^+$ (**23**) as the global minimum; from **23** C_2H_4 can be liberated to form platinum hydroxy complex [Pt(bipy)(OH)]$^+$ (**24**) as the ionic product. While C_2H_4 formation is thermochemically favored, the barrier **TS 10/17** for the initial methyl transfer process is 44 kJ mol^{-1} higher than the energy required to produce formaldehyde. Therefore, under kinetic conditions elimination of CH_2O clearly dominates the ion–molecule reaction of **1** with $(CH_3)_2O$ (see Figure 1). In distinct contrast, in the reaction of **1** with $(CH_3)_2S$ about 55% C_2H_4 and only 5% CH_2S are formed from the adduct complex.[12] The corresponding potential-energy surface, although already discussed in reference [12] using a different DFT functional, was, for comparison, recalculated at the BP86 level of theory. This new PES and structure **30** are given in Figures 4 and 5 (for a comprehensive presentation of all structures see Supporting Information SI 4 and SI 5). The most remarkable differences in the reactions of the couples **1**/$(CH_3)_2O$ versus **1**/$(CH_3)_2S$ are connected with the energy demands for isomerization of **10** and **30**, respectively, to intermediates from which CH_2X (X=O, S) and C_2H_4 are formed as well as the energetics of the two exit channels for the two systems in question (compare Figures 3 and 5). While for the ether ligand the isomerization **10**→**11** and the liberation of CH_2O are energetically significantly more favored than the initial methyl transfer in the process **10**→**TS 10/17**→**17**→→**24**+C_2H_4, the opposite holds for the thioether-containing system. Here, while the isomerization of **30** towards intermediates from which CH_2S loss can occur is energetically comparable with methyl transfer to the platinum atom (**30**→**TS 30/36**→**36**), the former process is disfavored by 149 kJ mol^{-1} with regard to the energetics of the exit channel as compared to formation of C_2H_4 and cationic [Pt(bipy)(SH)]$^+$ (**42**). A more quantitative analysis based on RRKM theory[29] is beyond the scope of this work and would require significantly more accurate PES calculations to make this exercise meaningful.

In spite of some fundamental differences, an interesting structural aspect we note for both substrates $(CH_3)_2X$ (X=O, S) is that their reactions with **1** proceed through three-membered metallacycles **10** (X=O) and **30** (X=S) as key intermediates; in the condensed phase, such species are rather common only for sulfur but quite rare for oxygen-bridged systems.[1e,f]

Conclusion

We have studied the ion–molecule reactions of dimethyl ether with cyclometalated [Pt(bipy−H)]$^+$ (**1**) in the gas phase. The application of DFT-based calculations as well as the analogous reactions 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 reaction pathways corresponds to transfer of a hydrogen atom to the (bipy−H) ligand forming three-membered metallacycles as intermediates. A comparison of the reactions of the ether with that of the analogous sulfur compound is rather instructive and points to delicate differences in the reactions with

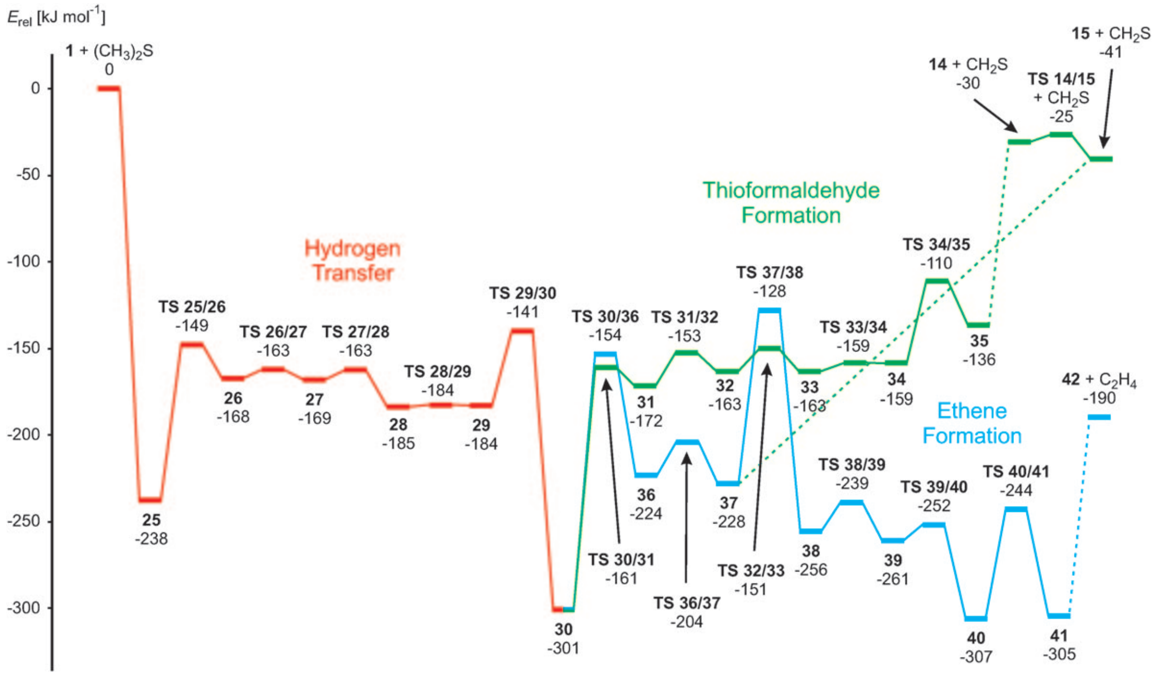


Figure 5. Simplified potential-energy surface for the ion–molecule reaction of [Pt(bipy−H)]$^+$ (**1**) with $(CH_3)_2S$ to generate CH_2S and C_2H_4 at the BP86 level of theory. The red part corresponds to the transfer of a hydrogen atom from the thioether to the bipyridyl ligand followed by a "retro-rollover" process to generate **30**. Intermediate **30** serves as a branching point to generate CH_2S (minor process; green part) and C_2H_4 (major reaction; blue part).

[Pt(bipy−H)]$^+$; most importantly, [Pt(bipy−H)]$^+$ does not give rise to oxidative C−C bond coupling of $(CH_3)_2O$, in contrast to the reaction of complex **1** with dimethyl sulfide; in the latter, dehydrosulfurization results in the formation of ethene as the major decomposition path. On the other hand, CH_2O loss dominates the reaction of [Pt(bipy−H)]$^+$ with dimethyl ether, whereas the elimination of CH_2S constitutes only a minor channel in the reaction with dimethyl sulfide. This distinct behavior is explained in terms of the corresponding potential-energy surfaces and has its origin in the weaker interaction of platinum with oxygen than with sulfur. An analogous study of the reaction of **1** with dimethyl ether and ethyl methyl ether is published elsewhere.[30]

Acknowledgements

We thank Dr. Xinhao Zhang and Professor Martin K. Beyer for enlightening discussions and are grateful for financial support to the Fonds der Chemischen Industrie as well as the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technische Universität Berlin and funded by the Deutsche Forschungsgemeinschaft.

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[27] The analogous reaction of the phen complex $[Pt(CH_3)(phen)]^+$ (**3**) + $(CH_3)_2O$ (**4**) $\rightarrow [Pt(phen)((CH_3)_2O{-}H)]^+ + CH_4$ is associated with $\Delta_R H = -111\ \mathrm{kJ\,mol^{-1}}$.

[28] If one assumes that the hydrogen exchange observed in the reactions of **1** and $[D_7]$**1** with $[D_3]$**4** involves **11** one has to consider the exchange within $[C_2,H_2,D_3,O]$ and $[C_2,H_3,D_2,O]$. Statistically, CH_2O, CHDO, and CD_2O are lost from the former in a ratio of 10:60:30 and from the latter in a ratio of 30:60:10. Due to a small kinetic isotope effect, $[C_2,H_2,D_3,O]$ is formed in small excess over $[C_2,H_3,D_2,O]$ in the initial hydrogen abstraction process. Therefore, it is expected that CH_2O, CHDO, and CD_2O are lost in a ratio that deviates slightly from 20:60:20, favoring CD_2O loss as observed in the experiment.

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Received: October 5, 2009
Revised: December 30, 2009