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Platinum(II)-mediated dehydrosulfurization and oxidative carbon–carbon coupling in the gas-phase decomposition of thioethers

Burkhard Butschke [a], Maria Schlangen [a], Detlef Schröder [b], Helmut Schwarz [a,*]

[a] Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
[b] Institute of Organic Chemistry and Biochemistry, Flemingovo nám 2, 16610 Prague 6, Czech Republic

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Dedicated, in friendship and with admiration, to Michael T. Bowers on the occasion of his 70th birthday.

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ABSTRACT

The ion/molecule reaction (IMR) of “roll-over” cyclometalated [Pt(bipy−H)]$^+$ (**1**) (bipy = 2,2′-bipyridine) with dimethyl sulfide (**2**) leads to the loss of ethene in the main reaction channel (55%); this corresponds to a formal dehydrosulfurization accompanied by the dehydrogenative (“oxidative”) C–C coupling of the two methyl groups in dimethyl sulfide to form ethene. In order to obtain deeper insight into this rare reaction, the IMRs of **1** with several symmetric, asymmetric as well as cyclic thioethers and some thiols are probed. Common to many substrates is the formal transfer of H_2S from the organic sulfur compound to the [Pt(bipy−H)]$^+$ core accompanied by the expulsion of one or more alkene units. In contrast to the behavior of [Pt(bipy−H)]$^+$ (**1**), bare Pt$^+$, diatomic PtH$^+$, and also the complex [Pt(phpy−H)]$^+$ (phpy = 2-phenyl pyridine) are not able to bring about dehydrosulfurization. It is accordingly suggested that the (bipy−H)-ligand does not only affect the electronic structure of the platinum(II) core but, moreover, plays an *active* role as an acceptor in the initial hydrogen transfer from the thioether ligand to the LPt$^+$ core (L = heterocyclic ligand).

1. Introduction

Catalytic hydrodesulfurization (HDS) is an extremely important process in petrochemical industry. In fact, the removal of sulfur from crude oils and coal liquids by conversion of the organic sulfur content into H_2S constitutes one of the largest-scale chemical processes of utmost ecological importance [1–4]. In view of the industrial importance of HDS, achievement of a better understanding of the basic principles of this process and the development of improved catalysts are subjects of intense research [5].

One approach for the study of the intrinsic features of catalytically active centers, i.e. the often invoked single-site of a catalyst, is the investigation of the reactions of atomic or metal-cluster ions, both as bare or partially ligated systems under well-defined conditions in the gas phase [6]. The advantage of this approach is that these experiments are not hampered with the problems of obscuring the intrinsic features of the reactants by ill-defined solvation, ion-pairing, or aggregation, all of which may strongly affect the condensed-phase behavior of a reactive species. Thus, it is not surprising that organometallic chemistry in the gas phase has emerged as an actively pursued topic which has been summarized in numerous review articles over the last decades [6,7].

With regard to metal-mediated dehydrosulfurization (and related reactions) of organic sulfur compounds in the gas phase, some previous reports have already indicated the kind of mechanistic insight provided by mass-spectrometry-based experiments [8–13], and the activation of the C–S bond in CS_2 has been studied systematically for a wide set of transition-metal ions [14–31]. Very recently, we discovered that the major product (55% of all neutral products formed) in the thermal ion/molecule reaction (IMR) of the cyclometalated platinum(II) complex [Pt(bipy−H)]$^+$ (**1**) with $(CH_3)_2S$ (**2**) corresponds to the formation of neutral ethene (**4**). This reaction thus can be considered as an example of a gas-phase dehydrosulfurization of the thio compound concomitant with C–C-bond formation via oxidative coupling of the two methyl groups in **2** (Scheme 1) [32].

Based on extensive labeling experiments and complementary DFT-based calculations, the crucial aspects of the mechanisms operative in the IMR of **1** with **2** have been uncovered as detailed in Refs. [32,33]. In the course of the investigation of this simple substrate, it deemed appropriate to extend the experiments to other organic sulfides in order to probe the scope and limitations of this process.

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[*] Corresponding author. Tel.: +49 30 314 23483; fax: +49 30 314 21102.
E-mail address: Helmut.Schwarz@mail.chem.tu-berlin.de (H. Schwarz).

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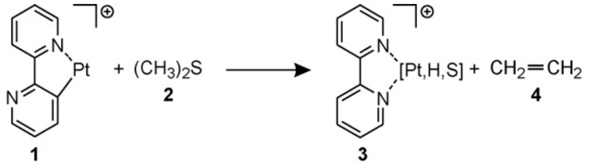


Scheme 1. Dehydrogenative coupling of the methyl groups in $(CH_3)_2S$ (**2**) by $[Pt(bipy{-}H)]^+$ (**1**).

The findings of the IMR of **1** with the compounds shown in Scheme 2 are reported in this study.

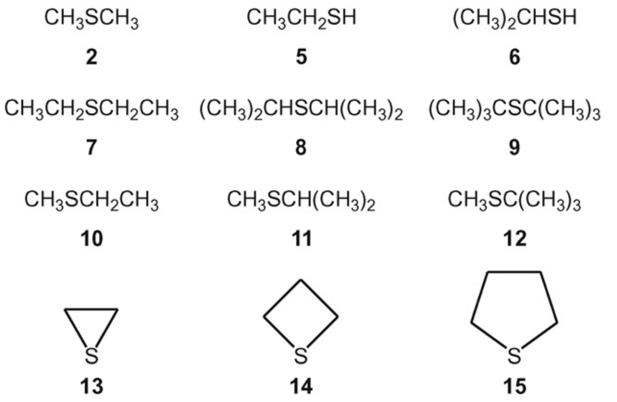
2. Experimental details

2.1. Chemicals

All sulfur-containing precursors (Scheme 2) were either commercially available or synthesized and purified according to standard laboratory procedures and fully characterized by adequate spectroscopic methods (^{1}H-NMR, IR, MS) [33].

2.2. Instrumentation

The mass-spectrometric experiments were performed with a *VG BIO-Q* mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization (ESI) [34,35] source as described in detail previously [36,37]. In brief, millimolar solutions of dimeric $[Pt(CH_3)_2(\mu\text{-}(CH_3)_2S)]_2$ (for preparation and structure see [38,39]) and 2,2′-bipyridine (bipy) (or its $[D_8]$-labeled analogue $[D_8]$-bipy) in pure methanol were introduced through a fused-silica capillary to the ESI source via a syringe pump (ca. 3 μL/min). Nitrogen was used as a nebulizing and drying gas at a source temperature of 80 °C. By adjusting the cone voltage (U_c) to around 20 V, the Pt(II) complex $[Pt(bipy)(CH_3)((CH_3)_2S)]^+$ was generated which – upon increasing U_c or by subjecting the mass-selected cation to collision-induced dissociation (CID) – decomposes via a "roll-over" cyclometalation [40] to yield the cationic species $[Pt(bipy{-}H)]^+$ (**1**) [32,33]. The identity of the ions was confirmed by comparison with the expected isotope pattern [41] as well as CID experiments, labeling studies, selected ion/molecule reactions, and extensive DFT-based calculations [32,33]. The isotope patterns also assisted in the choice of the adequate precursor in order to avoid coincidental mass overlaps of isobaric species in the mass selected ion beam [42]. The IMRs of mass-selected **1** and of $[Pt([D_8]\text{-bipy}{-}D)]^+$ ($[D_7]$-**1**) with the substrates shown in Scheme 2 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 [36] allows the investigation of quasi-thermal reactions, as demonstrated previously [43–47]. Best yields of **1** are obtained at a cone voltage of $U_c = 60$ V, because harsher conditions lead to further fragmentation and undesired overlap of isobaric signals, whereas lower cone voltages decrease the yield of the desired product ions **1** and $[D_7]$-**1**, respectively. For the generations of bare Pt^+ and diatomic PtH^+ the cone voltage was increased to about 180 V. The relative rates (k_{rel}) of the IMRs given below are referenced to the IMR of **1** with $(CH_3)_2S$ (**2**) with $k_{rel} = 100$.



Scheme 2. Sulfur-containing compounds used for ion/molecule reactions with $[Pt(bipy{-}H)]^+$ (**1**) in this study.

3. Results and discussion

3.1. General remarks

The focus of this work forms the screening of some sulfur-containing organic substrates (Scheme 2) with respect to dehydrosulfurization (i.e. formation of alkenes) and the associated problem of intraligand oxidative alkyl coupling. While C–C-bond formation is obvious to occur in the formation of C_2H_4 from $[Pt(bipy{-}H)]^+$ (**1**) and $(CH_3)_2S$ (**2**) (Scheme 1), simply on the ground that the alternative elimination of $2CH_2$ is energetically impossible under the reaction conditions employed, the coupling scenario is much less secured for the symmetric substrates **7**, **8**, and **9** (Scheme 2) as will be shown below. While characterization [48–50] or even preparative isolation [51] of the neutral product(s) of the ion/molecule reactions have been realized in selected cases, with regard to the IMRs of **1** with thiols and thioethers we will rely on indirect or circumstantial evidence in the structural assignment.

Even for the most simple system (Scheme 1), a rather complex reaction pattern has been established, which can be summarized as follows [32,33]. (i) In the IMR of **1** with $(CH_3)_2S$, about 75% of the encounter complexes undergo the exchange of one (and only one) hydrogen atom of the heterocycle with any of the hydrogen atoms of the dimethyl-sulfide ligand prior to the loss of ethene. For the remaining quarter of the ensemble, two hydrogen atoms from $(CH_3)_2S$ are transferred without any exchange to the $[Pt(bipy{-}H)]^+$ core. (ii) The hydrogen-atom transfers can be distinguished into a formal 1,1-elimination (i.e. both hydrogen atoms are delivered by the same CH_3 group) and a predominating, formal 1,3-transfer in which each methyl group of **2** delivers a hydrogen atom. (iii) The averaged kinetic isotope effects (KIEs) of about 1.1 for the hydrogen/deuterium transfers are rather small indicating other processes than the mere C–H(D)-bond activation as rate-determining step(s). In view of the complexity that already exists for the simple couple **1** + **2**, we will refrain from a detailed mechanistic analysis in the present work, but rather focus on the gross structural features and the trends in the reactions of **1** with the compounds shown in Scheme 2. Particular attention will be paid to the fundamental role of the heterocyclic ligand of **1** in the initial C–H-bond activation phase.

While many of the IMRs of **1** with the substrates **5**–**15** exhibit a rather rich chemistry [33], here we report only the major product channels and those relevant in the context of dehydrosulfurization.[1] Further, the IMRs of both **1** and $[D_7]$-**1** with the neutral substrates were probed, enabling an estimation of the extent of hydrogen exchange between the bipy-ligand and the incoming sulfur compound for each individual reaction channel. The amount of H/D exchange is represented by the value f_{exc}. For

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[1] For all systems studied, the branching ratios are given in % relative to Σ(products) = 100%. Note that not all reaction channels are listed; the complete set of data is available upon request.

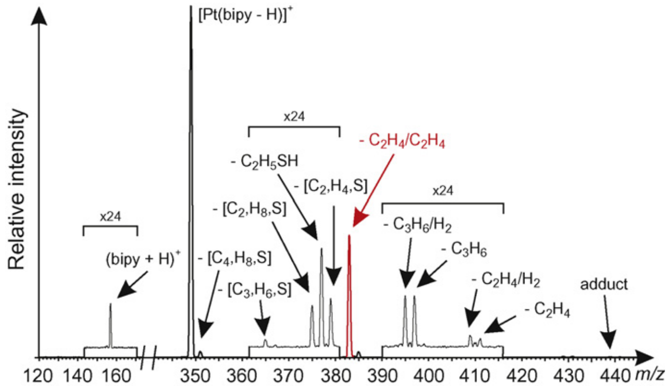


Fig. 1. Ion/molecule reaction of mass-selected $[Pt(bipy{-}H)]^+$ (**1**) with $(C_2H_5)_2S$ (**7**).

the calculation of f_{exc} the arbitrary assumption was made that the encounter complex initially formed consists of two components, the first one eliminating the neutral products after a formal complete scrambling of all hydrogen atoms of the thio compounds and exactly one hydrogen/deuterium atom from **1** or [D_7]-**1**, respectively, whereas in the second one no scrambling takes place prior to the neutral loss; f_{exc} stands for the first fraction (for further details see [33]). As in the main reaction channels of the central IMR **1** + **2** the f_{exc} values vary between 61% and 82%, respectively, values falling below 20% are regarded as small.

3.2. *Reactions of* ***1*** *with thiols*

The IMR of **1** with C_2H_5SH (**5**) occurs with $k_{rel} = 82 \pm 11$ and is dominated by the expulsion of neutral C_2H_4 (92%). Formation of $(bipy{+}H)^+$ is much less pronounced (8%) and losses of H_2S or C_2H_4S are very small (<1%). The labeling experiment with [D_7]-**1** reveals a fairly small propensity for the occurrence of interligand hydrogen exchange prior to product formation. This is indicated by $f_{exc} = 7\%$ for C_2H_4 loss and $f_{exc} = 19\%$ for the generation of $(bipy{+}H)^+$. The small values of f_{exc} suggest that the couple **1** + **5** possesses easily accessible dissociation channels.

This trend becomes even more obvious for the next higher homologue, i.e. the system **1** + $(CH_3)_2CHSH$ (**6**). Here, the product spectrum of the IMR ($k_{rel} = 73 \pm 10$) is dominated by the expulsion of C_3H_6 (95%), with minor contributions of H_2S loss (2%) and the formation of $(bipy{+}H)^+$ (3%). In the hydrogen-atom transfers to generate C_3H_6 and H_2S, respectively, exchange processes are negligible or small ($f_{exc} = 1\%$ and 9%, respectively).

3.3. *Reactions of* ***1*** *with symmetric acyclic thioethers*

In the IMR of **1** with $(CH_3)_2S$ (**2**) ($k_{rel} = 100 \pm 14$), the dominant reactions correspond to the oxidative C–C coupling of the two methyl groups of **2** to generate C_2H_4 (55%) and to the formation of $(bipy{+}H)^+$ (15%). Other processes relevant in the context of dehydrosulfurization are much less pronounced, e.g. losses of H_2 (<1%), H_2S (<1%) or CH_2S (5%) as well as the losses of CH_3 (7%), CH_4 (5%) and CH_3/H_2 (5%). Extensive labeling studies and DFT-based calculations revealed an extraordinarily complex mechanistic scenario [32,33].

The mass spectrum of the IMR of **1** with $(C_2H_5)_2S$ (**7**) ($k_{rel} = 61 \pm 9$), Fig. 1, may serve as a typical example for the reactions of the higher homologues of the thioethers. The dominant signal is due to loss of $\Delta m = 56$ (86%), and the central question in the present context is: does this neutral product correspond to a genuine, intact C_4H_8 hydrocarbon (e.g. cyclobutane or an acyclic butene isomer [52,53]) that is generated in an oxidative C–C-coupling step of the two C_2H_5 groups, or are we dealing with a stepwise process, Eq. (1), in which the first elimination of C_2H_4 (k_1) is orders of magnitude slower than the second one, i.e. $k_1 \ll k_2$? For the latter alternative there is not only precedence in numerous gas-phase reactions [54–58], but extensive labeling studies for the couple **1** + **7** also support the latter variant:

$$[Pt(bipy-H)]^+ + (C_2H_5)_2S \xrightarrow{k_1} [Pt(bipy)(C_2, H_5, S)]^+ + C_2H_4 \qquad (1a)$$

$$[Pt(bipy)(C_2, H_5, S)]^+ \xrightarrow{k_2} [Pt(bipy)(H, S)]^+ + C_2H_4 \qquad (1b)$$

For example, the investigation of the isotopologous diethyl thioethers **7a**–**7c** (**7a** = $(CH_3CD_2)S$, **7b** = $(C_2H_5)S(C_2D_5)$, **7c** = $(CD_3CH_2)S$) with $[Pt(bipy{-}H)]^+$ (**1**) as well as $[Pt([D_8]\text{-}bipy{-}D)]^+$ ([D_7]-**1**) leads to the following conclusions (Table 1): (i) the reactions of both cationic platinum precursors with the substrates **7**–**7c** give very similar H/D distributions in the elimination of "$C_4H_{8-x}D_x$" ($x = 0$–7), thus ruling out any extensive H/D exchange between the heterocyclic ligand on platinum and the thioether reactants; $f_{exc} < 3\%$. (ii) In marked contrast, the patterns for the labeled thioethers are quite different from each other. In the reactions with the unsymmetrically [D_5]-labeled isotopologue **7b**, the dominant elimination path corresponds to $\Delta m = 60$ (formally "$C_4H_4D_4$"). Thus, each of the two ethyl groups delivers one hydrogen/deuterium atom to the $[Pt(bipy{-}H)]^+$ core. This observation indicates an independent, consecutive elimination of two ethene units, Eq. (1). (iii) In contrast, if the double hydrogen-atom transfer from the $(C_2H_5)_2S$ ligand were to be accompanied by an α,α′-C–C coupling of the C_2H_5 groups to generate a C_4-species, e.g. 2-butene, due to the often observed proclivity of hydrogen-atom scrambling in Pt-alkyl systems [59], for the couple **1** + **7b** one would expect a distribution of $C_4H_5D_3$:$C_4H_4D_4$:$C_4H_3D_5$ in a ratio 17:66:17. As this expectation clearly deviates from the experimental finding (3:95:1), such a coupling scenario can be ruled out. (iv) However, as indicated by the label distributions obtained for the IMR with $(CD_3CH_2)_2S$ (**7c**), H/D exchange within each ethyl group is rather extensive, and a detailed kinetic modelling reveals the existence of a complex superposition of both specific and unspecific mechanistic variants for the platinum-mediated dehydrogenation of the ethyl groups of **7**. (v) Finally, while C–C coupling between the two ethyl groups of **7** occurs to some extent, as indicated by the minor losses of C_3H_6 and C_3H_6/H_2 (see Fig. 1), they cannot efficiently compete with the obviously much more facile decomposition of the separated alkyl chains.

A similar situation holds true for the ion/molecule reactions of $[Pt(bipy{-}H)]^+$ with the higher homologues $(CH_3)_2CHSCH(CH_3)_2$ (**8**) and $(CH_3)_3CSC(CH_3)_3$ (**9**) which proceed with $k_{rel} = 36 \pm 5$ and 9 ± 1, respectively. The reaction of **1** with **8** is dominated by losses of $\Delta m = 76$ (9%) and $\Delta m = 84$ (89%); for the *t*-butyl substituted system (**1** + **9**), the corresponding neutral losses correspond to $\Delta m = 90$ (13%) and $\Delta m = 112$ (85%). Given the structures of the two thioethers and taking into account the reaction of **1** with the lower homologue $(C_2H_5)_2S$, these eliminations most likely correspond to the formations of RSH (R = C_3H_7, C_4H_9) and of "C_nH_{2n}" (with $n = 6$ for compound **8** and $n = 8$ for **9**). With respect to the generation of these olefins, we suggest once more the consecutive eliminations of $2C_3H_6$ and $2C_4H_8$, respectively, from either alkyl groups of **8** and **9** without any (significant) contribution of interligand oxidative C–C coupling. In fact, for the *t*-butyl substituted thioether **9**, due to the absence of a C(α)-hydrogen, such an oxidative coupling anyhow appears unlikely on structural grounds. For both substrates, hydrogen exchange between the bipy unit and the thioether ligands is negligible in the olefin loss channel as indicated by the small f_{exc} values of about 1%.

Table 1
Isotope distributions for the losses of "$C_4H_{8-x}D_x$" ($x = 0$–7) in the ion/molecule reactions of $[Pt(bipy-H)]^+$ and $[Pt([D_8]\text{-}bipy-D)]^+$, respectively, with the isotopologous diethyl thioethers **7**–**7c**[a].

	$[Pt(bipy-H)]^+$				$[Pt([D_8]\text{-}bipy-D)]^+$			
	$(C_2H_5)_2S$ (**7**)	$(CH_3CD_2)_2S$ (**7a**)	$(C_2H_5)S(C_2D_5)$ (**7b**)	$(CD_3CH_2)_2S$ (**7c**)	$(C_2H_5)_2S$ (**7**)	$(CH_3CD_2)_2S$ (**7a**)	$(C_2H_5)S(C_2D_5)$ (**7b**)	$(CD_3CH_2)_2S$ (**7c**)
C_4H_8	100				98			
C_4H_7D					2			
$C_4H_6D_2$		14	1			14		
$C_4H_5D_3$		55	3			54	4	
$C_4H_4D_4$		31	95	18		30	94	17
$C_4H_3D_5$			1	58		2	2	56
$C_4H_2D_6$				24				24
C_4HD_7								3

[a] Intensities are normalized and expressed in % according to $\Sigma(C_4H_{8-x}D_x) = 100\%$.

3.4. *Reactions of **1** with the unsymmetric thioethers **10**–**12***

While oxidative C–C coupling, which is intimately related to the topic of dehydrosulfurization, can only be probed indirectly in the reactions of *symmetric* thioethers, e.g. **7**–**9**, the investigation of thioethers bearing two different alkyl groups, as in **10**–**12**, is more revealing. Particularly insightful in this respect are CH_3-substituted precursors as the decomposition of, e.g. $CH_3SCH_2CH_3$ (**10**) according to Eq. (2a) is by >254 kJ mol^{-1} more endothermic than the formation of a coupling product, Eq. (2b) [60]; formal generation of H_2S or its transfer to the metal-ion core in the course of the Pt-mediated activation of the thioether therefore strongly suggest the formation of a C_3-coupling product:

$$CH_3SCH_2CH_3 \rightarrow H_2S + CH_2 + CH_2{=}CH_2 \qquad (2a)$$

$$CH_3SCH_2CH_3 \rightarrow H_2S + CH_2{=}CHCH_3 \qquad (2b)$$

In fact, in the IMR of **1** with $CH_3SC_2H_5$ (**10**) ($k_{rel} = 63 \pm 9$), Fig. 2, the rather rich product-ion distribution includes a signal due to loss of $\Delta m = 42$ (9%), which indicates the oxidative coupling of the CH_3 and C_2H_5 units of **10** according to Eq. (2b). The exchange factor, f_{exc}, of this particular process amounts to 24%, which is significantly larger than that ($f_{exc} < 2\%$) for the more facile C_2H_4 loss (33%) from the same substrate. This finding may indicate a complex mechanistic scenario of the interligand C–C coupling, but due to overlap of isobaric ions in the product channels in the reactions with labeled substrates, an unambiguous data analysis of the isotope distributions is impossible and the data are therefore neither presented nor discussed here [33].

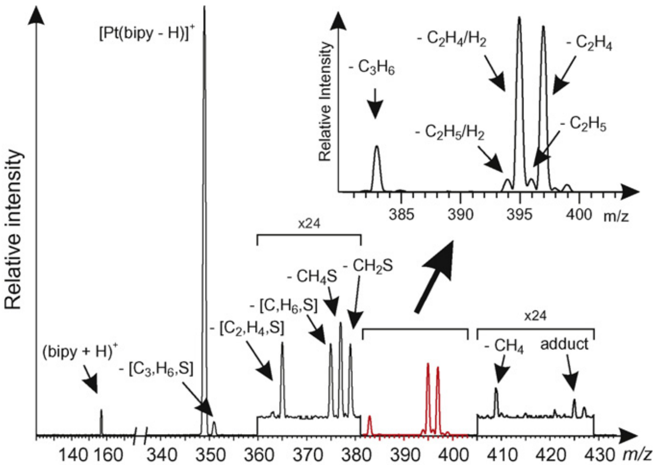


Fig. 2. Ion/molecule reaction of mass-selected $[Pt(bipy-H)]^+$ (**1**) with $CH_3SC_2H_5$ (**10**).

Some oxidative C–C coupling is also observed in the reaction of **1** with $CH_3SCH(CH_3)_2$ (**11**) ($k_{rel} = 56 \pm 8$), $\Delta m = 56$ (7%), while in the reaction of **1** with $CH_3SC(CH_3)_3$ (**12**) ($k_{rel} = 60 \pm 8$) the analogous channel ($\Delta m = 70$) is not important (1%). This finding indicates that $\Delta m = 56$ in the reaction of **1** and **11** is due to α,α′-C–C coupling, whereas this reaction is not feasible for the **1** + **12** couple due to the absence of a C(α)-hydrogen atom in the *t*-butyl group. For either substrates, the dominant decompositions involve losses of CH_4S (7%), C_3H_6 (48%) and C_3H_6/H_2 (25%) from **11** and of CH_4S (11%), C_4H_8 (63%) and C_4H_8/H_2 (21%) from **12**. Once more, the processes in which C_3H_6 (from **11**) or C_4H_8 (from **12**) are eliminated proceed without any significant hydrogen exchange with the bipy ligand as indicated by f_{exc} values of 4% and <1%, respectively. In contrast, the reactions which require more extensive rearrangements, e.g. C–C coupling or involvement of different sites of the alkyl groups as in the formation of CH_4S or in the combined alkene/H_2 loss, all exhibit $f_{exc} > 25\%$. Clearly, while oxidative C–C coupling of the alkyl fragments in thioethers is feasible in most systems studied, this reaction cannot efficiently compete with the combined hydrogen-transfer/olefin-elimination process involving only *one* alkyl group larger than methyl.

3.5. *Reactions of **1** with cyclic thioethers **13**–**15***

As shown in Table 2, the by far most prominent process in the ion/molecule reaction of **1** with the three cyclic thioethers **13**–**15** corresponds to the formal "H_2S" transfer to the $[Pt(bipy-H)]^+$ core concomitant with expulsions of C_2H_2 (from **13**: 74%), C_3H_4 (from **14**: 82%), and C_4H_6 (from **15**: 80%), respectively. Obviously, dehydrosulfurization is facile in these systems, as indicated by the rather small amount of H/D exchange ($f_{exc} = 6$–13%). In the case of **15**, also the isotopologue $[D_4]$-**15** ([2,2,5,5-D_4]-tetrahydrothiophene) was reacted with **1**. This precursor yields the formal transfer of H_2S, HDS, and D_2S to the $[Pt(bipy-H)]^+$ core in a ratio of 3:66:31 which is far from

Table 2
Selected neutral products generated in the ion/molecule reactions of $[Pt(bipy-H)]^+$ with the cyclic thioethers **13**–**15**[a].

	c-$(CH_2)_2S$ (**13**)	*c*-$(CH_2)_3S$ (**14**)	*c*-$(CH_2)_4S$ (**15**)
C_2H_2	74	–	–
C_2H_4	17[b]	2	1
C_3H_4	–	82	–
C_3H_6	–	<1	2
C_4H_6	–	–	80
H_2S	2	2	1
CH_2S	–	<1	8
k_{rel}[c]	51 ± 7	71 ± 10	80 ± 11

[a] Intensities of the reaction channels are expressed in % with $\Sigma(\text{products}) = 100\%$.

[b] May also correspond to combined loss of C_2H_2/H_2.

[c] k_{rel} is expressed relative to the IMR of **1** + $(CH_3)_2S = 100$.

the statistical distribution (21:58:21) including all eight hydrogen/deuterium atoms of [D$_4$]-**15**. According to the rather small value of $f_{\mathrm{exc}} = 6\%$ for this channel, the distribution for the reaction with [D$_7$]-**1** is nearly the same (4:65:31). Already without performing a detailed analysis of these results, some conclusions can be drawn. (i) In comparison to the reaction of **1** with **7a** (formal transfer of H_2S, HDS, and D_2S in a ratio of 31:55:14), hydrogen transfer in the reaction with **15** is much more selective, i.e. less intraligand H/D-scrambling takes place prior to the neutral loss. (ii) Secondly, a direct 3,4-H/H transfer to the [Pt(bipy−H)]$^+$ core which would result in the elimination of a thermodynamically favoured [1,1,4,4-D$_4$]-1,3-butadiene is only a minor process, thus pointing to a kinetic control of the decomposition pathway. (iii) The main channel corresponds to either a 2,3- or a 2,4-hydrogen transfer. There are quite a few mechanistic variants to account for this labeling result; for example, in the course of a 2,3-H/D-transfer [1,4,4-D$_3$]-cyclobutene could be generated. For the 2,4-H/D transfer, there are at least two possible pathways. In the first one, a formal diradical may be generated with the option to collapse into bicyclo[1.1.0]butane, while in an alternative path allylcarbene could be generated which may undergo exothermic isomerization to 1,3-butadiene. From a thermodynamical point of view, the two latter paths are rather energy demanding due to the high heats of formation of the C_4H_6 isomers suggested ($\Delta_f H = 157\,\mathrm{kJ\,mol^{-1}}$ for cyclobutene; $\Delta_f H = 217\,\mathrm{kJ\,mol^{-1}}$ for bicyclo[1.1.0]butane; ca. $\Delta_f H = 110\,\mathrm{kJ\,mol^{-1}}$ for 1,3-butadiene) [60,61]. (iv) As to the D_2S transfer (31%), formal 2,2- or 2,5-hydrogen transfer appear as feasible pathways, the latter formally yielding neutral cyclobutene.

3.6. Other systems and concluding remarks

The present study demonstrates that oxidative C–C coupling of alkyl groups in the dehydrosulfurization of organic sulfur compounds is most pronounced for the reaction of [Pt(bipy−H)]$^+$ (**1**) with $(CH_3)_2S$ (**2**) (Scheme 1), and one wonders whether this process is confined to platinum(II) complexes with a (bipy−H) ligand. To this end, the IMRs of **2** were also investigated with bare Pt$^+$, diatomic PtH$^+$, and the complex [Pt(phpy−H)]$^+$ (**16**) (phpy = 2-phenyl pyridine). Both, atomic Pt$^+$ and diatomic PtH$^+$ do not show any products due to C–C-bond formation; rather, the spectra are dominated by efficient charge-transfer reactions according to Eqs. (3), (4), and secondary products derived thereof. Occurrence of electron transfer with these "bare" cations can be attributed to the relatively low ionization energy of dimethyl sufide (*IE* = 8.69 eV), which is lower than *IE*(Pt) = 9.0 eV [60].

$$Pt^+ + (CH_3)_2S \rightarrow Pt + (CH_3)_2S^+ \tag{3}$$

$$PtH^+ + (CH_3)_2S \rightarrow PtH + (CH_3)_2S^+ \tag{4}$$

Most revealing is the active role that the heterocyclic ligand exerts as demonstrated by a comparison of Fig. 3a and b. While in the reaction of the 2,2′-bipyridine complex (Fig. 3a) the formation of C_2H_4 constitutes the most prominent process, this reaction is below the detection limit for the structurally related complex derived from 2-phenyl pyridine (phpy), Fig. 3b.

An explanation for this unexpected observation may be found in the assumption that the heterocyclic ligands do not only affect the electronic structure of the platinum(II) core but, moreover, play an *active* role as an acceptor in the crucial hydrogen transfer from the thioether ligand to the LPt$^+$ core (L = heterocyclic ligand) such that the initially present C–Pt bond is cleaved (Scheme 3) and a new aryl–H bond is formed. For a system like **1**, DFT calculations suggest an energetic assistance of the reaction by a "retro-roll-over" mechanism [32,33], in the course of which there is an energy gain of ca. 105 kJ mol^{-1} due to re-complexation of

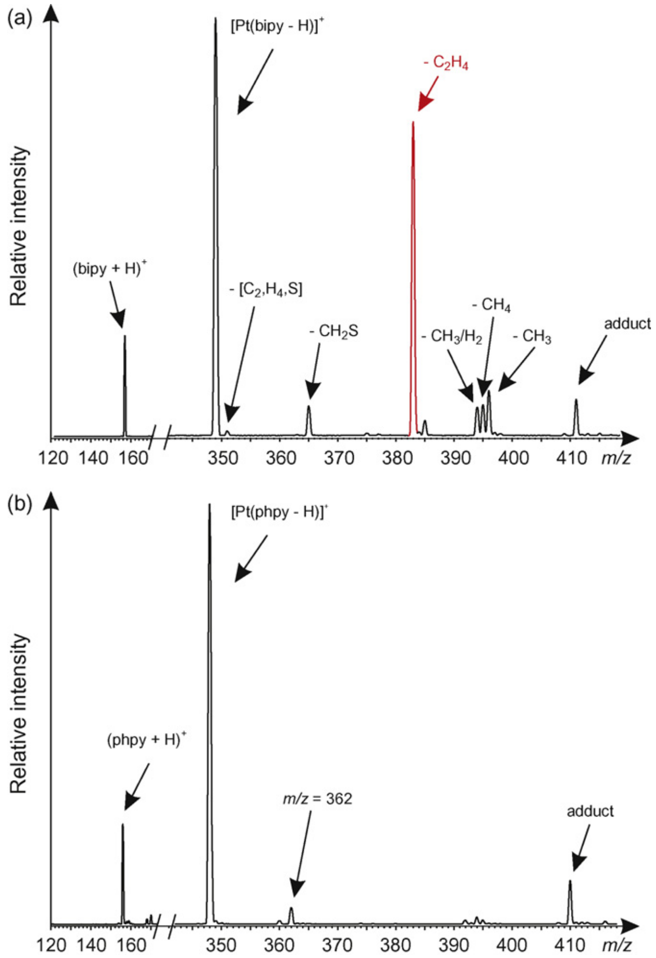
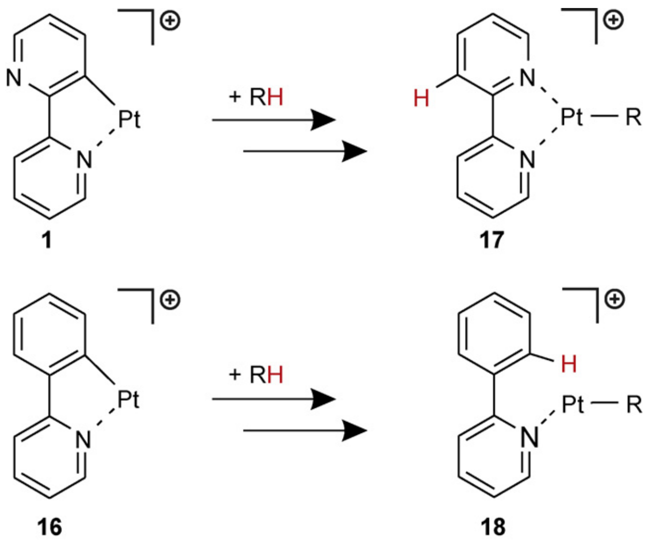


Fig. 3. Ion/molecule reactions of $(CH_3)_2S$ (**2**) with (a) mass-selected [Pt(bipy−H)]$^+$ (**1**) and (b) mass-selected [Pt(phpy−H)]$^+$ (**16**).



Scheme 3. Proposed "active" role of heterocyclic ligands in the initial hydrogen-atom transfer from a substrate R–H.

the platinum core by the nitrogen atom of the second pyridine ring (Scheme 3: **1** → **17**). In the related $[\mathrm{Pt(phpy{-}H)}]^+$ complex **16**, no such stabilization is possible in the course of any conceivable H-transfer and, therefore, the channel for R–H-bond activation by platinum-based complexes, e.g. **16** → **18**, would be higher in energy by this amount. The consequences of this observation for (catalytic) bond activation by platinum-based heterocyclic complexes in desulfurization processes remain to be probed in further experiments.

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