International Journal of Mass Spectrometry 306 (2011) 108–113

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

On the Activation of Chloromethanes by Cyclometalated [Pt(bipy – H)]$^+$ in the Gas Phase: A Mechanistic Study

Burkhard Butschke, Helmut Schwarz*

Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

ARTICLE INFO

Article history:
Received 22 June 2010
Accepted 31 August 2010
Available online 15 September 2010

Dedicated to Professor Tino Gäumann, an extraordinary mentor, on the occasion of his 85th birthday.

Keywords:
2,2′-bipyridine
Bond activation
Cyclometalation
Platinum complexes
Chloromethanes

ABSTRACT

The gas-phase ion/molecule reactions of cyclometalated [Pt(bipy – H)]$^+$ (bipy = 2,2′-bipyridine) with the chloromethanes $CH_{4-n}Cl_n$ (n = 1–4) were investigated and mechanistic features were derived from deuterium labeling experiments. The initial step corresponds to an insertion of the platinum center into the C–Cl bond of the chloromethanes which is either followed by an intramolecular migration of the (halogenated) methyl group to the platinum-bound carbon atom of the aryl ring or for the substrates $CHCl_3$ and CCl_4 by the losses of neutral or cationic $CHCl_2$ and CCl_3 fragments. In all reactions, apart from that with CH_3Cl, transfer of $CH_{2-n}Cl_n$ (n = 0–2) to the (bipy – H) ligand is observed; this process corresponds to a platinum-mediated C–C bond formation.

1. Introduction

The oxidative additions of neutral Pt(II)-complexes [1] to C–X bonds (X = Cl, Br, I) of halogen-substituted methanes [2–7], higher haloalkanes [6–10], and even metal-containing substrates [11] have been investigated quite extensively over the last four decades, and also in the reactions of chloroolefins and -alkanes with Pt(0)-complexes insertions into C–Cl bonds were observed [12]. In most of the examples mentioned above, nitrogen-donor ligands were employed with [Pt(CH$_3$)$_2$(bipy)] (bipy = 2,2′-bipyridine) as the mostly used structural motif [1,4,5,9–11]. Van Koten and co-workers have investigated in detail the reaction of CH_3I with cyclometalated [Pt(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o*′)(H$_2$O)][BF$_4$] (**A** in Scheme 1); however, instead of generating the oxidative-addition product [Pt(CH$_3$)(I)(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o*′)][BF$_4$] (**B**), the complex [Pt(I)(CH$_3$C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o*′)][BF$_4$] (**C**) was isolated; obviously, a carbon-platinum bond had been replaced by a carbon-carbon bond [13,14]. An intramolecular 1,2-methyl shift **B** → **C** was suggested [15], and mechanistic aspects of this process were analyzed in a comprehensive theoretical study by the Hoffmann group [16]. Cyclometalated transition-metal complexes [17–41] are encountered as intermediates in different organic transformations such as the Heck reaction and the Suzuki coupling [42–44], and these compounds have also been employed in the synthesis of various heterocyclic products [45–49].

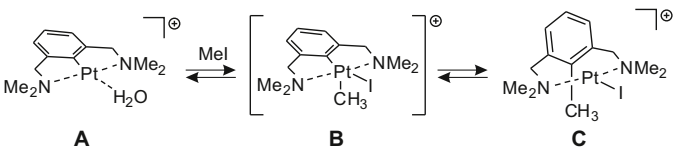
More recently, we have studied in quite some detail the gas-phase reactions of the "rollover"-cyclometalated Pt(II) complex [Pt(bipy – H)]$^+$ (**1**) with various substrates [50–53]; this Pt(II) cation can be conveniently produced via the consecutive losses of methane and dimethyl sulfide from [Pt(CH$_3$)(bipy)((CH$_3$)$_2$S)]$^+$ [50]. Here, we present the results of ion/molecule reactions (IMRs) of the chloromethanes $CH_{4-n}Cl_n$ (n = 1–4) with cyclometalated **1**. Mechanistic insight is gained through comparative reactions with the deuterium labeled complexes [Pt([D$_8$]-bipy – D)]$^+$ ([D$_7$]-**1**) and [Pt([D$_2$]-bipy – D)]$^+$ ([D$_1$]-**1**) ([D$_2$]-bipy = 3,3′-dideutero-2,2′-bipyridine), and with the methylated complexes [Pt(CH$_3$)(bipy)]$^+$ (**2**), [Pt(CH$_3$)([D$_8$]-bipy)]$^+$ ([D$_8$]-**2**), and [Pt(CH$_3$)(bipyrm)]$^+$ (**3**) (bipyrm = 2,2′-bipyrimidine) (Scheme 2).

2. Experimental Details

The experiments were performed with a *VG BIO-Q* mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization (ESI) source as described in detail previously [54,55]. In brief, millimolar methanolic solutions of dimeric [Pt(CH$_3$)$_2$(μ-(CH$_3$)$_2$S)]$_2$ (prepared according to Ref. [56]) and the desired ligands, i.e. 2,2′-bipyridine (bipy), the deuterated analogues 3,3′-dideutero-2,2′-bipyridine ([D$_2$]-bipy) and

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

1387-3806/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2010.08.030



Scheme 1. Mechanism for the formation of $[Pt(I)(CH_3C_6H_3(CH_2NMe_2)_2\text{-}o,o')][BF_4]$ (**C**) in the reaction of cyclometalated $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)][BF_4]$ (**A**) with MeI as suggested in Refs. [13–15]. The counter ion $[BF_4]^-$ has been omitted for the sake of clarity.

perdeutero-2,2′-bipyridin ([D_8]-bipy) as well as 2,2′-bipyrimidine (bipyrm), were introduced through a fused-silica capillary to the ESI source via a syringe pump (ca. 3 μL min^{-1}) in order to produce the ligated Pt(II) cations under investigation (Scheme 2). Apart from [D_2]-bipy, the heterocyclic ligands were purchased. [D_2]-bipy was synthesized via palladium-mediated coupling [57] of 2-chloro-3-deuteropyridine which was synthesized according to [58]. The deuterium incorporation was determined to [D_0]: [D_1]: [D_2] = 2: 19: 79 by analyzing the resulting isotope patterns of the complexes $[Pt(CH_3)([D_n]\text{-bipy})((CH_3)_2S)]^+$ and $[Pt(CH_3)([D_n]\text{-bipy})]^+$ (n = 0 - 2). Analogously, a ratio of 77: 23 for the species [D_1]-**1** and **1** was determined. This implies that mass selection of the ion at m/z = 352 yields [D_1]-**1** in 97% purity. The same analysis for the purchased [D_8]-bipy ligand reveals a distribution of [D_7]-bipy: [D_8]-bipy = 12: 88. [D_6]-**1** and [D_7]-**1** are produced in a ratio of 84: 16, and mass selection of the signal at m/z = 358 resulted in [D_7]-**1** in 98% purity.

In the ESI experiments, 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 [59]. The identity of the ions was already confirmed earlier [50,60]. 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 [54] allows the investigation of quasi-thermal reactions, as demonstrated previously [61–65]. All chloromethanes were purchased. The rates (k_{rel}) of the IMRs shown below are given relative to that of $[Pt(bipy - H)]^+$ with CH_2Cl_2 (k_{rel} = 100).

3. Results and Discussion

3.1. Reactions with CH_3Cl

The mass spectrum for the reaction of mass-selected $[Pt(bipy - H)]^+$ (**1**) with CH_3Cl (k_{rel} = 85) is shown in Fig. 1. From the adduct complex (18% rel. intensity) HCl is eliminated nearly as the only product (79%). When [D_7]-**1** is reacted with CH_3Cl, losses of HCl and DCl are observed. In Table 1, the HCl/DCl-loss ratios for the IMRs of mass selected **1**, [D_1]-**1**, and [D_7]-**1** with CH_3Cl and CD_3Cl are given.

The ratios for the losses of HCl and DCl in the reactions of [D_1]-**1** and [D_7]-**1** with CH_3Cl are within error bars identical. This implies that from the heterocyclic ligand nearly exclusively the hydrogen

Table 1
Experimentally observed ratios for the losses of HCl and DCl (in %) in the IMRs of mass selected **1**, [D_1]-**1**, and [D_7]-**1** with CH_3Cl and CD_3Cl[a].

	1	[D_1]-**1**	[D_7]-**1**
CH_3Cl	100: 0	56: 44	55: 45
CD_3Cl	54: 46	2: 98[b]	1: 99 [b]

[a] The distributions are normalized to Σ = 100%.
[b] The observed signal for the loss of HCl is the result of incomplete deuteration of [D_2]-bipy and [D_8]-bipy (see Experimental Details).

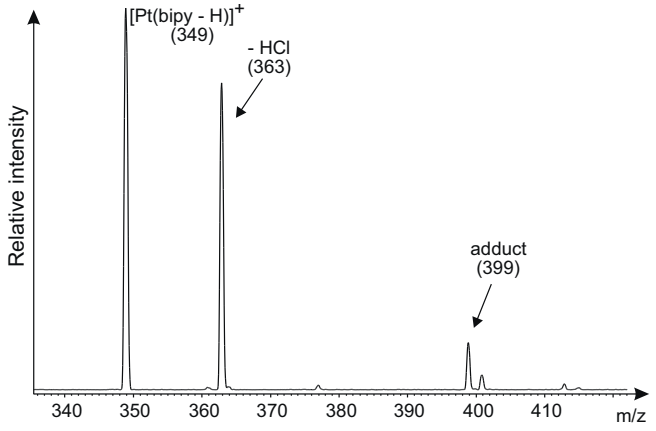
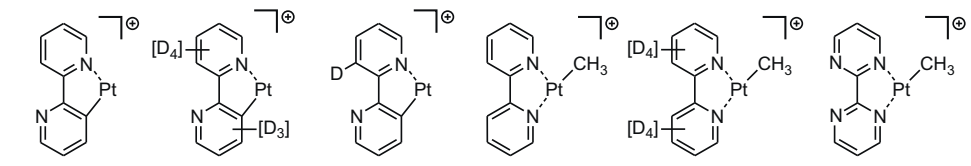


Fig. 1. Ion/molecule reaction of mass-selected $[Pt(bipy - H)]^+$ (**1**) with CH_3Cl. m/z values are given in parentheses for the lightest isotopomer.

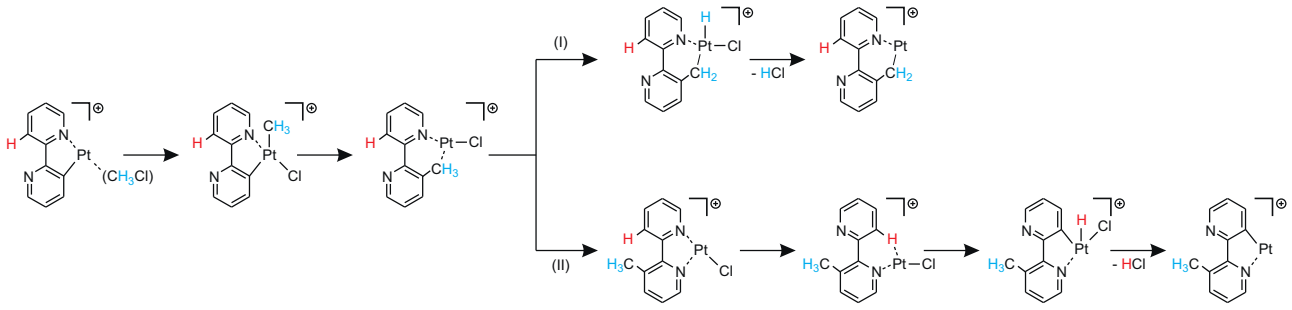
atom from position C(3′) is involved in the formation of hydrogen chloride. This is also supported by the fact that for the couple [D_1]-**1**/CD_3Cl < 2% HCl are lost. However, there must exist a further independent pathway for HCl formation as indicated by the HCl/DCl ratio of 56: 44 for the couple [D_1]-**1**/CH_3Cl. Obviously, the incoming CH_3Cl ligand also serves as a hydrogen-atom source. The observed HCl/DCl ratio can be explained by a mechanistic scenario in which both processes, the activation of the C(3′)–D bond and C–H abstraction from the methyl group of CH_3Cl compete, and a mechanism which accounts for this scenario is shown in Scheme 3.[1] The initially formed adduct complex $[Pt(bipy - H)(CH_3Cl)]^+$ undergoes first C–Cl bond insertion that is followed by a 1,2-methyl shift to the platinum-bound carbon atom of the heterocyclic ligand. For both steps, precedent exists in solution-phase reactions as mentioned in the Introduction. Elimination of HCl can then occur by hydrogen abstraction from the methyl group (path I), while for the formation of HCl including the hydrogen atom from position C(3′) the heterocyclic ligand has to undergo a sequence of "retro-rollover" and "rollover" processes (path II).

There is further experimental support for this scenario: *i*) in the reaction of $[Pt(CH_3)(bipy)]^+$ (**2**) with CH_3Cl, from the adduct complex the elimination of CH_4 as well as the consecutive losses of CH_4 and HCl are observed (see Fig. 2a); *ii*) when the deuterated analogue $[Pt(CH_3)([D_8]\text{-bipy})]^+$ ([D_8]-**2**) is reacted with CH_3Cl one observes CH_4 elimination as well as the combined eliminations of CH_4/HCl and CH_4/DCl; the latter occurs in a ratio of 56: 44; *iii*) in the reaction of $[Pt(CH_3)(bipyrm)]^+$ (**3**) with CH_3Cl, the loss of CH_4 is observed but not the combined formations of CH_4 and HCl (see Fig. 2b). In all cases, methane loss must have initially produced the species $[Pt(L)(CH_2Cl)]^+$ (L = bipy, [D_8]-bipy, bipyrm) because in the reaction with [D_8]-**2** no elimination of CH_3D is observed and for **3** no HCl loss occurs as a consequence of the fact that no hydrogen atoms are accessible for an abstraction process [60] (see Scheme 4). However, only in the first two cases an isomerization producing $[Pt(bipy - H)(CH_3Cl)]^+$ and $[Pt([D_8]\text{-bipy} - D)(CH_2DCl)]^+$ is, in principle, feasible and from these intermediates HCl elimination can be explained according to Scheme 3; indeed, only in these two cases the consecutive losses of CH_4 and HCl (or DCl) take place. Moreover, inspection of Table 1 reveals that for the couples **1**/CD_3Cl and [D_7]-**1**/CH_3Cl loss of HCl is slightly favored as compared with DCl elimination. This, implies that for the former pair, path II in Scheme 3 is preferred and for the latter path I. Thus, most likely, a kinetic isotope

[1] H/D scrambling between position C(3′) and the incoming CH_3Cl can be ruled out as this would result in an HCl/DCl ratio of 3 : 1.



Scheme 2. Pt(II) complexes employed in the gas-phase IMRs with the chloromethanes $CH_{4-n}Cl_n$ (n = 1 - 4).



Scheme 3. Proposed mechanisms for the HCl loss in the IMR of $[Pt(bipy - H)]^+$ (**1**) with CH_3Cl.

effect is associated with the rate-limiting steps of C–H/D bond activation.

We note in passing that in the IMR of **1** with chloroethane loss of HCl is unimportant. Rather, elimination of neutral ethene constitutes the dominant process; this can be easily explained by a facile β-hydrogen elimination from the platinum bound ethyl group after initial C–Cl bond insertion. Quite likely, a "retro-rollover" process that results in the formation of $[Pt(bipy)(Cl)]^+$ serves as a driving force.

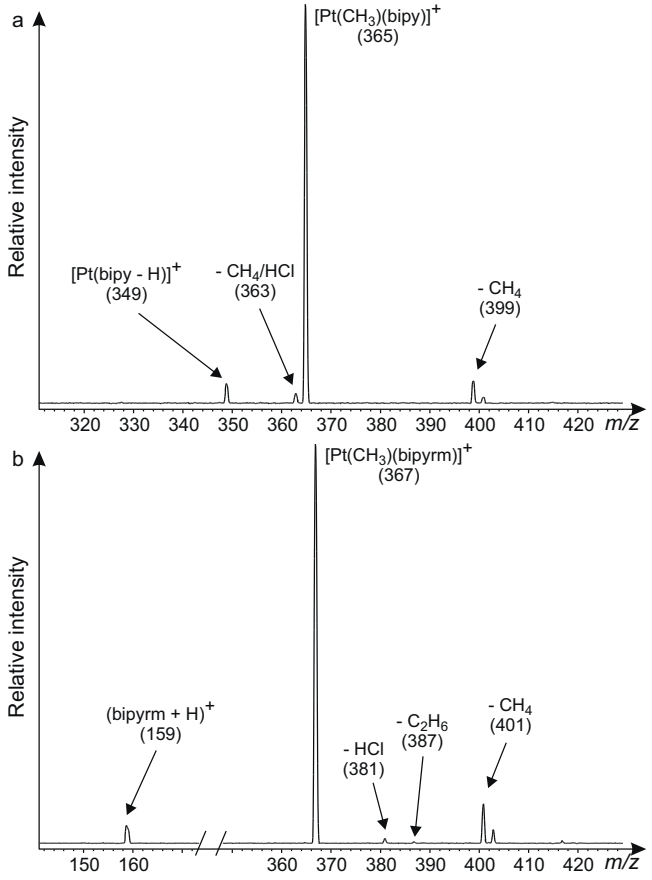


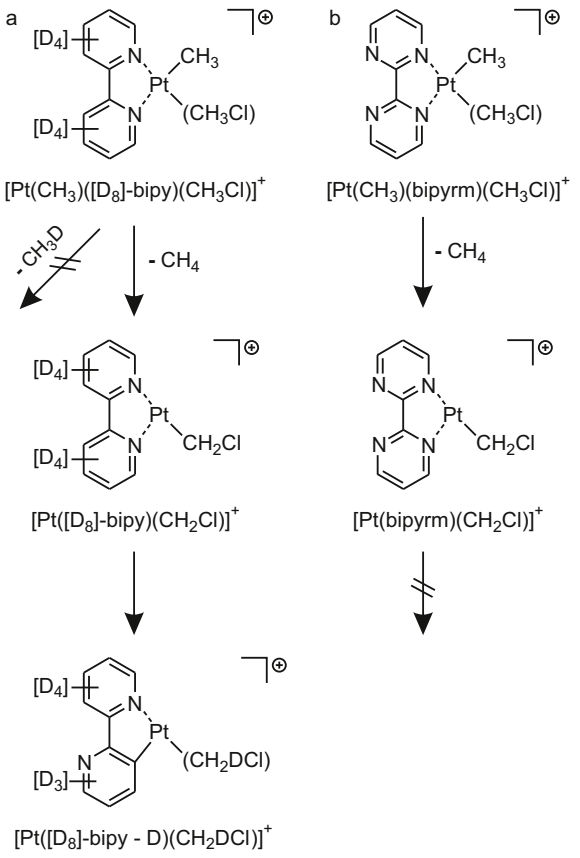
Fig. 2. Comparison of the ion/molecule reactions of mass-selected a) $[Pt(CH_3)(bipy)]^+$ (**2**) and b) $[Pt(CH_3)(bipyrm)]^+$ (**3**) with CH_3Cl. m/z values are given in parentheses for the lightest isotopomer.

3.2. Reactions with CH_2Cl_2

In the IMR of mass-selected $[Pt(bipy - H)]^+$ (**1**) with CH_2Cl_2 (k_{rel} = 100, Fig. 3) the most important reaction channels correspond to the eliminations of HCl (9%), 2HCl (16%) and $PtCl_2$ (50%) from the adduct complex (20%) (Fig. 3). For the formation of HCl, we suggest the same mechanistic scenario as illustrated in Scheme 3 for the couple **1**/CH_3Cl; this is justified because in the IMR of the deuterium labeled precursor complex $[Pt([D_8]-bipy - D)]^+$ with CH_2Cl_2 losses of HCl and DCl are observed in a ratio of 74: 26 (pathways (I) and (II) in Scheme 5). This ratio is significantly higher than in the reaction of **1** with CH_3Cl, and this is consistent with the proposed mechanism as coordination of the CH_2Cl-group to the platinum center can be assumed to be stronger than that of the CH_3 group for the couple **1**/CH_3Cl; therefore, pathway (II) should be connected with a higher barrier for the aryl-aryl rotation. The combined losses of two HCl molecules, on the other hand, cannot be explained as easily as implied by path (III) in Scheme 5 because this scenario contradicts the findings for the reaction with $[Pt([D_8]-bipy - D)]^+$ where both 2HCl and HCl/DCl are eliminated in a ratio of 57: 43. Obviously, partial hydrogen/deuterium exchange between the incoming CH_2Cl_2 substrate and the heterocyclic ligand occurs; however, it is not clear if this takes place prior or after the first HCl-elimination step. The fact that only one deuterium atom is incorporated into the neutral product suggests that only the highlighted hydrogen atom in (bipy – H) is involved in the reactions (Scheme 5). The elimination of neutral $PtCl_2$ can be explained through the steps indicated by pathway (IV) in Scheme 5; Cl-atom transfer (instead of H-atom transfer) from the CH_2Cl-group to the platinum center following the 1,2-methyl shift generates $PtCl_2$ as a thermodynamically favorable leaving group.

3.3. Reactions with $CHCl_3$

In the reaction of $[Pt(bipy - H)]^+$ with $CHCl_3$ (k_{rel} = 66, Fig. 4) the losses of HCl (44%), $PtCl_2$ (10%) and neutral $CHCl_2$ (18%) from the adduct complex (2%) are observed as well as the formation of



Scheme 4. Proposed mechanisms for the losses of CH_4 and the ongoing steps in the IMRs of a) $[Pt(CH_3)([D_8]\text{-bipy})]^+$ ($[D_8]$-**2**) and b) $[Pt(CH_3)(\text{bipyrm})]^+$ (**3**) with with CH_3Cl.

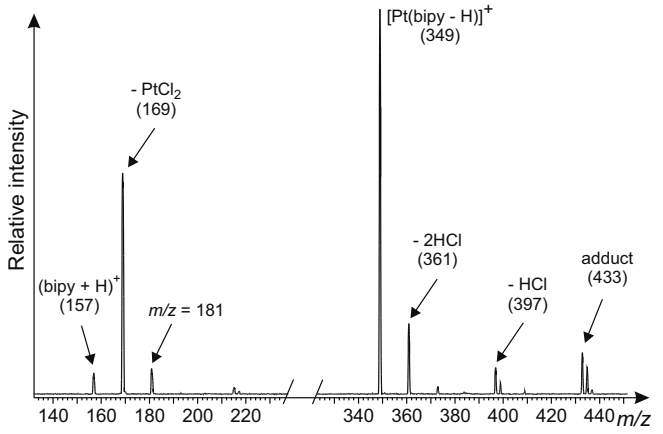


Fig. 3. Ion/molecule reaction of mass-selected $[Pt(bipy - H)]^+$ (**1**) with CH_2Cl_2. *m/z* values are given in parentheses for the lightest isotopomer.

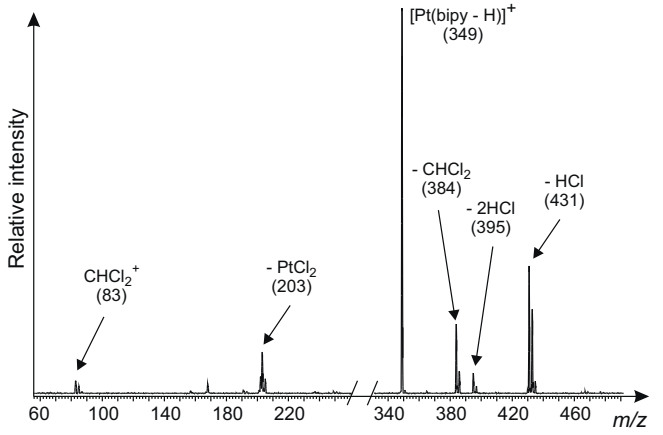
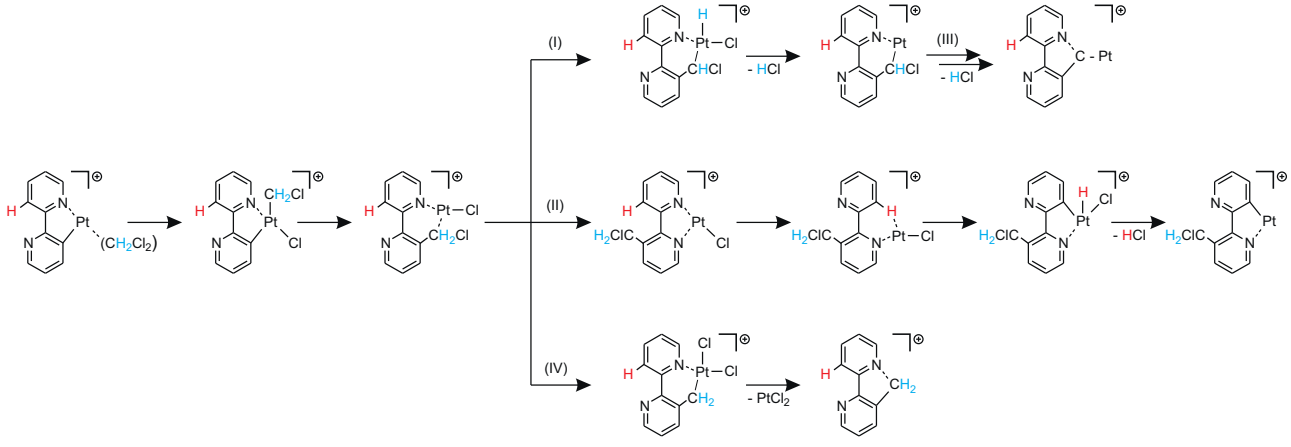


Fig. 4. Ion/molecule reaction of mass-selected $[Pt(bipy - H)]^+$ (**1**) with $CHCl_3$. *m/z* values are given in parentheses for the lightest isotopomer.

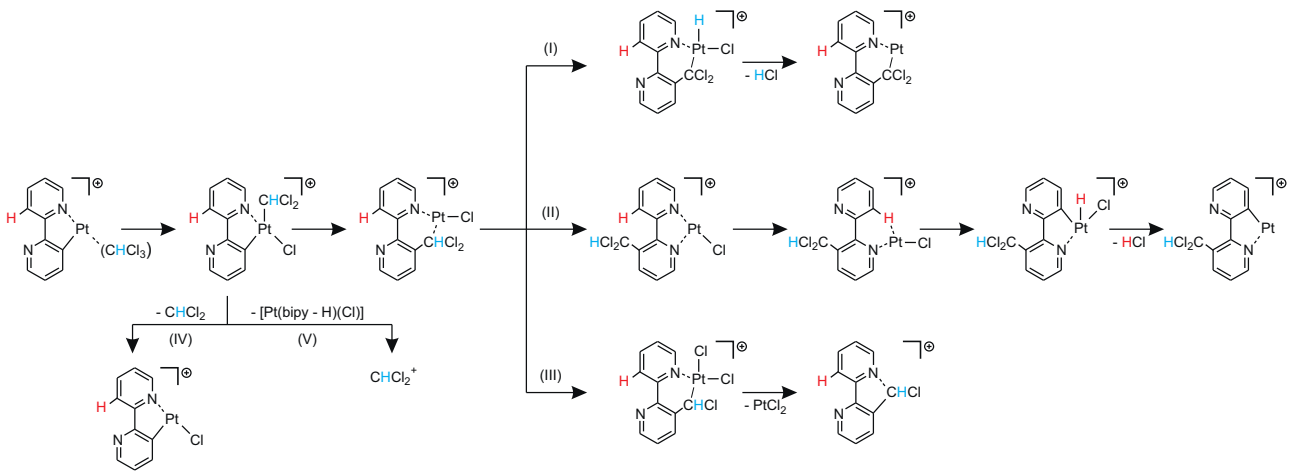
cationic $CHCl_2^+$ (5%). In the reaction of $[Pt([D_8]\text{-bipy} - D)]^+$ with $CHCl_3$, HCl and DCl are formed in a ratio of 95: 5; this is consistent with the trend already noted for the elimination of HCl in the reactions of **1** with CH_3Cl and CH_2Cl_2, respectively (compare pathways (I) and (II) in Scheme 6). Formation of $PtCl_2$ from the adduct can be explained analogously as for the couple **1**/CH_2Cl_2 (pathway (III) in Scheme 6). In addition to the channels which were already observed in the reactions of **1** with CH_3Cl and CH_2Cl_2 there are two new processes which are linked by a formal charge-transfer process, i.e. formation of $[Pt(bipy - H)(Cl)]^+ + CHCl_2$ versus $[Pt(bipy - H)(Cl)] + CHCl_2^+$.

3.4. Reactions with CCl_4

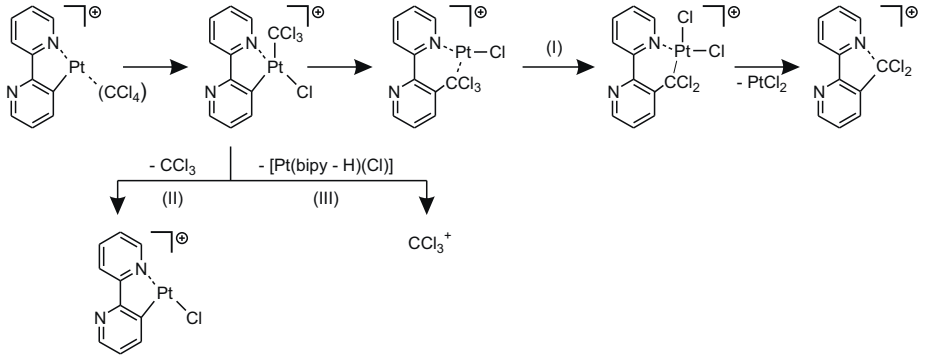
In the reaction of **1** with CCl_4 (k_{rel} = 98, Fig. 5) after adduct formation (4%) the main processes correspond to the losses of neutral $PtCl_2$ (28%) and CCl_3 (27%) as well as to the formation of cationic CCl_3^+ (27%). A mechanistic scenario for these processes is suggested in Scheme 7.



Scheme 5. Proposed mechanisms for the main reactions in the IMR of $[Pt(bipy - H)]^+$ (**1**) with CH_2Cl_2.



Scheme 6. Proposed mechanisms for the main reactions in the IMR of $[Pt(bipy - H)]^+$ (**1**) with $CHCl_3$.



Scheme 7. Proposed mechanisms for the main reactions in the IMR of $[Pt(bipy - H)]^+$ (**1**) with CCl_4.

In passing, we would like to mention that also in the reactions of **1** with benzylchloride and *tert*-butylchloride abstraction of Cl^- from the neutral substrates occurs to give rise to the formations of $C_7H_7^+$ and $t\text{-}C_4H_9^+$ cations, respectively; however, in these cases no signal for $[Pt(bipy - H)(Cl)]^+$ is observed. This, together with the above mentioned results implies a series of decreasing stability for $C_7H_7^+$, $t\text{-}C_4H_9^+ > CCl_3^+ > CHCl_2^+ > CH_2Cl^+, CH_3^+$ which is in line with the trends known from carbocation stabilities [66].

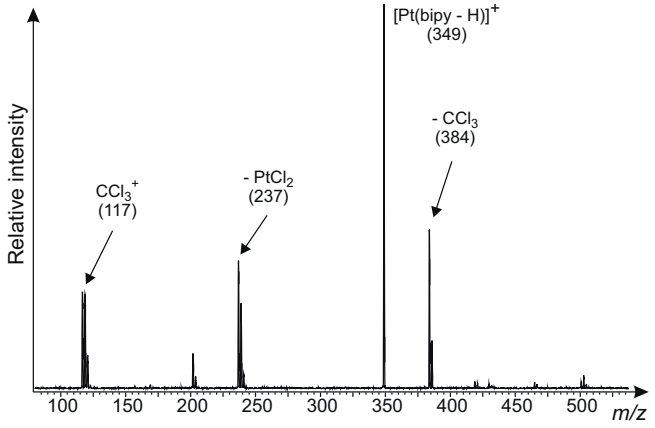


Fig. 5. Ion/molecule reaction of mass-selected $[Pt(bipy - H)]^+$ (**1**) with CCl_4. *m/z* values are given in parentheses for the lightest isotopomer.

4. Conclusion

In the reactions of cyclometalated $[Pt(bipy - H)]^+$ with CH_3Cl the elimination of HCl corresponds to the most dominant process. Two mechanisms are operative which have both in common the initial insertion of the platinum center into the C–Cl bond followed by an intramolecular migration of the methyl group to the platinum-bound carbon atom of the heterocyclic ligand. Next, HCl is formed either after hydrogen abstraction from the methyl group or in a specific fashion from the C(3′) position of the aryl ring after two consecutive ring rotations of the pyridyl rings. In the reaction of $[Pt(bipy - H)]^+$ with CH_2Cl_2 the transfer of CH_2 to the (bipy – H) ligand constitutes the most important process concomitant with formation of neutral $PtCl_2$. In the reactions with $CHCl_3$ and CCl_4 couples of $CHCl_2$ and $CHCl_2^+$ as well as CCl_3 and CCl_3^+ are generated; this is likely due to the decreasing C–Cl bond dissociation energies in the series CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

Acknowledgements

We thank Dr. Xinhao Zhang 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*.

References

[1] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.

[2] J.D. Ruddick, B.L. Shaw, J. Chem. Soc. A (1969) 2801.
[3] J.D. Ruddick, B.L. Shaw, J. Chem. Soc. A (1969) 2964.
[4] J. Kuyper, Inorg. Chem. 16 (1977) 2171.
[5] J. Kuyper, Inorg. Chem. 17 (1978) 77.
[6] G.B. Young, G.M. Whiteside, J. Am. Chem. Soc. 100 (1978) 5808.
[7] P.K. Monaghan, R.J. Puddephatt, Organometallics 4 (1985) 1406.
[8] M. Rashidi, B.Z. Momeni, J. Organomet. Chem. 574 (1999) 286.
[9] S.M. Nabavizadeh, S.J. Hoseini, B.Z. Momeni, N. Shahabadi, M. Rashidi, A.H. Pakiari, K. Eskandari, Dalton Trans. (2008) 2414.
[10] B.Z. Momeni, Z. Moradi, M. Rashidi, F. Rominger, Polyhedron 28 (2009) 381.
[11] G.J. Arsenault, M. Crespo, R.J. Puddephatt, Organometallics 6 (1987) 2255.
[12] W.J. Bland, R.D.W. Kemmitt, J. Chem. Soc. A (1968) 1278.
[13] G. van Koten, K. Timmer, J.G. Noltes, A.L. Spek, J. Chem. Soc., Chem. Commun. (1978) 250.
[14] D.M. Grove, G. van Koten, J.N. Louwen, J.G. Noltes, A.L. Spek, H.J.C. Ubbels, J. Am. Chem. Soc. 104 (1982) 6609.
[15] J. Terheijden, G. van Koten, I.C. Vinke, A.L. Spek, J. Am. Chem. Soc. 107 (1985) 2891.
[16] J.V. Ortiz, Z. Havlas, R. Hoffmann, Helv. Chim. Acta. 67 (1984) 1.
[17] J. Dehand, M. Pfeffer, Coord. Chem. Rev. 18 (1976) 327.
[18] M.I. Bruce, Angew. Chem. Int. Ed. Engl. 16 (1977) 73.
[19] R.J. Watts, J.S. Harrington, J. Van Houten, J. Am. Chem. Soc. 99 (1977) 2179.
[20] I. Omae, Coord. Chem. Rev. 28 (1979) 97.
[21] I. Omae, Chem. Rev. 79 (1979) 287.
[22] I. Omae, Coord. Chem. Rev. 32 (1980) 235.
[23] W.A. Wickramasinghe, P.H. Bird, N. Serpone, J. Chem. Soc. Chem. Commun. (1981) 1284.
[24] E.C. Constable, K.R. Seddon, J. Chem. Soc. Chem. Commun. (1982) 34.
[25] S. Dholakia, R.D. Gillard, F.L. Wimmer, Inorg. Chim. Acta. 69 (1983) 179.
[26] G. Nord, A.C. Hazell, R.G. Hazell, O. Farver, Inorg. Chem. 22 (1983) 3429.
[27] P.J. Spellane, R.J. Watts, C.J. Curtis, Inorg. Chem. 22 (1983) 4060.
[28] E.C. Constable, Polyhedron 3 (1984) 1037.
[29] P.S. Braterman, G.A. Heath, A.J. MacKenzie, B.C. Noble, R.D. Peacock, L.J. Yellowlees, Inorg. Chem. 23 (1984) 3425.
[30] I.P. Rothwell, Polyhedron 4 (1985) 177.
[31] G. Minghetti, A. Doppiu, A. Zucca, S. Stoccoro, M.A. Cinellu, M. Manassero, M. Sansoni, Chem. Heterocycl. Comp. 35 (1999) 992.
[32] Y. Wu, S. Huo, J. Gong, X. Cui, L. Ding, K. Ding, C. Du, Y. Liu, M. Song, J. Organomet. Chem. 27 (2001) 637.
[33] M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750.
[34] A. Zucca, A. Doppiu, M.A. Cinellu, S. Stoccoro, G. Minghetti, M. Manassero, Organometallics 21 (2002) 783.
[35] G. Minghetti, S. Stoccoro, M.A. Cinellu, B. Soro, A. Zucca, Organometallics 22 (2003) 4770.
[36] I. Omae, Coord. Chem. Rev. 248 (2004) 995.
[37] A. Zucca, M.A. Cinellu, G. Minghetti, S. Stoccoro, M. Manassero, Eur. J. Inorg. Chem. (2004) 4484.
[38] S. Stoccoro, A. Zucca, G.L. Petretto, M.A. Cinellu, G. Minghetti, M. Manassero, J. Organomet. Chem. 691 (2006) 4135.
[39] F. Mohr, S.H. Priver, S.K. Bhargava, M.A. Bennett, Coord. Chem. Rev. 250 (2006) 1851.
[40] G. Minghetti, S. Stoccoro, M.A. Cinellu, G.L. Petretto, A. Zucca, Organometallics 27 (2008) 3415.
[41] A. Zucca, G.L. Petretto, S. Stoccoro, M.A. Cinellu, M. Manassero, C. Manassero, G. Minghetti, Organometallics 28 (2009) 2150.
[42] Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen, Z. Yang, Org. Lett. 19 (2004) 3337.
[43] G.D. Frey, J. Schütz, E. Herdtweck, W.A. Herrmann, Organometallics 24 (2005) 4416.
[44] S.P. Mulcahy, P.J. Carroll, E. Meggers, Tetrahedron Letters 47 (2006) 8877.
[45] M. Pfeffer, Pure Appl. Chem. 64 (1992) 335.
[46] J. Vicente, J.-A. Abad, R. Bergs, P.G. Jones, M.C. Ramrez de Arellano, Organometallics 15 (1996) 1422.
[47] W. Ferstl, I.K. Sakodinskaya, N. Beydoun-Sutter, G. de Borgne, M. Pfeffer, A.D. Ryabov, Organometallics 16 (1997) 411.
[48] S.J. Hwang, S.H. Cho, S. Chang, J. Am. Chem. Soc. 130 (2008) 16158.
[49] K.L. Hull, M.S. Sanford, J. Am. Chem. Soc. 131 (2009) 9651.
[50] B. Butschke, M. Schlangen, D. Schröder, H. Schwarz, Chem. Eur. J. 14 (2008) 11050.
[51] B. Butschke, M. Schlangen, D. Schröder, H. Schwarz, Int. J. Mass Spectrom. 283 (2009) 3.
[52] B. Butschke, S. Ghassemi Tabrizi, H. Schwarz, Chem. Eur. J. 16 (2010) 3962.
[53] B. Butschke, S. Ghassemi Tabrizi, H. Schwarz, Int. J. Mass Spectrom. 291 (2010) 125.
[54] D. Schröder, T. Weiske, H. Schwarz, Int. J. Mass Spectrom. 219 (2002) 729.
[55] C. Trage, D. Schröder, H. Schwarz, Chem. Eur. J. 11 (2005) 619.
[56] G.S. Hill, M.J. Irwin, C.J. Levy, L.M. Rendina, R.J. Puddephatt, Inorg. Synth. 32 (1998) 149.
[57] P. Bamfield, P.M. Quan, Synthesis (1978) 537.
[58] L. Bérillon, A. Leprêtre, A. Turck, N. Plé, G. Quéguiner, G. Cahiezc, P. Knochel, Synlett (1998) 1359.
[59] N.B. Cech, C.G. Enke, Mass Spectrom. Rev. 20 (2001) 362.
[60] B. Butschke, D. Schröder, H. Schwarz, Organometallics 28 (2009) 4340.
[61] D. Schröder, H. Schwarz, S. Schenk, E. Anders, Angew. Chem. Int. Ed. 42 (2003) 5087.
[62] C. Trage, M. Diefenbach, D. Schröder, H. Schwarz, Chem. Eur. J. 12 (2006) 2454.
[63] D. Schröder, M. Engeser, H. Schwarz, E.C.E. Rosenthal, J. Döbler, J. Sauer, Inorg. Chem. 45 (2006) 6235.
[64] P. Gruene, C. Trage, D. Schröder, H. Schwarz, Eur. J. Inorg. Chem. (2006) 4546.
[65] B. Jagoda-Cwiklik, P. Jungwirth, L. Rulíšek, P. Milko, J. Roithová, J. Lemaire, P. Maitre, J.M. Ortega, D. Schröder, ChemPhysChem. 8 (2007) 1629.
[66] G.A. Olah, G.K.S. Prakash (Eds.), Carbocation Chemistry, Wiley-Interscience, Hoboken, N.J., 2004.