Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 237 (2004) 19–23

www.elsevier.com/locate/ijms

Short communication

# C–H- and N–H-activation by gaseous $Rh_2^+$ and $PtRh^+$ cluster ions

Konrad Koszinowski[1], Maria Schlangen, Detlef Schröder, Helmut Schwarz*

*Institut für Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*

Received 14 June 2004; accepted 21 June 2004

Dedicated to Professor Giorgio Modena on the occasion of his 80th birthday.

## Abstract

The gas-phase reactions of the cluster ions $Rh_2^+$ and $PtRh^+$ with methane and ammonia are studied by Fourier-transform ion-cyclotron-resonance mass spectrometry. The dehydrogenation reactions observed closely resemble processes previously found for $Pt_2^+$. In the presence of ammonia, the carbene species $Rh_2CH_2^+$ and $PtRhCH_2^+$ formed in the primary dehydrogenation of methane yield the carbide complexes $Rh_2C^+(NH_3)$ and $PtRhC^+(NH_3)$, respectively. Again, this behavior is analogous to that of the corresponding platinum cluster. The generation of carbide complexes in the gas phase mimics unwanted soot formation in the heterogeneous DEGUSSA process which employs platinum and rhodium for the catalytic conversion of methane and ammonia to hydrogen cyanide.

*Keywords:* Bond activation; Gas-phase reactions; Metal clusters; Platinum; Rhodium

## 1. Introduction

Fueled by a strong economic interest, the activation of methane and other simple, inert substrates by transition metals receives much attention [1–4]. Although important progress has been made in the past decade [5–7], many questions remain open and thus call for further efforts to understand the fundamental prerequisites of the activation process. Particularly, one has to find out which transition metals are suited best for this purpose.

One possible method to unravel the intrinsic reactivities of the d-block elements relies on gas-phase techniques [8]. By the rigorous exclusion of any environmental effects, the chemical behavior of a transition metal can be probed under well-defined conditions. As far as mass spectrometry is used as experimental technique, this approach is limited to charged species, in the simplest case monocationic metal atoms $M^+$. For these, the entire d-block has been screened with respect to reactivity toward methane [9–11]. With the exception of $Zr^+$ [12,13], none of the 3d or 4d elements achieves $CH_4$ activation under thermal conditions. Instead, the 5d metal ions $Ta^+$, $W^+$, $Os^+$, $Ir^+$, and $Pt^+$ spontaneously dehydrogenate methane according to reaction 1. This striking difference has been traced back to different stabilities of the resulting metal-carbene species which originate from different sd-promotion energies of the metal ions and ultimately reflect the different extents of relativistic effects [10,14].

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 \qquad (1)$$

Besides mononuclear metal ions $M^+$, several cluster ions $M_n^+$ have been investigated as well. These experiments provide valuable additional information because they allow the exploration of different electronic structures and probe species with lower charge densities that should be better comparable to systems of practical interest. For instance, it could be shown that small platinum clusters $Pt_n^{+/-}$, $n \leq 9$, dehydrogenate $CH_4$ in analogy to the behavior of mononuclear $Pt^+$ [15–17]. In other cases, only for specific clusters sizes high reactivities are observed. Whereas, e.g., $Rh_2^+$ accomplishes

---

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

[1] Present address: Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA.

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.06.009

$CH_4$ activation, neither mononuclear $Rh^+$ nor the larger clusters $Rh_n{}^+$ do so [18].

Interestingly, both platinum and rhodium are used in one of the few established industrial processes for methane activation, namely the DEGUSSA process. This procedure employs heterogeneous platinum or platinum/rhodium catalysts for the generation of hydrogen cyanide from $CH_4$ and $NH_3$ at elevated temperatures, reaction 2 [19–21].

$$CH_4 + NH_3 \xrightarrow{[Pt] \vee [Pt/Rh]} HCN + 3H_2 \qquad (2)$$

Previous work from our group has shown that the reactivity of gaseous $Pt^+$ mimics that of the DEGUSSA catalyst in that it mediates C–N coupling of methane and ammonia, the carbene species $PtCH_2{}^+$ being the key intermediate [22,23]. In contrast, the analogous reactions of platinum clusters $Pt_n{}^+$ lead to carbide species $Pt_nC^+(NH_3)$ and may thus be interpreted as gas-phase equivalents of unwanted soot formation on the heterogeneous catalyst [24].

Given that rhodium displays catalytic activity in the DEGUSSA process as well, the gas-phase reactivities of $Rh_2{}^+$ and $Rh_2CH_2{}^+$ also deserve attention. Moreover, the mixed dinuclear cluster $PtRh^+$ offers the possibility to study eventual cooperative effects of the two metals that could be relevant to the heterogeneous process as well. Such cooperative effects have been observed for the dinuclear platinum-coinage metal cations $PtM^+$, M = Cu, Ag, and Au [25–27]. To probe whether a similar situation applies to the system platinum/rhodium as well, we now have studied the reactivities of $Rh_2{}^+$ and $PtRh^+$ toward methane and ammonia by means of Fourier-transform ion-cyclotron-resonance mass spectrometry.

## 2. Experimental

Experiments were performed using a Spectrospin CMS 47X FT-ICR mass spectrometer [28] equipped with a Smalley-type [29] cluster-ion source developed by Bondybey, Niedner-Schatteburg, and co-workers [30,31]. In brief, the fundamental of a pulsed Nd:YAG laser ($\lambda = 1064$ nm, Spectron Systems) is focused onto a rotating target of a platinum-rhodium alloy (1:1 molar ratio). The metal plasma thereby generated is entrained in a synchronized helium pulse and cooled by supersonic expansion to achieve cluster formation. After passing a skimmer, the ionic components of the molecular beam are transferred into the analyzer cell where they are trapped in the field of a 7.05 T superconducting magnet.

After mass selection of the $^{103}Rh_2{}^+$ or $^{195}Pt^{103}Rh^+$ ion, respectively, by means of the FERETS ion-ejection technique [32] and ion thermalization by pulsing-in argon as a buffer gas, ion-molecule reactions are studied by leaking-in the neutral reactant at $p \approx 10^{-8}$ mbar. Based on the pseudo first-order kinetic approximation, kinetic analysis of the decline of the reactant clusters and evolution of the corresponding product ions yield bimolecular rate constants $k$. The errors in $k$ are estimated to ±30% in the case of $CH_4$ [33] and ±50% for $NH_3$ because of the unfavorable pumping characteristics of the latter that render the maintenance of a constant pressure throughout the whole experiment difficult. Reaction efficiencies $\varphi = k/k_{cap}$ are calculated according to capture theory [34]. To study the reactions of the metal-carbene ions, these are generated by subjecting the mass-selected, thermalized bare metal dimers to pulsed-in methane followed by a second mass selection. For collision-induced dissociation (CID) experiments, the ion of interest is mass-selected, kinetically excited, and collided with pulsed-in argon gas prior to detecting the fragment ions.

## 3. Results

As already reported by Albert et al. [18], $Rh_2{}^+$ efficiently dehydrogenates $CH_4$, reaction 3. The rate constant derived from the present experiments, $k = (5.9 \pm 1.8) \times 10^{-10}$ cm$^3$ s$^{-1}$, agrees with the value measured by these authors, $k = (7.0 \pm 2.1) \times 10^{-10}$ cm$^3$ s$^{-1}$, within the error margins.

$$Rh_2{}^+ + CH_4 \rightarrow Rh_2CH_2{}^+ + H_2 \qquad (3)$$

$Pt_2{}^+$ undergoes an analogous reaction with methane that is even more efficient (Table 1) [16,17]. Hence, a simple interpolation suggests a similar behavior of $PtRh^+$ which is indeed observed in experiment, reaction 4. Apparently, it makes no difference if the metal cluster has an even (like $PtRh^+$) or odd (like $Rh_2{}^+$ and $Pt_2{}^+$) number of valence electrons.

$$PtRh^+ + CH_4 \rightarrow PtRhCH_2{}^+ + H_2 \qquad (4)$$

Clearly, the dehydrogenation accomplished in reactions 3 and 4 corresponds to the activation of methane. In the context of the DEGUSSA process, the crucial question now is whether the resulting metal carbene species react with ammonia under C–N bond formation. We find that both $Rh_2CH_2{}^+$ and

Table 1
Bimolecular rate constants $k$ and efficiencies $\varphi$ for the reactions of $Rh_2{}^+$, $RhPt^+$, and $Pt_2{}^+$ with methane and ammonia

| Reaction | $k$ ($\times 10^{-10}$ cm$^3$ s$^{-1}$) ($\varphi$) | | |
|---|---|---|---|
| | $MM'^+ = Rh_2{}^+$ | $RhPt^+$ | $Pt_2{}^+$ |
| $MM'^+ + CH_4$<br>$\rightarrow MM'CH_2{}^+ + H_2$ | 5.9 (0.60)[a] | 7.1 (0.74) | 8.2 (0.85)[b,c] |
| $MM'CH_2{}^+ + NH_3$<br>$\rightarrow [M,M',C,H_3,N]^+ + H_2$ | 12.8 (0.63) | 9.4 (0.47) | 9.7 (0.49)[d] |
| $MM'^+ + NH_3$<br>$\rightarrow MM'NH^+ + H_2$ | 2.6 (0.12) | 0.8 (0.04) | 5.4 (0.27)[b] |

[a] Compare to $k = (7.0 \pm 2.1) \times 10^{-10}$ cm$^3$ s$^{-1}$ [18].

[b] Taken from [17].

[c] Compare to $k = (7.0 \pm 0.6) \times 10^{-10}$ cm$^3$ s$^{-1}$ [16].

[d] Taken from [24].

$PtRhCH_2^+$ undergo ready dehydrogenation in the presence of $NH_3$, reactions 5 and 6.

$$Rh_2CH_2^+ + NH_3 \rightarrow [Rh_2, C, H_3, N]^+ + H_2 \qquad (5)$$

$$PtRhCH_2^+ + NH_3 \rightarrow [Pt, Rh, C, H_3, N]^+ + H_2 \qquad (6)$$

These observations alone do not give clear clues with respect to the ion structures because dehydrogenation can be associated with C–N coupling, but can also involve the carbene unit only. Specifically, two markedly different patterns for the dehydrogenation of platinum carbenes have been distinguished. Mononuclear $PtCH_2^+$ as well as the dinuclear platinum-coinage metal-carbene species $PtMCH_2^+$, M = Cu, Ag, and Au, form metal-aminocarbene complexes in their reactions with $NH_3$, i.e., they do mediate C–N coupling [22,23,25–27]. In contrast, the seemingly equivalent reactions of the $Pt_nCH_2^+$ clusters ($n$ = 2–5) with $NH_3$ yield carbide structures $Pt_nC^+(NH_3)$ and thus do not accomplish C–N bond formation [24]. Experimentally, a distinction between both reaction pathways can be achieved by isotopic labeling. For the present problem, this approach implies consideration of $Rh_2CD_2^+$ and $PtRhCD_2^+$. In the presence of ammonia, both these ions exclusively lose $D_2$, reactions 5a and 6a, which is clear evidence for the formation of the corresponding carbide species $Rh_2C^+(NH_3)$ and $PtRhC^+(NH_3)$, respectively.

$$Rh_2CD_2^+ + NH_3 \rightarrow [Rh_2, C, H_3, N]^+ + D_2 \qquad (5a)$$

$$PtRhCD_2^+ + NH_3 \rightarrow [Pt, Rh, C, H_3, N]^+ + D_2 \qquad (6a)$$

In the case of the rhodium dimer, additional support for this structural assignment comes from CID of the $[Rh_2,C,H_3,N]^+$ product ion which leads to $Rh_2C^+$ as sole ionic fragment, reaction 7. For a hypothetical aminocarbene complex, one would expect a different fragmentation behavior, e.g., losses of $H_2$ or HCN [22].

$$[Rh_2, C, H_3, N]^+ \rightarrow Rh_2C^+ + NH_3 \qquad (7)$$

While both $Rh_2^+$ and $PtRh^+$ activate methane but do not mediate coupling with ammonia in the second step, it remains to be probed whether the bare metal clusters react with $NH_3$. Among the platinum clusters $Pt_n^+$, $n \leq 5$, only $Pt_2^+$ dehydrogenates ammonia. The resulting imine species $Pt_2NH^+$ then rapidly transfers its proton to a further $NH_3$ molecule in a second step ($k = 6.6 \times 10^{-10}$ cm$^3$ s$^{-1}$, $\varphi = 0.33$) [17]. Again, the reactivities of $Rh_2^+$ and $PtRh^+$ resemble that of their $Pt_2^+$ counterpart. Both ions react with ammonia under dehydrogenation as well, reactions 8 and 9. However, the efficiencies of these processes are significantly smaller compared to the corresponding reaction of $Pt_2^+$ (Table 1). Moreover, the reaction efficiencies do not follow a continuous trend when going from $Rh_2^+$ via $PtRh^+$ to $Pt_2^+$ but show a minimum for the heteronuclear cluster ion.

$$Rh_2^+ + NH_3 \rightarrow Rh_2NH^+ + H_2 \qquad (8)$$

$$PtRh^+ + NH_3 \rightarrow PtRhNH^+ + H_2 \qquad (9)$$

Regarding secondary processes, no reaction is found for $Rh_2NH^+$ whereas $PtRhNH^+$ slowly protonates ammonia concomitant with loss of neutral PtRhN ($k \approx 1.7 \times 10^{-11}$ cm$^3$ s$^{-1}$, $\varphi \approx 8 \times 10^{-3}$). This implies that $Rh_2N$ is a stronger gas-phase base than $NH_3$ whereas the opposite holds true for PtRhN. In addition, the mixed cluster ion yields the consecutive products $RhNH_3^+$ and $[Pt,Rh,H_4,N_2]^+$ with similarly low efficiencies.

As all three diatomic clusters $Rh_2^+$, $PtRh^+$, and $Pt_2^+$ accomplish $NH_3$ activation, reaction of the resulting imine species with $CH_4$ might be considered as an alternative route for C–N coupling. In the case of $Pt_2NH^+$, however, a major drawback of this approach arises from the competition of the efficient proton transfer to $NH_3$. This very reaction also prohibits an unambiguous experimental elucidation of the reactivity of $Pt_2NH^+$ toward $CH_4$. Owing to the unfavorable pumping characteristics of ammonia, $Pt_2NH^+$ cannot be generated by exposure of $Pt_2^+$ to a short $NH_3$ pulse but only by reaction with continuously leaked-in ammonia that inevitably also gives rise to the consecutive proton transfer. Suppressing this unwanted reaction by applying a high pressure of $CH_4$ is not feasible either, because this measure would mainly lead to the build-up of $Pt_2CH_2^+$ and consecutively formed $Pt_2C^+(NH_3)$ instead of generating $Pt_2NH^+$. For $Rh_2NH^+$ and $PtRhNH^+$, the situation is more favorable because of their much lower tendency to undergo secondary reactions with $NH_3$. The reactivities of these ions can be qualitatively probed by exposing the mass-selected imine species to a sequence of methane pulses that rapidly raise the $CH_4$ pressure. Despite the thus obtained high number of collisions between the metal imines and $CH_4$ no reaction products are observed which rules out appreciable reactivities of $Rh_2NH^+$ and $PtRhNH^+$ toward methane. Hence, starting with $NH_3$ activation does not achieve C–N coupling of methane and ammonia either.

## 4. Discussion

The present experiments reveal several parallels in the reactivities of $Rh_2^+$, $PtRh^+$, and $Pt_2^+$. To some extent, this alikeness might be expected, given the well-known general similarities in the chemical behavior of rhodium and platinum that are reflected in the term "platinum metals" coined for these two elements together with Ru, Os, Ir, and Pd [35]. However, it is common wisdom that the reactivities of small metal clusters can be strongly modulated by electronic and geometric effects [36]. Whereas the geometric situation most probably remains nearly constant in the progression $Rh_2^+$, $PtRh^+$, and $Pt_2^+$, the electronic structure certainly changes, the number of valence electrons alternating between odd and even. Apparently, the differences in electronic structure essentially do not affect the clusters' chemical reactivities.[1]

---

[1] A slight difference might be perceived in the reactions with ammonia. Here, the rate constants found for the clusters do not display a monotonous trend but pass through a minimum for the even-electron cluster $PtRh^+$ (Table 1).

In marked contrast, going from $Pt_2^+$ to $PtM^+$ or $M_2^+$, M = Cu, Ag, and Au, leads to qualitative changes in chemical behavior [25–27]. Thus, it seems that filling-up the d-electron shells of the clusters increases their sensitivity to further electronic changes. This trend agrees with expectation in that the coinage metals only have a limited number of free valences that are required for substrate binding and thereby crucially influence the reactivities of the clusters. A full understanding of these relations must remain reserved to a rigorous computational treatment, however.

Additional insight can be gained from comparing the metal dimers to clusters of other sizes. For rhodium and platinum, the dinuclear clusters display distinct reactivities in terms of bond activation. The dehydrogenation of both methane and ammonia achieved by the dimers is unparalleled for all other cluster sizes $Rh_n^+$ and $Pt_n^+$ investigated so far (with respect to mixed platinum-rhodium clusters, no further data is available for comparison). We have suggested that the elevated reactivities of the dinuclear species might result from two opposing trends [17]. On the one hand, an increase of the cluster size enhances intra-cluster binding and thus saturates open valences, thereby lowering the tendency towards substrate activation. On the other hand, the presence of more than a single metal atom opens the possibility of forming bridging bonds towards the substrate. Such multifold interactions should stabilize carbene or imine species and thus facilitate their formation. While in the case of late transition metals like rhodium and platinum, the optimum reactivity seems to be reached for $n = 2$, the situation may be different for earlier *d*-block elements whose valence-shells are populated by less electrons.

The question of $CH_4$ and $NH_3$ activation by rhodium and platinum attracts further interest against the background of the DEGUSSA process. Like in the case of homonuclear platinum clusters $Pt_n^+$, $n = 2–5$ [24], methane dehydrogenation by $Rh_2^+$ and $PtRh^+$ and reaction with ammonia exclusively leads to carbide complexes. This finding indicates that this reaction pathway is not just limited to platinum clusters but operative in general if the cluster contains at least two metal centers capable of forming strong bonds to carbon. These interactions with the metal core stabilize the carbon fragment sufficiently such that it is no longer available for C–N coupling with ammonia.

Finally, the present experiments do not provide any evidence for cooperative effects in the reactivity of $PtRh^+$ as they were found for the dinuclear platinum-coinage metal clusters $PtM^+$, M = Cu, Ag, and Au [25,26]. Likewise, there is no indication that $PtRh^+$ could mediate C–N bond formation by a novel reaction type via the initial formation of imine species. Hence, gas-phase experiments do not find a superior intrinsic reactivity of the heteronuclear $PtRh^+$ cluster ion compared to the “pure” clusters $Rh_2^+$ and $Pt_2^+$. Certainly, this result by no means rules out the possibility that rhodium additives enhance the performance of the heterogeneous DEGUSSA catalyst by modifying its surface structure, lattice geometry etc. Nevertheless, systematic investigations of the heterogeneous process demonstrate that platinum and rhodium almost behave identically, the reactivity of the latter being slightly stronger affected by the formation of carbon-atom monolayers in the presence of excess methane [19,20].

## 5. Conclusion

Gas-phase experiments reveal high intrinsic reactivities of the cluster ions $Rh_2^+$ and $PtRh^+$. Both species activate methane and ammonia in dehydrogenation reactions that are analogous to processes observed for $Pt_2^+$. This remarkable similarity implies that the reactivities of these clusters are not very sensitive to changes in their electronic structure. Interestingly, this behavior contrasts with the situation encountered for the dinuclear platinum-coinage metal clusters $PtM^+$ M = Cu, Ag, and Au, whose reactivities significantly differ from both those of $Pt_2^+$ and $M_2^+$. Presumably, once the metals’ d-shells are filled up to a certain level, the clusters can no longer provide enough free valence sites for easy substrate binding and activation. While the high reactivities of $Rh_2^+$ and $PtRh^+$ allow efficient methane activation, the resulting metal-carbene species do not undergo C–N coupling with ammonia. The strong interactions of both metal atoms in the dinuclear clusters are assumed to facilitate the first reaction step by raising its exothermicity, but the thus achieved stabilization of the intermediates lowers their tendencies towards consecutive bond formation with $NH_3$. Precisely the same behavior has been observed for $Pt_2CH_2^+$ and the homologous heavier clusters. Thus, the present gas-phase experiments do not suggest major differences between the performance of platinum and rhodium in the heterogeneous DEGUSSA process for HCN generation. Indeed, it was shown that both metals have quite similar catalytic activities under heterogeneous conditions [19,20].

With a larger amount of data emerging for the gas-phase reactivities of transition-metal cluster ions, the classification of new experimental results becomes more and more straightforward. Continued systematic efforts promise to achieve a full understanding of the truly fascinating properties of metal clusters and are expected to provide important stimuli to other areas within chemistry as well.

## Acknowledgements

Support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Degussa AG is gratefully acknowledged.

## References

[1] J.H. Lunsford, Catal. Today 63 (2000) 165.

[2] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 101 (2001) 953.

[3] R.H. Crabtree, J. Chem. Soc., Dalton Trans. (2001) 2437.

[4] J.A. Labinger, J.E. Bercaw, Nature 417 (2002) 507.

[5] M. Lin, A. Sen, Nature 368 (1994) 613.

[6] R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, Science 280 (1998) 560.

[7] R.A. Periana, O. Mironov, D. Taube, G. Bhalla, C.J. Jones, Science 301 (2003) 814.

[8] K. Eller, H. Schwarz, Chem. Rev. 91 (1991) 1121.

[9] K.K. Irikura, J.L. Beauchamp, J. Am. Chem. Soc. 113 (1991) 2769.

[10] K.K. Irikura, J.L. Beauchamp, J. Phys. Chem. 95 (1991) 8344.

[11] H. Schwarz, D. Schröder, Pure Appl. Chem. 72 (2000) 2319.

[12] Y.A. Ranasinghe, T.J. MacMahon, B.S. Freiser, J. Phys. Chem. 95 (1991) 7721.

[13] P.B. Armentrout, M.R. Sievers, J. Phys. Chem A 107 (2003) 4396.

[14] H. Schwarz, Angew. Chem. 115 (2003) 4580;
H. Schwarz, Angew. Chem. Int. Ed. 42 (2003) 4442.

[15] A. Kaldor, D.M. Cox, Pure Appl. Chem. 62 (1990) 79.

[16] U. Achatz, C. Berg, S. Joos, B.S. Fox, M.K. Beyer, G. Niedner-Schatteburg, V.E. Bondybey, Chem. Phys. Lett. 320 (2000) 53.

[17] K. Koszinowski, D. Schröder, H. Schwarz, J. Phys. Chem. A 107 (2003) 4999.

[18] G. Albert, C. Berg, M. Beyer, U. Achatz, S. Joos, G. Niedner-Schatteburg, V.E. Bondybey, Chem. Phys. Lett. 268 (1997) 235.

[19] D. Hasenberg, L.D. Schmidt, J. Catal. 91 (1985) 116.

[20] D. Hasenberg, L.D. Schmidt, J. Catal. 97 (1986) 156.

[21] A. Bockholt, I.S. Harding, R.M. Nix, J. Chem. Soc., Faraday Trans. 93 (1997) 3869.

[22] M. Aschi, M. Brönstrup, M. Diefenbach, J.N. Harvey, D. Schröder, H. Schwarz, Angew. Chem. 110 (1998) 858;
M. Aschi, M. Brönstrup, M. Diefenbach, J.N. Harvey, D. Schröder, H. Schwarz, Angew. Chem. Int. Ed. 37 (1998) 829.

[23] M. Diefenbach, M. Brönstrup, M. Aschi, D. Schröder, H. Schwarz, J. Am. Chem. Soc. 121 (1999) 10614.

[24] K. Koszinowski, D. Schröder, H. Schwarz, Organometallics 22 (2003) 3809.

[25] K. Koszinowski, D. Schröder, H. Schwarz, J. Am. Chem. Soc. 125 (2003) 3676.

[26] K. Koszinowski, D. Schröder, H. Schwarz, Angew. Chem. 116 (2004) 124;
K. Koszinowski, D. Schröder, H. Schwarz, Angew. Chem. Int. Ed. 43 (2004) 121.

[27] K. Koszinowski, D. Schröder, H. Schwarz, Organometallics 23 (2004) 1132.

[28] K. Eller, W. Zummack, H. Schwarz, J. Am. Chem. Soc. 112 (1990) 621.

[29] S. Maruyama, L.R. Anderson, R.E. Smalley, Rev. Sci. Instrum. 61 (1990) 3686.

[30] C. Berg, T. Schindler, M. Kantlehner, G. Niedner-Schatteburg, V.E. Bondybey, Chem. Phys. 262 (2000) 143.

[31] M. Engeser, T. Weiske, D. Schröder, H. Schwarz, J. Phys. Chem. A 107 (2003) 2855.

[32] R.A. Forbes, H.F. Laukien, J. Wronka, Int. J. Mass Spectrom. Ion Processes 83 (1998) 23.

[33] D. Schröder, H. Schwarz, D.E. Clemmer, Y.-M. Chen, P.B. Armentrout, V.I. Baranov, D.K. Böhme, Int. J. Mass Spectrom. Ion Processes 161 (1997) 175.

[34] T. Su, J. Chem. Phys. 88 (1988) 4102;
T. Su, J. Chem. Phys. 89 (1988) 5355.

[35] A.F. Holleman, E. Wiberg, Lehrbuch der Anorganischen Chemie, 101th ed., de Gruyter, Berlin, 1995.

[36] J.A. Alonso, Chem. Rev. 100 (2000) 637.