Platinum-Mediated Coupling of Methane and Small Nucleophiles (H_2O, PH_3, H_2S, CH_3NH_2) as a Model for C−N, C−O, C−P, and C−S Bond Formation in the Gas Phase[†]

Mark Brönstrup, Detlef Schröder, and Helmut Schwarz*

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

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The reactions of Pt^+ and $PtCH_2^+$ with the nucleophiles H_2O, PH_3, H_2S, HCl, CH_3NH_2, and CH_3OH are studied by Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometry. In the reactions of $PtCH_2^+$, carbon−heteroatom bond formation can be accomplished for all substrates except CH_3OH and HCl. The reaction of $PtCH_2^+$ with two molecules of water yields $Pt(CO)(H_2O)^+$ and constitutes a gas-phase model for the platinum-mediated generation of water gas according to $CH_4 + H_2O \rightarrow CO + 3H_2$. In the reactions with PH_3 and H_2S, carbon−phosphorus and carbon−sulfur bond formation to $PtCPH^+$ and $PtCS^+$ competes with demethanation and dehydrogenation of the substrates to yield PtS_n^+ ($n = 1-4$) and $PtP_nH_m^+$ ($n = 1-6$; $m = 0-3$) compounds, respectively. For organic nucleophiles such as CH_3NH_2 and CH_3OH, C−N and C−O coupling is much less efficient than platinum-mediated C−H bond activation of the substrates.

Introduction

In organometallic chemistry, numerous experimental and theoretical methods are applied to unravel principal reaction pathways and their mechanistic details. Among them, gas-phase experiments performed in advanced mass spectrometers have gained considerable attention during the last two decades.[1] This approach allows the study of the intrinsic chemical behavior of metals at a molecular level under rigorous exclusion of many complicating factors such as solvent and aggregation effects, counterions, ligands, or even enzyme backbones.

Recently, we have established a detailed reaction mechanism for the Pt^+ mediated coupling of methane and ammonia, which can be regarded as a gas-phase analogue of the DEGUSSA-process for the synthesis of HCN.[2,3] The sequence of elementary steps can be summarized as follows (reactions 1 and 2).

$$Pt^+ + CH_4 \longrightarrow PtCH_2^+ + H_2 \quad (100\%) \qquad (1)$$

$$PtCH_2^+ + NH_3 \longrightarrow \begin{cases} NH_4^+ + PtCH & (5\%) & (2a) \\ CH_2NH_2^+ + PtH & (70\%) & (2b) \\ [Pt,C,N,H_3]^+ + H_2 & (25\%) & (2c) \end{cases}$$

In the first step, methane is activated by “bare” Pt^+ to yield $PtCH_2^+$ and H_2.[4] Subsequently, a nucleophilic attack of ammonia at the platinum carbene cation gives three ionic products (2a−2c). Whereas eq 2a is a simple acid−base reaction, C−N bond formation is achieved in reactions 2b and 2c. From $CH_2NH_2^+$, the liberation of HCN is feasible after dehydrogenation and deprotonation. Various experiments[2,5] as well as detailed theoretical calculations[5] indicate that the ionic product of reaction 2c, i.e., $[Pt,C,N,H_3]^+$, has an aminocarbene structure $PtC(H)NH_2^+$.[6] A collision-induced dehydrogenation of $PtC(H)NH_2^+$ yields a platinum-isocyanide complex $PtCNH^+$, which can eventually dissociate into Pt^+ and HCN.

A key feature of the $Pt^+/CH_4/NH_3$ system is that the carbon atom in the cationic platinum carbene can be attacked by a nucleophile (Nu) under C−N bond formation. In the present study, we investigated whether this concept for C−Nu coupling is general and can be extended to both harder and softer nucleophiles, i.e.,

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[†] Dedicated to Prof. R. W. Hoffmann, Marburg, on the occasion of his 65th birthday.

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(5) Diefenbach, M.; Brönstrup, M.; Aschi, M.; Schröder, D.; Schwarz, H. Manuscript in preparation.

(6) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (c) Herrmann, W. A.; Köcher, C. *Angew. Chem.* **1997**, *109*, 2257; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

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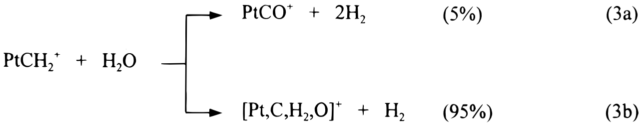
H_2O, PH_3, H_2S, and HCl, or to the carbon-substituted N and O nucleophiles CH_3NH_2 and CH_3OH, respectively.

Results and Discussion

The reactions of $PtCH_2^+$ with the element hydrides EH_n (E = O, P, S, Cl) are presented first,[7] followed by a discussion of the reactions with the carbon-substituted analogues CH_3NH_2 and CH_3OH. For comparison, the reactions of bare Pt^+ with these nucleophiles are also included in this study.

Water. The reaction of $PtCH_2^+$ with H_2O yields $PtCO^+$ and $[Pt,C,H_2,O]^+$ (reactions 3a and 3b) with a rate constant of $k = 0.04 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1}. The reaction efficiency ϕ, defined as the ratio between the measured rate constant k and the gas kinetic collision rate k_C,[8] is very low ($\phi = k/k_C = 0.002$).



$$PtCH_2^+ + H_2O \rightarrow PtCO^+ + 2H_2 \quad (5\%) \qquad (3a)$$
$$PtCH_2^+ + H_2O \rightarrow [Pt,C,H_2,O]^+ + H_2 \quad (95\%) \qquad (3b)$$

Although reaction 3b is the major channel, the stationary concentration of $[Pt,C,H_2,O]^+$ remains small due to a fast consecutive reaction with water to $[Pt,C,H_2,O_2]^+$ (reaction 4).

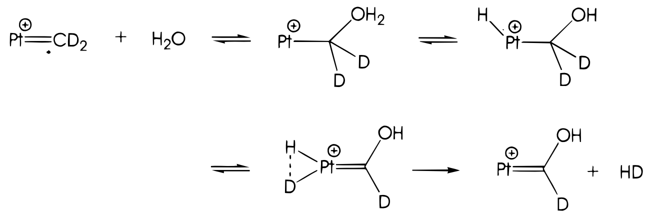
$$[Pt,C,H_2,O]^+ + H_2O \rightarrow [Pt,C,H_2,O_2]^+ + H_2$$
$$k = 2.0 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (4)$$

Two experiments were performed in order to elucidate the structural connectivity of the final product $[Pt,C,H_2,O_2]^+$: (i) Ligand-exchange of mass-selected $[Pt,C,H_2,O_2]^+$ with deuteriobenzene yields $Pt(CO)(C_6D_6)^+$ (100%) along with small amounts of $Pt(H_2O)(C_6D_6)^+$ (10%) and $Pt(C_6D_6)^+$ (7%); all three ionic products continue to react with deuteriobenzene to yield $Pt(C_6D_6)_2^+$. (ii) Collision-induced dissociation (CID) of $[Pt,C,H_2,O_2]^+$ leads to Pt^+ (100%), $PtCO^+$ (50%), and $Pt(H_2O)^+$ (25%). These findings strongly support a $Pt(CO)(H_2O)^+$ connectivity for the ionic product formed in reaction 4.

To probe if $[Pt,C,H_2,O_2]^+$ is formed via either $PtCO^+$ or $[Pt,C,H_2,O]^+$, the $[Pt,C,H_2,O_2]^+$ signal intensities are monitored during continuous double-resonance ejection[9] of both conceivable intermediates. Whereas removal of $PtCO^+$ induced a decrease of the $[Pt,C,H_2,O_2]^+$ intensity by about only 5%, its formation was almost completely suppressed upon double-resonance ejection of $[Pt,C,H_2,O]^+$. Thus, reaction 4 represents the by far dominant pathway to $[Pt,C,H_2,O_2]^+$, whereas the association reaction of $PtCO^+$ and H_2O is slow, as expected.

Further insight into the elementary steps is obtained by studying the reaction of $PtCD_2^+$ and H_2O, which reveals several interesting features: First, isotopic scrambling of the reagent to $PtCHD^+$ and $PtCH_2^+$ competes with product formation. The H/D equilibration is about 0.4 times as fast as the extremely slow first reaction step to produce $[Pt,C,H_2,O]^+$ ($\phi = 0.002$). Next, in the first reaction step, a specific loss of HD to yield $[Pt,C,H,D,O]^+$ is observed, whereas $[Pt,C,H_2,O]^+$ is not formed.[10] The final product of the $PtCD_2^+/H_2O$ system shows no label incorporation and has the elemental composition $[Pt,C,H_2,O_2]^+$.

Scheme 1



A key species being crucial for the understanding of the reaction mechanism probably is the intermediate $[Pt,C,H_2,O]^+$, for which several structures are conceivable, e.g., (i) a hydroxycarbene $PtC(H)OH^+$, (ii) a platinum−formaldehyde complex $Pt(CH_2{=}O)^+$, (iii) a bisligated platinum−oxo−carbene structure $O{=}Pt{=}CH_2^+$, (iv) a platinumcarbonyl-hydrogen complex H_2-$PtCO^+$, (v) a hydrido formyl complex $H{-}Pt{-}CHO^+$, or (vi) a hydroxy carbyne $HO{-}Pt{-}CH^+$. However, all structures having equivalent hydrogen atoms like ii−iv can readily be discarded, because otherwise the specific HD loss from the $PtCD_2^+/H_2O$ couple together with the complete loss of deuterium of the system $[Pt,C,H,D,O]^+/H_2O$ in reaction 4 cannot be accounted for. Structure v has two nonequivalent hydrogen atoms, but a regiospecific sequence leading to it is hardly conceivable. Finally, vi is assumed to be much higher in energy, as it formally involves a high-valent Pt(V) species that would have to support four covalent bonds, which is improbable on electronic grounds. Thus, the most straightforward sequence involves nucleophilic attack of H_2O at the carbon atom of $PtCD_2^+$, followed by regiospecific loss of HD to yield a hydroxycarbene $PtC(D)OH^+$. The reaction is completely analogous to that found for the $PtCH_2^+/NH_3$ system, and we assume a similar mechanism. Therefore, the sequence of elementary steps for H_2-elimination displayed in Scheme 1 is analogous to the lowest energy path found for reaction 2c, although we cannot exclude alternative variants at this stage. The low efficiency of reaction 3 indicates that the relative height of the exit channel or of the associated barriers is close to or slightly above that of the entrance channel. The indicated reversibility of the steps also provides a rationale for the H/D equilibration of the platinum carbene reactant (Scheme 2). Further, the fact that a fraction of $[Pt,C,H_2,O]^+$ possesses enough internal energy to undergo subsequent dehydrogenation to $PtCO^+$ indicates that the activation energy required for the second step is rather small. Following this line of reasoning, the complexation energy gained upon the addition of the second water molecule (reaction 4) is sufficient to dehydrogenate the hydroxycarbene yielding $(H_2O)Pt(CO)^+$ as the final product.

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[7] For a related study about reactions of FeO^+ with EH_n compounds, see: Brönstrup, M.; Schröder, D.; Schwarz, H. *Chem. Eur. J.* **1999**, *5*, 1176.

[8] (a) Su, T.; Chesnavich, W. *J. Chem. Phys.* **1982**, *76*, 5183. (b) Su, T. *J. Chem. Phys.* **1988**, *89*, 5355. (c) Su, T. *J. Chem. Phys.* **1994**, *100*, 4703.

[9] Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413.

[10] The reported regioselectivity of H/D losses was corrected for scrambling of $PtCD_2^+$ to $PtCHD^+$ and $PtCH_2^+$.

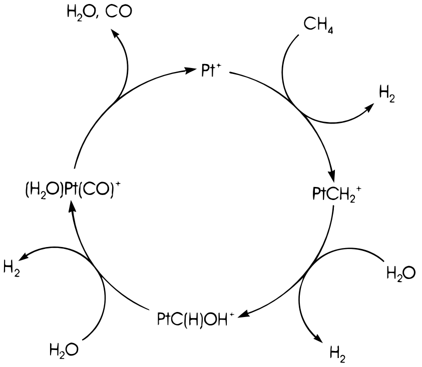
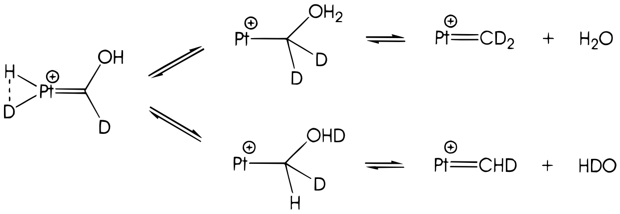


Figure 1. Gas-phase model for the Pt^+-mediated conversion of CH_4 and H_2O into CO and H_2.

Scheme 2



The overall sequence, i.e., reactions 1, 3b, and 4, represents a gas-phase model for the metal-catalyzed generation of water gas. The elementary steps of the Pt^+-mediated conversion of CH_4 and H_2O into CO and H_2 are depicted in Figure 1. As thermalized ions undergo only exothermic or almost thermoneutral reactions under the low-pressure conditions prevailing in an ICR spectrometer ($p \approx 10^{-6}-10^{-9}$ mbar), the overall reaction cannot be observed in our experiment on principle grounds, simply because it is endothermic by 49 kcal mol^{-1}.[11] Thus, the reaction stops after formation of $Pt(CO)(H_2O)^+$, and according to theoretical calculations, the final ligand detachment to Pt^+, CO, and H_2O has to be induced by an external energy input of about 102 kcal mol^{-1}.[4f] Interestingly, it is not the activation of methane but the addition of H_2O to $PtCH_2^+$ that constitutes the rate-determining step in the exothermic sequence to produce $Pt(CO)(H_2O)^+$. Except for the minor channel 3a that yields $PtCO^+$ directly, two water molecules are required for the generation of the main product $Pt(CO)(H_2O)^+$.

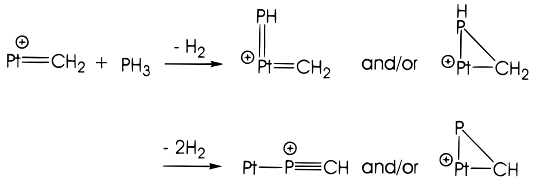
Phosphine. The reaction of $PtCH_2^+$ with PH_3, the third-row congener of ammonia, yields $PtPH^+$, $[Pt,C,H,P]^+$, and $[Pt,C,H_3,P]^+$ as the primary products (reactions 5a−5c) with an overall rate constant of $k = 6.9 \times 10^{-10}$ cm^3 $molecules^{-1}$ s^{-1}, corresponding to an efficiency of $\phi = 0.62$.

$$PtCH_2^+ + PH_3 \rightarrow PtPH^+ + CH_4 \quad (65\%) \quad (5a)$$

$$PtCH_2^+ + PH_3 \rightarrow [Pt,C,H,P]^+ + 2H_2 \quad (25\%) \quad (5b)$$

$$PtCH_2^+ + PH_3 \rightarrow [Pt,C,H_3,P]^+ + H_2 \quad (10\%) \quad (5c)$$

Scheme 3



Compared to NH_3 (reactions 2a−2c), the differences in product distributions can be ascribed to two major factors: (i) Due to less favorable π-bonding and the lower basicity of phosphorus, the formations of PH_4^+ and $CH_2PH_2^+$ are not observed. (ii) As the cleavage of P−H bonds requires much less energy than the cleavage of N−H bonds (83.9 ± 0.5 kcal mol^{-1} vs 108.2 ± 0.3 kcal mol^{-1}),[11b] dehydrogenation processes are much more facile. For example, PH_3 can also be dehydrogenated by bare Pt^+ cations (see below), while this process is endothermic for NH_3. The occurrence of reaction 5a implies that $D(Pt^+-PH)$ is larger than 59 ± 5 kcal mol^{-1}.

In the reaction of PH_3 with $PtCD_2^+$ a mixture of $[Pt,C,D,P]^+$ and $[Pt,C,H,P]^+$ in a 82:18 ratio is observed in channel 5b, and only $[Pt,C,H,D_2,P]^+$ is formed in 5c.[10] The competing H/D equilibration of $PtCD_2^+$ to $PtCHD^+$ and then $PtCH_2^+$ is about 0.15 times as fast as reactions 5a−5c. In contrast to the regiospecific losses of two HD molecules from the $PtCD_2^+/NH_3$ couple, reaction 5c presumably involves a dehydrogenation of phosphine at platinum without participation of the carbene moiety. Nevertheless, a connectivity with a carbon−phosphorus bond is also conceivable (Scheme 3). The fact that $[Pt,C,H,D_2,P]^+$ loses HD and D_2 indicates that hydrogen shifts precede the second dehydrogenation to $[Pt,C,X,P]^+$ (X = H, D). As far as the atom connectivity in $[Pt,C,H,P]^+$ is concerned, the labeling distribution and the assumed structure of the precursor $[Pt,C,H_3,P]^+$ point to a three-membered metallacycle or a Pt^+-PCH complex (Scheme 3) rather than to the carbene structure $Pt{=}C{=}PH^+$. A high-valent bisligated $P-Pt-CH^+$ complex without a C−P bond is presumably much higher in energy, as Pt^+ can support only three covalent bonds without involving a participation of p orbitals. The occurrence of reaction 5b and supplementary thermochemical data predict that the binding energy of the [C,H,P] unit to Pt^+ exceeds 61 ± 16 kcal mol^{-1}.[11a] The primary product $[Pt,C,H,P]^+$ reacts with a further equivalent of PH_3 to produce $[Pt,C,H_2,P_2]^+$. Compared to the Pt^+-mediated methane−ammonia coupling, carbon−heteroatom bond formation is achieved by a completely different mechanistic sequence.

Interestingly, the main product $PtPH^+$ reacts consecutively with excess PH_3 to yield PtP_2^+, then PtP_3H^+, etc. (see below).[12] Although the same products are formed when bare Pt^+ is reacted with PH_3, the intermediate formation of Pt^+ in the $PtCH_2^+/PH_3$ reaction can be excluded from analysis of the kinetic data; further, thermodynamical data predict the formation of Pt^+ and CH_3PH_2 from $PtCH_2^+$ and PH_3 to be endothermic by 16 ± 4 kcal mol^{-1}.

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[11] Thermochemical data are taken from ref 2 and from: (a) Lias, S. G.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 695. (b) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744. (c) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

[12] For further FT-ICR studies involving transition metal−phosphorous compounds, see: (a) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 4228. (b) Bjarnason, A.; Arnason, I. *Inorg. Chem.* **1996**, *35*, 3455. (c) Fisher, K.; Henderson, W.; Dance, I.; Willett, G. *J. Chem. Soc., Dalton Trans.* **1996**, 4109. (d) Fisher, K.; Dance, I.; Willett, G. *Polyhedron* **1997**, *16*, 2731. (e) Fisher, K. Dance, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2381.

The generation of platinum polyphosphides $PtP_nH_m^+$ has been investigated in more detail using bare Pt^+ and PH_3 as precursors. The alternating addition of PH and P_2 fragments to Pt^+ nicely demonstrates the preference for generating closed-shell products (reactions 6a–6f) and yields platinum phosphides up to PtP_6^+.[13,14]

$$Pt^+ + PH_3 \rightarrow PtPH^+ + H_2 \qquad k = 6.0 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (6a)$$

$$PtPH^+ + PH_3 \rightarrow PtP_2^+ + 2H_2 \qquad k = 7.5 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (6b)$$

$$PtP_2^+ + PH_3 \rightarrow PtP_3H^+ + H_2 \qquad k = 3.3 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (6c)$$

$$PtP_3H^+ + PH_3 \rightarrow PtP_4^+ + 2H_2 \qquad k = 5.5 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (6d)$$

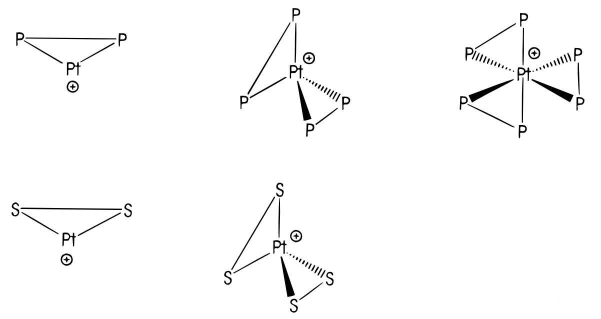
$$PtP_4^+ + PH_3 \rightarrow PtP_5H^+ + H_2 \qquad k = 1.2 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (6e)$$

$$PtP_5H^+ + PH_3 \rightarrow PtP_6^+ + 2H_2 \qquad k = 4.0 \times 10^{-10}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}} \quad (6f)$$

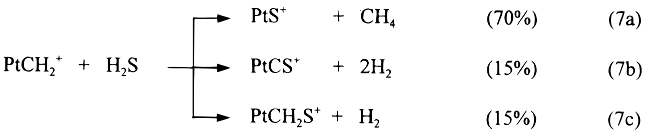
The relative rates of the consecutive reactions reveal that the hydrogen-containing species $PtPH^+$, PtP_3H^+, and PtP_5H^+ react more readily with excess PH_3 than their precursors Pt^+, PtP_2^+, and PtP_4^+; the difference becomes more pronounced with increasing size of the system. The comparison of rates among hydrogen-containing and hydrogen-free phosphides shows that the reaction rates decrease with increasing system size, i.e., $k(6a) > k(6c) > k(6e)$ and $k(6b) > k(6d) > k(6f)$. In the consecutive reactions of PtP_2^+ and higher species, simple adduct formation competes with dehydrogenation; for example, next to PtP_3H^+ also $PtP_3H_3^+$ is observed. In the reactions of PtP_3H^+ and PtP_4^+ with PH_3, about 15% of $PtP_4H_2^+$ and $PtP_5H_3^+$, respectively, are formed in addition to complete dehydrogenation.

Interestingly, no species higher than PtP_6^+ could be detected, indicating a saturation after addition of six phosphorus atoms. This saturation effect is inconsistent with a propagating phosphorus chain that is only partially bound to platinum, but clearly points to a structure with a central platinum atom. However, the fact that addition of PH_3 to $PtPH^+$ yields primarily PtP_2^+ and only minor amounts of $PtP_2H_2^+$ is indicative for P–P bond formation. Therefore, we propose the presence of P_2 units in PtP_2^+, PtP_4^+, and PtP_6^+ (Scheme 4). This hypothesis is supported by CID and the reactions with benzene (Table 1). In all CID experiments losses of P_2 units are much more favored compared to losses of odd-membered P_n (n = 1, 3, 5). The CID spectrum of PtP_6^+ has two additional features, i.e., a much more facile overall dissociation compared to PtP_4^+ and PtP_2^+ at similar collision energies, and a dominant loss of P_4 instead of P_2. Further, the reactions of PtP_2^+ and PtP_4^+ with benzene yield the corresponding adducts $PtP_2(C_6H_6)^+$ and $PtP_4(C_6H_6)^+$, respectively. In contrast, association is negligible for PtP_6^+, and ligand-exchange reactions occur in which P_2, P_3, and especially P_4 are replaced by benzene. The absence of an association product for the PtP_6^+/C_6H_6 couple as well as the kinetics of the Pt^+/PH_3 reaction is indicative for a coordinative saturation of PtP_6^+, whereas PtP_2^+ and PtP_4^+ still have vacant coordination sites. Moreover, the almost exclusive association processes observed for PtP_2^+ and PtP_4^+ as well as the overall CID efficiencies suggest that the binding energy of P_n units to platinum increases in the order $PtP_6^+ < PtP_4^+ < PtP_2^+$. A structural assignment on the basis of CID experiments is difficult to derive, however, because rearrangements might precede dissociation. For example, the prevalent loss of P_4 in the PtP_6^+ units is probably thermochemically driven, and we do not assume the presence of an intact P_4 tetrahedron in PtP_6^+, as this is not in line with the saturation effect. Finally, the preferential loss of P_2 and not of atomic P indicates that $D(Pt^+{-}P) < D(P{-}P) = 116.9 \pm 0.6$ kcal mol^{-1}.

Scheme 4



Hydrogen Sulfide. The reaction of $PtCH_2^+$ with H_2S yields PtS^+, $PtCS^+$, and $[Pt,C,H_2,S]^+$ as primary products (reactions 7a – 7c) with an overall rate constant of $k = 3.9 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} corresponding to $\phi = 0.32$.



$$PtCH_2^+ + H_2S \rightarrow PtS^+ + CH_4 \quad (70\%) \quad (7a)$$

$$PtCH_2^+ + H_2S \rightarrow PtCS^+ + 2H_2 \quad (15\%) \quad (7b)$$

$$PtCH_2^+ + H_2S \rightarrow PtCH_2S^+ + H_2 \quad (15\%) \quad (7c)$$

Reaction 7c yields $[Pt,C,H_2,S]^+$, which also serves as a precursor for $PtCS^+$. Both species react consecutively with H_2S to afford $[Pt,C,H_2,S_2]^+$ and subsequently $[Pt,C,S_3]^+$. Experiments with labeled $PtCD_2^+$ show an H/D scrambling to $PtCHD^+$ and $PtCH_2^+$, which is about 0.2 times as fast as product formation. Further, the first dehydrogenation is not regiospecific, as a mixture of $[Pt,C,H_2,S]^+$, $[Pt,C,D,H,S]^+$, and $[Pt,C,D_2,S]^+$ is formed in a 9:58:33 ratio.[10] Preferential losses of H_2 and HD from the $PtCD_2^+/H_2S$ couple could imply either favorable dehydrogenation of the substrate at platinum or the operation of sizable kinetic isotope effects. For the time being, we cannot resolve this dichotomy. Thus, several structural isomers are conceivable for $[Pt,C,H_2,S]^+$, whereas the product of reaction 7b quite certainly is the platinum–thiocarbonyl complex $PtCS^+$, thus indicating carbon–sulfur bond formation.[15]

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(13) Corbridge, D. E. L. *Studies in Inorganic Chemistry, Vol. 20: Phosphorous*, 5th ed.; Elsevier: Amsterdam, 1995; p 82.

(14) For organometallic platinum–phosphido complexes in solution, see: Wicht, D. K.; Paisner, S. N.; Lew, B. M.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Haar, C. M.; Nolan, S. P. *Organometallics* **1998**, *17*, 652, and references therein.

Table 1. Collision-Induced Dissociation (CID) and Ligand-Exchange Experiments with Platinum Sulfide and Platinum Phosphide Cations[a]

	neutral fragments lost upon CID						neutral fragments lost and added upon ligand exchange with C_6H_6			
species	$-P$	$-P_2$	$-P_3$	$-P_4$	$-P_5$	$-P_6$	$+C_6H_6$	$+C_6H_6 - P_4$	$+C_6H_6 - P_3$	$+C_6H_6 - P_2$
PtP_2^+	10	100					100			
PtP_4^+	4	100	4	16			100			5
PtP_6^+	8	40	8	100	4	10		100	20	20
	$-S$	$-S_2$	$-S_3$	$-S_4$			$+C_6H_6$	$+C_6H_6 - S_2$	$+C_6H_6 - S_4$	electron transfer
PtS_2^+	20	100					100			50
PtS_4^+	8	100	16	53				100		

[a] The most intensive fragment is normalized to $I = 100$.

The main product PtS^+ reacts consecutively with excess H_2S to yield PtS_2^+. From the occurrence of reaction 7a, a lower limit of $D(Pt^+{-}S) > 71$ kcal mol^{-1} can be derived. As the reaction of naked Pt^+ ions with H_2S also yields PtS^+ (see below), we have to consider the possibility that the product PtS^+ in the $PtCH_2^+ + H_2S$ reaction is formed via Pt^+ as an intermediate. However, this route was ruled out by double-resonance experiments, as continuous ejection of Pt^+ during the reaction was found to have no effect on the observed product distribution. The generation of Pt^+ and CH_3SH from $PtCH_2^+$ and H_2S is also predicted to be endothermic by 20 ± 4 kcal mol^{-1} and should therefore not be feasible under the experimental conditions.

The Pt^+/H_2S couple was explored in order to gain further insight into cationic platinum sulfides. In a large excess of H_2S, up to four sulfur atoms are transferred sequentially to platinum (reactions 8a−8d).[16]

$$Pt^+ + H_2S \rightarrow PtS^+ + H_2$$
$$k = 2.1 \times 10^{-10}\ \text{cm}^3\ \text{molecules}^{-1}\ \text{s}^{-1} \quad (8a)$$

$$PtS^+ + H_2S \rightarrow PtS_2^+ + H_2$$
$$k = 4.1 \times 10^{-10}\ \text{cm}^3\ \text{molecules}^{-1}\ \text{s}^{-1} \quad (8b)$$

$$PtS_2^+ + H_2S \rightarrow PtS_3^+ + H_2$$
$$k = 0.10 \times 10^{-10}\ \text{cm}^3\ \text{molecules}^{-1}\ \text{s}^{-1} \quad (8c)$$

$$PtS_3^+ + H_2S \rightarrow PtS_4^+ + H_2$$
$$k = 0.69 \bullet 10^{-10}\ \text{cm}^3\ \text{molecules}^{-1}\ \text{s}^{-1} \quad (8d)$$

The relative rate constants of 8a−8d exhibit two features: (i) PtS^+ and PtS_2^+ react much faster with H_2S than PtS_3^+ and PtS_4^+. (ii) Compounds with an odd number of ligands react faster than those with an even number, i.e., $k(8b) > k(8a)$ and $k(8d) > k(8c)$. This order of rate constants is not in line with previously observed trends for transition-metal sulfides[18,19] and can be rationalized in terms of a high stability of ligands with S_2 units. Thus, the addition of a sulfur atom to PtS^+ and PtS_3^+ coincides with the favorable formation of PtS_2^+ and PtS_4^+ and is therefore rapid. Following this line of reasoning, the slow addition of sulfur to the stable molecules PtS_2^+ and to PtS_4^+ indicates a low relative stability of the products PtS_3^+ and PtS_5^+. Alternatively, it is conceivable that the addition of sulfur to PtS_2^+ and PtS_4^+ requires rearrangement processes which might be associated with significant activation barriers.

This is also reflected by the CID behavior as well as by the reactions with benzene (Table 1). Both PtS_2^+ and PtS_4^+ preferentially lose S_2 and S_4 rather than S and S_3 upon CID.[20] PtS_2^+ is coordinatively unsaturated and undergoes adduct formation with benzene as well as electron transfer (ET); a ligand exchange does not occur. For PtS_4^+, however, adduct formation is not observed; rather an S_2 unit is replaced by benzene. To a first approximation, this finding implies that $D(Pt^+{-}S_2)$ is higher than $D(S_2Pt^+{-}S_2)$. Both platinum sulfides exhibit a lower reactivity toward benzene than bare Pt^+, which promotes facile dehydrogenation to give $Pt(C_6H_4)^+$. The relative rates of PtS_n^+ formation, the CID and ligand-exchange experiments are in line with the presence of S−S bonds, and we therefore assume structures analogous to the platinum phosphides as proposed above (Scheme 4).

Dehydrogenation of H_2S stops after formation of PtS_4^+.[21,22] This cannot be ascribed to a steric congestion, as the Pt^+/PH_3 reaction has shown that hexacoordinate platinum compounds such as PtP_6^+ are viable in the gas phase.[23] In this context, let us briefly mention preliminary data on the limits for the formation of the related PtO_n^+ and $PtSi_nH_m^+$ compounds. Thus, the oxidation of Pt^+ by N_2O yields no higher species than PtO_2^+, while two molecules of SiH_4 can be rapidly dehydrogenated by Pt^+ to yield $PtSi_2^+$ (80%) and $PtSi_2H_2^+$ (20%). In slower consecutive reactions of both species with excessive silane, $PtSi_nH_m^+$ compounds with n as large as 13 can be obtained; the precise termination of the sequence is difficult to determine.[24−28] Thus, the maximum number of ligands $n_{\max}$ at Pt^+ is 2 for oxygen, 4 for sulfur, 6 for phosphorus, and at least 13 for silicon. We propose that $n_{\max}$ correlates with the electronegativity

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[15] For ligated platinum−thiocarbonyl complexes in solution, see: (a) Werner, H. *Angew. Chem.* **1990**, *102*, 1109; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (b) Ebner, M.; Werner, H. *Chem. Ber.* **1988**, *121*, 1449. (c) Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.

[16] An earlier study of reaction 8 (ref 17), reporting only adduct formation, is incorrect due to a misinterpretation of data. Private communication of the authors.

[17] El-Nakat, J. H.; Dance, I. G.; Fisher, K. J.; Willett, G. D. *Polyhedron* **1993**, *12*, 2477.

[18] For example, the formation of FeS_n^+ compounds from Fe^+ and COS shows a reversed order, i.e., $k(Fe^+ \rightarrow FeS^+) \gg k(FeS^+ \rightarrow FeS_2^+)$ and $k(FeS_2^+ \rightarrow FeS_3^+) \gg k(FeS_3^+ \rightarrow FeS_4^+)$. Kretzschmar, I.; Schröder, D.; Schwarz, H. Unpublished results.

[19] Carlin, T. J.; Wise, M. B.; Freiser, B. S. *Inorg. Chem.* **1981**, *20*, 2743.

[20] For the CID behavior of FeS_n^+ ($n = 1{-}6$), see: MacMahon, T. J.; Jackson, T. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 421.

[21] Note that the reaction of Pt^+ with S_8 yields higher platinum sulfides PtS_n with $n = 3{-}10$ (ref 22). This difference is ascribed to the mode of generation, which probably involves transfer of S_n chains instead of S atoms. The reaction of Pt^+ and COS stops after PtS_4^+ formation, in complete analogy to the Pt^+/H_2S couple.

[22] Dance, I. G.; Fisher, K. J.; Willett, G. D. *Inorg. Chem.* **1996**, *35*, 4177.

[23] In the condensed phase, hexacoordinate platinum compounds with polysulfide ligands such as $(NH_4)_2Pt(S_5)_3{\cdot}2H_2O$ have been observed: Draganjac, M.; Rauchfuss, T. B. *Angew. Chem.* **1985**, *8897*, 745; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

of the elements and their ability to form element−element bonds. The high electron-withdrawing capability of two oxygen atoms lowers the electron density at platinum, rendering a further oxidation beyond PtO_2^+ unfavorable. For $PtSi_2^+$, the electron density at the metal is higher.[29] Moreover, the addition of SiH_m fragments does not require an increase of the oxidation state at platinum due to the possibility of forming extended Si−Si bonds. However, this explanation is based on few experimental data and should therefore be regarded as an approximate guideline. For a better description, high-level electronic structure calculations of the geometries and energetics of ligated Pt^+ compounds are desirable, but these are beyond the scope of the present study.

Hydrogen Chloride. Neither atomic Pt^+ nor $PtCH_2^+$ shows any reaction with gaseous HCl ($\phi < 0.001$). From the absence of a reaction with Pt^+, upper limits for $D(Pt^+{-}H)$[30] and $D(Pt^+{-}Cl)$ of 103 kcal mol^{-1} can be derived. Thermochemical reasons might also be responsible for the fact that $PtCH_2^+$ is completely unreactive toward HCl. A nucleophilic addition/H_2-elimination mechanism analogous to reaction 2c yielding a chlorocarbene (reaction 9) is only feasible if the resonance stabilization of the carbene unit by the heteroatom is high enough to render the overall reaction exothermic. For example, according to theoretical calculations the reaction of CH_2 with NH_3 to give the aminocarbene $C(H)NH_2$ and H_2 is exothermic by about 14 kcal mol^{-1}.[11,31] In contrast, the analogous reaction of CH_2 and HCl to C(H)Cl and H_2 is only thermoneutral due to the much lower donor capability of chlorine compared to an amino group. This difference is expected to increase if an electron-deficient fragment like a cation has to be stabilized by the carbene. Therefore, we assume that the formation of $PtC(H)Cl^+$ is hampered on thermochemical grounds. All other conceivable reactions of $PtCH_2^+$ and HCl involve radical products that are expected to be more energy-demanding.

$$PtCH_2^+ + HCl \nrightarrow PtC(H)Cl^+ + H_2 \qquad (9)$$

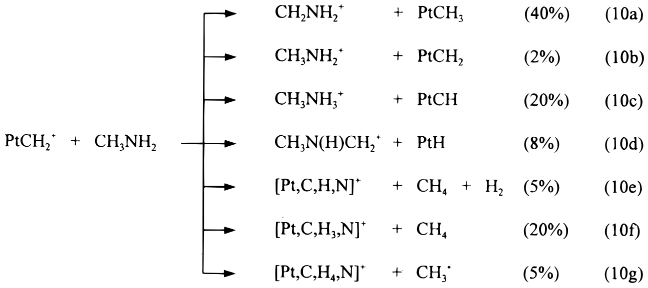
Methylamine. A straightforward modification of the $Pt^+/CH_4/NH_3$ system consists of the substitution of one hydrogen atom at ammonia by a methyl group. However, this seemingly simple structural change induces a much more complex product distribution in the $PtCH_2^+$ reactions compared to NH_3. The reaction efficiency ϕ is high ($k/k_C = 0.4$), and as much as seven primary products are obtained, i.e., $CH_2NH_2^+$, $CH_3NH_2^+$, $CH_3NH_3^+$, $CH_3N(H)CH_2^+$, $[Pt,C,H,N]^+$, $[Pt,C,H_3,N]^+$, and $[Pt,C,H_4,N]^+$ (reactions 10a−10g).

Table 2. Distribution of Deuterium Labels for the Reaction of Platinum Carbene Cations with Methylamine and Methanol[a]

	$PtCH_2^+/CH_3NH_2$	$PtCD_2^+/CH_3NH_2$	$PtCH_2^+/CD_3NH_2$
$[C,H_4,N]^+$	100	>90	<5
$[C,D_2,H_2,N]^+$		<10	>95
$[C,H_6,N]^+$	100	>60	
$[C,D,H_5,N]^+$		<40	
$[C,D_3,H_3,N]^+$			100
$[C_2,H_6,N]^+$	100		
$[C_2,D_2,H_4,N]^+$		100	
$[C_2,D_3,H_3,N]^+$			100
$[Pt,C,H_3,N]^+$	77	80	5
$[Pt,C,D,H_2,N]^+$, $[Pt,C,H_4,N]^+$	23	12	80
$[Pt,C,D_2,H,N]^+$, $[Pt,C,H_3,D,N]^+$		8	15

	$PtCH_2^+/CH_3OH$	$PtCD_2^+/CH_3OH$	$PtCH_2^+/CD_3OH$
$[C,H_3,O]^+$	100	100	
$[C,H,D_2,O]^+$			100
$[C,H_5,O]^+$ [b]	100	100	
$[C,H_2,D_3,O]^+$ [b]			75
$[C,H,D_4,O]^+$ [b]			25
$[Pt,C,H_2,O]^+$	95	>95	6
$[Pt,C,H,D,O]^+$	3	<5	86
$[Pt,C,D_2,O]^+$	2		8

[a] For each product channel, the intensities are normalized to 100%. [b] Protonated methanol is a secondary product; see text.



The major primary process corresponds to the formation of the imminium ion $CH_2NH_2^+$ (10a). When the reaction is carried out with $PtCH_2^+$ and CD_3NH_2, traces of $CH_2NH_2^+$ (<5%) are detected next to the main product $CD_2NH_2^+$ (>95%) (Table 2). Thus, the dominant reaction is a hydride transfer from methylamine to the platinum carbene cation, which is suggested to proceed via coordination of the amino group at platinum (Scheme 5, reaction 10a). In a side pathway the methylene unit at platinum is coupled to the amino group of the substrate. This minor channel can be rationalized by assuming a four-membered intermediate, which undergoes a metathesis-like reaction to yield both $CD_2NH_2^+$ and $CH_2NH_2^+$.

Electron transfer from CH_3NH_2 to $PtCH_2^+$ is observed as a minor process (10b). The discrepancy between the ionization energy of platinum carbene of 8.1 eV derived from theoretical calculations using the PCI-80 method[4e,32] and that of methylamine (8.97 ± 0.02 eV) either is due to an underestimation of the theoretical value or arises from a small fraction of nonthermalized ions in the experiment.

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[24] The metal-mediated sequential dehydrogenation of silane is not restricted to Pt^+, but can also be induced by Sc^+ (ref 25), Y^+ (ref 26), W^+ (ref 27), and Os^+ (ref 28).

[25] Azzaro, M.; Breton, S.; Decouzon, M.; Geribaldi, S. *Rapid Commun. Mass Spectrom.* **1992**, *6*, 306.

[26] Decouzon, M.; Gal, J.-F.; Geribaldi, S.; Rouillard, M.; Sturla, J.-M. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 298.

[27] (a) Ferhati, A.; McMahon, T. B.; Ohanessian, G. *Bull. Soc. Chim. Fr.* **1993**, *130*, 3. (b) Ferhati, A.; McMahon, T. B.; Ohanessian, G. *J. Am. Chem. Soc.* **1996**, *118*, 5997.

[28] Irikura, K. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 75.

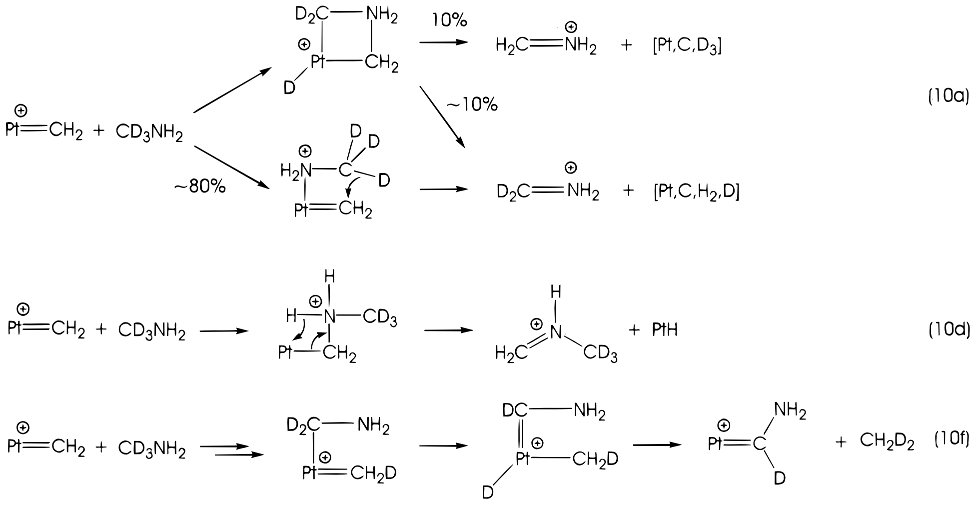
[29] The dependence of partial charges at the metal on the nature and the number of ligands is discussed in: Kretzschmar, I.; Fiedler, A.; Harvey, J. N.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1997**, *101*, 6252.

[30] A theoretical value of $D(Pt^+{-}H) = 62.9$ kcal mol^{-1} was reported in: Ohanessian, G.; Goddard, W. A., III. *Acc. Chem. Res.* **1990**, *23*, 386.

[31] Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11.

[32] Carroll, J. J.; Weisshaar, J. C.; Siegbahn, P. E. M.; Wittborn, C. A. M.; Blomberg, M. R. A. *J. Phys. Chem.* **1995**, *99*, 14388.

Scheme 5



An acid−base reaction with methylamine yields $CH_3NH_3^+$ and neutral PtCH (10c). As the proton affinity of CH_2NH (PA = 203.8 kcal mol^{-1}) is lower than that of the background gas, methylamine (PA = 214.8 kcal mol^{-1}), the overall fraction of $CH_3NH_3^+$ rises rapidly at higher reaction times due to proton transfer from $CH_2NH_2^+$ and other ionic products, which are formed with excess internal energy. However, continuous double-resonance ejection of $CH_2NH_2^+$ ensured that $CH_3NH_3^+$ is also formed as a primary product. Accordingly, $CH_3NH_2D^+$ is formed when the reaction is carried out with $PtCD_2^+$. With respect to C−N bond formation, the acid−base reaction represents an undesired pathway. Therefore, we have not attempted to extend the series of nucleophiles to substrates with even higher PAs, e.g., secondary or tertiary amines. Reactions 10a and 10c nicely demonstrate the amphoteric character of $PtCH_2^+$, i.e., its ability to act as a proton donor and as a hydride acceptor.

For $PtCH_2^+/CD_3NH_2$ or $PtCD_2^+/CH_3NH_2$, reaction 10d proceeds without any isotopic scrambling and definitely demonstrates that a coupling of the platinum-bound methylene unit and methylamine is feasible. The mechanistic sequence depicted in Scheme 5 (reaction 10d) involves nucleophilic attack of the nitrogen atom at the cationic platinum carbene and a subsequent β-hydride transfer to yield neutral platinum hydride and N-protonated *N*-methylformimine. From a combination of thermochemical data and theoretical calculations,[5] an exothermicity of about 34 kcal mol^{-1} is predicted.

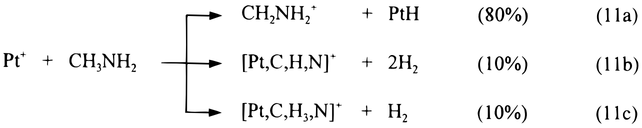
Next to the metal-free ionic products, three platinum-containing species are formed in reactions 10e−10g. For the main product, $[Pt,C,H_3,N]^+$, labeling experiments indicate that the C−N bond in methylamine remains intact during the course of the reaction, as the $PtCD_2^+/CH_3NH_2$ couple yields mainly $[Pt,C,H_3,N]^+$, whereas $[Pt,C,H_2,D,N]^+$ is the major product for $PtCH_2^+/CD_3NH_2$. A precise determination of selectivities is, however, not feasible due to a mass overlap with $[Pt,C,H_4,N]^+$. The dominant pathway can be explained by an initial C−H bond activation of methylamine by platinum followed by hydrogen shifts to the carbene group and eventual expulsion of methane as the neutral product; one possible course of steps for reaction 10f is shown in Scheme 5. A fraction of $[Pt,C,H_3,N]^+$ molecules possesses enough internal energy to dissociate unimolecularly to $[Pt,C,H,N]^+$ and molecular hydrogen (10e). The fact that in experiments with the labeled components $PtCD_2^+$ and CD_3NH_2 no deuterium is incorporated in $[Pt,C,H,N]^+$ is indicative for a platinum−isonitrile complex.

Finally, let us compare the product distribution of the $PtCH_2^+/CH_3NH_2$ reaction with that obtained for two closely related systems, i.e., $PtCH_2^+/NH_3$ (reaction 2) and Pt^+/CH_3NH_2. Whereas analogues of reactions 10a and 10g do not exist for the $PtCH_2^+/NH_3$ reaction, most other channels can be related to reaction 2. For the $PtCH_2^+/CH_3NH_2$ couple, the dominant product at higher reaction times is the protonated substrate $CH_3NH_3^+$ arising from the primary reaction 10c as well as from secondary processes. In contrast, acid−base reactions to yield NH_4^+ are negligible in the $PtCH_2^+/NH_3$ system. This difference is ascribed to the increased proton affinity (PA) of methylamine compared to ammonia (PA(CH_3NH_2) = 214.8 kcal mol^{-1} vs PA(NH_3) = 204.0 kcal mol^{-1}), which according to theoretical calculations[5] renders reaction 10c exothermic by about 11 kcal mol^{-1}, whereas reaction 2a is thermoneutral and therefore slow.

In the $PtCH_2^+/CH_3NH_2$ reaction, $CH_3N(H)CH_2^+$ is formed via hydride transfer (10d), which is completely analogous to the hydride transfer to give $CH_2NH_2^+$ in the Pt^+-mediated coupling of methane and ammonia (2b).

On the basis of the labeling experiments, we propose that the $[Pt,C,H_3,N]^+$ ion produced in reaction 10f is identical to the aminocarbene $PtC(H)NH_2^+$ formed in reaction 2c. In the $Pt^+/CH_4/NH_3$ system, a spontaneous dehydrogenation of $[Pt,C,H_3,N]^+$ to $[Pt,C,H,N]^+$ is prevented by a kinetic barrier that is 11 kcal mol^{-1} higher than the entrance channel, but can be brought about by CID.[5] In contrast, $[Pt,C,H_3,N]^+$ generated by reaction 10f possesses an internal energy of about 12 kcal mol^{-1} *above* the barrier for dehydrogenation according to theoretical calculations,[5] and the total reaction is predicted to be exothermic by about 32 kcal mol^{-1}. Thus, the more favorable energetic situation in reaction 10f compared to 2c enables a further dehydrogenation of $[Pt,C,H_3,N]^+$ to $[Pt,C,H,N]^+$ (10e). Both the occurrence of reaction 10e and the labeling experiments are in full agreement with the barrier height for a dehydrogenation pathway from the aminocarbene to a Pt−CNH$^+$ complex established by theoretical calculations.[5]

The reaction of bare Pt$^+$ with methylamine has been reported before[2] and is briefly summarized here for the sake of comparison: $CH_2NH_2^+$, $[Pt,C,H_3,N]^+$, and $[Pt,C,H,N]^+$ are formed as ionic products (reactions 11a−11c).

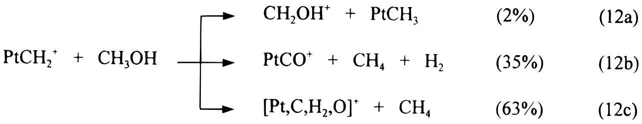


$$\mathrm{Pt^+ + CH_3NH_2} \longrightarrow \begin{cases} \mathrm{CH_2NH_2^+ + PtH} & (80\%) & \text{(11a)}\\ \mathrm{[Pt,C,H,N]^+ + 2H_2} & (10\%) & \text{(11b)}\\ \mathrm{[Pt,C,H_3,N]^+ + H_2} & (10\%) & \text{(11c)} \end{cases}$$

In perfect analogy with the regioselectivity observed for the $PtCH_2^+/CH_3NH_2$ and $PtCH_2^+/NH_3$ systems, only PtD, D_2, and D_2 + HD are lost as neutral fragments when CD_3NH_2 is used. Thus, the labeling experiments indicate that the ionic product $[Pt,C,H_3,N]^+$ generated in reactions 2c, 10f, and 11c probably has an identical structure in all three reactions. Apparently, the fact that the entrance energy of the reactants is somewhat higher for the Pt^+/CH_3NH_2 couple ($\sum\Delta H°_f = 328$ kcal mol^{-1}) than for $PtCH_2^+/NH_3$ ($\sum\Delta H°_f = 303$ kcal mol^{-1}) is sufficient to surmount the barriers associated with double dehydrogenation to afford $[Pt,C,N,H]^+$. Further, formation of $[Pt,C,N,H]^+$ rather than $[Pt,C,N,D]^+$ from Pt^+/CD_3NH_2 implies a $Pt(CNH)^+$ structure.

In summary, the reaction of $PtCH_2^+$ with methylamine yields a broad range of products due to the efficient competition of several reactive sites at $PtCH_2^+$ like the acidic proton, the electrophilic carbon, and a metal center which is prone to bring about C−H bond activation. All these sites are attacked efficiently by methylamine, which already possesses too many functionalities for maintaining high selectivity. Nevertheless, the systems $PtCH_2^+/CH_3NH_2$, Pt^+/CH_3NH_2, and $PtCH_2^+/NH_3$ are closely related to each other. In all three systems, $[Pt,C,H_3,N]^+$ ions are formed, which probably possess an aminocarbene connectivity. Whereas $[Pt,C,H_3,N]^+$ ions can be dehydrogenated unimolecularly to $[Pt,C,H,N]^+$ from the $PtCH_2^+/CH_3NH_2$ and the Pt^+/CH_3NH_2 entrance channels, this reaction is not accessible without external excitation for $PtCH_2^+/NH_3$ due to the lower internal energy of the system.

Methanol. The reaction of $PtCH_2^+$ with CH_3OH yields $PtCO^+$, $[Pt,C,H_2,O]^+$, and traces of CH_2OH^+ with a rate constant of $k = 4.2 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} and an efficiency of $\phi = 0.24$ (reactions 12a−12c). The regiochemistry of the reactions was investigated by performing labeling experiments with $PtCD_2^+/CH_3OH$ and $PtCH_2^+/CD_3OH$ (Table 2).



$$\mathrm{PtCH_2^+ + CH_3OH} \longrightarrow \begin{cases} \mathrm{CH_2OH^+ + PtCH_3} & (2\%) & \text{(12a)}\\ \mathrm{PtCO^+ + CH_4 + H_2} & (35\%) & \text{(12b)}\\ \mathrm{[Pt,C,H_2,O]^+ + CH_4} & (63\%) & \text{(12c)} \end{cases}$$

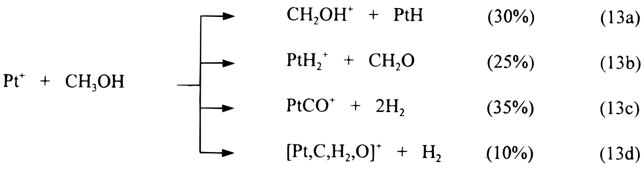
As the reaction of $PtCH_2^+$ and CD_3OH yields $[C,D_2,H,O]^+$ and not $[C,D_3,O]^+$, the product of reaction 12a is a hydroxymethyl cation rather than a methoxy cation, which is in line with the fact that CH_2OH^+ is about 86 kcal mol^{-1} more stable than the triplet ground state of CH_3O^+.[33]

Although protonated methanol is observed even at short reaction times, it is not assigned as a primary product, as no CH_3OHD^+ is formed from $PtCD_2^+/CH_3OH$. In contrast, the $PtCH_2^+/CD_3OH$ couple yields a mixture of $CD_3OH_2^+$ and CD_3OHD^+. Double-resonance experiments reveal that protonated methanol is partially formed by proton-transfer reactions from CH_2OH^+ ($PA(CH_2O) = 170.4$ kcal mol^{-1} $<$ $PA(CH_3OH) = 180.2$ kcal mol^{-1}). The overall amount of protonated methanol is further increased by proton-transfer reactions from secondary or tertiary products of reaction 12c (see below); these processes also account for the observation of CD_3OHD^+ from the $PtCH_2^+/CD_3OH$ couple.

Labeling experiments reveal that $[Pt,C,H_2,O]^+$ is formed via 1,1-elimination, as almost exclusively $[Pt,C,H,D,O]^+$ is obtained from the $PtCH_2^+/CD_3OH$ couple. Moreover, the fact that the products for $PtCH_2^+/CH_3OH$ and $PtCD_2^+/CH_3OH$ are identical indicates that the carbene unit acts as a hydrogen acceptor in the C−H bond activation processes and is eventually liberated as methane. According to these labeling experiments, channel 12c probably yields a platinum-bound hydroxycarbene $PtC(H)OH^+$. A fraction of $PtC(H)OH^+$ molecules possess enough internal energy for further dehydrogenation to $PtCO^+$ (12b). Note that none of the primary reactions can be ascribed to a nucleophilic attack of methanol to the platinum carbene.

Both $[Pt,C,H_2,O]^+$ and $PtCO^+$ react with CH_3OH to yield $[Pt,C_2,H_n,O_2]^+$ (n = 0, 2, 4).[34] When labeled CD_3OH is employed, a mixture of $Pt(CO)_2^+$, $[Pt,C_2,H,D,O_2]^+$, and $[Pt,C_2,H,D_3,O_2]^+$ is formed. The latter species becomes the dominant product at higher reaction times and arises from addition of CD_3OH to $PtCO^+$ as well as from addition of $[C,D_2,O]$ to $[Pt,C,H,D,O]^+$.

As the carbene unit in $PtCH_2^+$ is not incorporated in the ionic products of reaction 12, it is instructive to compare the product distribution with that obtained for the reaction of bare Pt$^+$ and methanol. In the latter system, CH_2OH^+, PtH_2^+, $PtCO^+$, and $[Pt,C,H_2,O]^+$ are formed with a rate constant of $k = 10 \times 10^{-10}$ cm^3 molecules^{-1} s^{-1} ($\phi = 0.57$).



$$\mathrm{Pt^+ + CH_3OH} \longrightarrow \begin{cases} \mathrm{CH_2OH^+ + PtH} & (30\%) & \text{(13a)}\\ \mathrm{PtH_2^+ + CH_2O} & (25\%) & \text{(13b)}\\ \mathrm{PtCO^+ + 2H_2} & (35\%) & \text{(13c)}\\ \mathrm{[Pt,C,H_2,O]^+ + H_2} & (10\%) & \text{(13d)} \end{cases}$$

The reaction yields similar products compared to the $PtCH_2^+/CH_3OH$ couple, although in different ratios. Hydride abstraction yielding CH_2OH^+ is much more pronounced, indicating that Pt$^+$ is a stronger hydride acceptor than $PtCH_2^+$. From the occurrence of reaction 13a a lower limit for $D(\mathrm{Pt{-}H}) > 69$ kcal mol^{-1} can be derived, which is in line with the theoretically predicted value of 71 kcal mol^{-1}.[5] Distinct differences between Pt^+/CH_3OH and $PtCH_2^+/CH_3OH$ can be discerned as far as reactions 13b and 13c are concerned. Only traces of PtH_2^+ (<2%) are observed in the $PtCH_2^+/CH_3OH$ reaction, whereas PtH_2^+ accounts for 30% of the products for the Pt^+/CH_3OH couple. In the reaction of Pt$^+$ with

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(33) Aschi, M.; Harvey, J. N.; Schalley, C. A.; Schröder, D.; Schwarz, H. *J. Chem. Soc., Chem. Commun.* **1998**, 531.

(34) The unsaturated species $[Pt,C_2,H,O_2]^+$, $[Pt,C_2,H_3,O_2]^+$, and $[Pt,C_2,H_5,O_2]^+$ are formed to a smaller extent (<25%) compared to $[Pt,C_2,O_2]^+$, $[Pt,C_2,H_2,O_2]^+$, and $[Pt,C_2,H_4,O_2]^+$.

CD_3OH, a mixture of $PtHD^+$ and PtD_2^+ in a ratio of about 4:1 is obtained. Channel 13d yields a mixture of $[Pt,C,D,H,O]^+$ and $[Pt,C,D_2,O]^+$ in a 4:1 ratio, whereas the $[Pt,C,D,H,O]^+$ to $[Pt,C,D_2,O]^+$ ratio is 11:1 for the $PtCH_2^+/CD_3OH$ couple. The labeling distribution for reactions 13b and 13d indicates that next to the 1,1-elimination of molecular hydrogen from methanol, a 1,2-elimination mechanism is also operating. The 1,2-elimination yields an intermediate $Pt(HD)(CD_2O)^+$ complex that readily dissociates into $PtHD^+$ and formaldehyde.

The ratio $PtCO^+:[Pt,C,H_2,O]^+$ of 4:1 for Pt^+/CH_3OH is distinctly different from the value of 1:1.8 obtained for $PtCH_2^+/CH_3OH$. This finding can be rationalized by two factors: (i) The products of reaction 13d possess about 5 kcal mol^{-1} more excess energy than those of 12c. (ii) The overall excess energy remains mainly in the ionic fragment $[Pt,C,H_2,O]^+$ and not in the neutral fragment H_2 in reaction 13d. In reaction 12c, a larger fraction of excess energy can be stored in the neutral fragment CH_4. Thus, due to the higher amount of internal excess energy of the $[Pt,C,H_2,O]^+$ fragment, the unimolecular dehydrogenation is more pronounced in reaction 13 than in (12).

Finally, the characteristics of the reaction of $PtCH_2^+$ with CH_3OH should be demonstrated by a comparison with the related systems $PtCH_2^+/H_2O$ and $PtCH_2^+/CH_3NH_2$. The reactions with H_2O and CH_3OH both yield the structurally identical primary products $PtCO^+$ and $[Pt,C,H_2,O,]^+$, although the mechanisms of formation are completely different. Moreover, both reactions are 27 ± 0.2 kcal mol^{-1} more exothermic for CH_3OH than for H_2O. This is reflected in a higher $PtCO^+/[Pt,C,H_2,O]^+$ ratio, indicating that more internal energy to overcome the barrier for dehydrogenation is available, and in a significantly higher overall reaction efficiency ($\phi(CH_3OH) = 0.3$ vs $\phi(H_2O) = 0.002$). The replacement of the hydroxy group in methanol with an amino function might appear as a rather small structural change, but induces a distinctly different product distribution in the reaction with $PtCH_2^+$ (see reaction 10). The oxygen atom in methanol is a weaker donor compared to nitrogen in methylamine. Hence, hydride abstraction and electron abstraction from the substrate (10a and 10b), proton transfer from $PtCH_2^+$ (10c), and in particular nucleophilic attack at the carbene (10d) are almost completely suppressed. In contrast, a close analogy between both substrates exists as far as the platinum-containing ionic products are concerned. Double C−H bond activation and expulsion of methane are feasible for both methanol and methylamine and yield a hydroxycarbene and an aminocarbene, respectively. The internal energy suffices in both cases to dehydrogenate these carbenes unimolecularly to $PtCO^+$ and $PtCNH^+$, respectively. In summary, the reaction of $PtCH_2^+$ and methanol is by and large determined by C−H bond activation of the substrate, whereas nucleophilic attack at the carbon atom does not occur.

Conclusions

The present study has demonstrated that the concept of carbon−heteroatom bond formation by nucleophilic attack at $PtCH_2^+$ can be extended to other nucleophiles than ammonia. Four general types of reactions can be distinguished: (i) Carbon−heteroatom coupling by nucleophilic attack at the carbene analogous to the $PtCH_2^+/NH_3$ reaction is found for H_2O (3a and 3b) and partially for CH_3NH_2 (10d). The reaction of $PtCH_2^+$ with H_2O helps to establish a gas-phase model for the platinum-mediated generation of water gas according to $CH_4 + H_2O \rightarrow CO + 3H_2$. (ii) For PH_3 and H_2S, carbon−heteroatom bond formation is feasible, but the dehydrogenation probably proceeds via initial activation of the heteroatom−hydrogen bonds at the platinum center. (iii) The activation of element−hydrogen bonds at platinum is followed by loss of methane instead of the H_2-loss as mentioned in (ii). For H_2S and PH_3, this process and subsequent dehydrogenations yield PtS_n^+ and $PtP_nH_m^+$ compounds. For substrates with organic substituents (CH_3NH_2, CH_3OH), C−H bond activation at platinum followed by loss of methane to give aminocarbenes and hydroxycarbenes is much more efficient than nucleophilic attack of the heteroatom at the carbene (process (i)). Therefore, (i) cannot be applied for the generation of N-substituted and O-substituted aminocarbenes and hydroxycarbenes, respectively. (iv) For basic nucleophiles such as methylamine or methanol, proton abstraction from $PtCH_2^+$ and the primary reaction products is favored.

Whereas the present study has helped to extend the potential of carbon−heteroatom bond formation reactions via $PtCH_2^+$, several of the encountered intermediates such as $Pt{-}XY^+$ ($X = CH_2$, $Y = O$, S, PH) and products such as the platinum phosphides and sulfides have been characterized only qualitatively. In this respect, more detailed investigations of the structural isomers and their energetics, e.g., by using quantum chemical methods, are highly indicated.

Experimental Section

The experiments were performed with a Spectrospin CMS 47X FTICR-mass spectrometer, which has been described previously.[35,36] Briefly, Pt^+ ions were generated via laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (Spectron Systems, $\lambda = 1064$ nm) onto a platinum target. The ions were extracted from the source, transferred into the analyzer cell by a system of electrostatic potentials and lenses, decelerated, and trapped in the field of a superconducting magnet (maximum field strength 7.05 T); prior to ion/molecule reactions, the $^{195}Pt^+$ isotope was mass selected by using the FERETS technique.[37] $PtCH_2^+$ and $PtCD_2^+$ were generated by pulsing-in CH_4 or CD_4, respectively, and subsequently mass selected by FERETS. For the purpose of thermalization and removal of excess energy, the ions were collided by pulsing-in methane/argon mixtures (for $PtCH_2^+$) or pure argon (for Pt^+) with a maximum pressure of about 5×10^{-5} mbar (ca. 2000 collisions). The neutral reactants H_2O, PH_3, H_2S, HCl, CH_3NH_2, and CH_3OH were leaked-in at partial pressures of $p = (3-100) \times 10^{-9}$ mbar. Ionic reaction products were monitored as a function of reaction time and reactant pressure. The data were accumulated and processed by means of an ASPECT 3000 minicomputer. Analysis of the kinetics of the ion/molecule reactions, which show a pseudo-first-order behavior for all

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[37] Forbes, R. A.; Laukien, F. H.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.

systems, provides branching ratios and effective bimolecular rate constants *k*, which are reported within experimental errors of ±5% and ±40%, respectively. For the modeling of more complex kinetics in consecutive reactions, a computer program was used which solves the set of differential equations by numerical methods.[38]

The neutral reagents CH_4, CD_4, CH_3NH_2, H_2O, CH_3OH, PH_3, H_2S, and HCl are commercially available in high purity and were used without further purification. CD_3NH_2 was generated on-line by treatment of $CD_3NH_2{\cdot}HCl$ with wet NaOH. CD_3OH was prepared by reduction of ethylene carbonate with $LiAlD_4$.[39]

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