Probing Cooperative Effects in Bimetallic Clusters: Indications of C−N Coupling of CH$_4$ and NH$_3$ Mediated by the Cluster Ion PtAu$^+$ in the Gas Phase

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The Degussa process for the large-scale synthesis of hydrogen cyanide from methane and ammonia (reaction 1) is of considerable economic importance. Nevertheless, mechanistic knowledge on the elementary steps involved and possible cocatalysts in addition to platinum is poor.[1]

$$CH_4 + NH_3 \xrightarrow{\langle Pt \rangle,\ 1500\ K} HCN + 3\ H_2 \qquad (1)$$

Recently, our group has shown that gaseous Pt$^+$ effects C−N bond coupling between CH$_4$ and NH$_3$ with the carbene PtCH$_2^+$ as a key intermediate.[2] Among the carbenes of several other late transition metals investigated, a particularly high reactivity with respect to C−N coupling was found for AuCH$_2^+$.[2b] Unlike PtCH$_2^+$, however, AuCH$_2^+$ is not spontaneously formed in reaction of the bare metal cation with CH$_4$. These observations aroused our interest in a system consisting of both metals and, thus, possibly combining their positive effects in terms of C−N coupling. Here, we report on the corresponding reactivity of PtAu$^+$ in comparison with Pt$_2^+$, Au$_2^+$, and Pt$^+$ as studied by Fourier transform ion-cyclotron resonance (FT-ICR) mass spectrometry.[3−6]

Like atomic Pt$^+$,[7] Pt$_2^+$ and also the larger clusters Pt$_n^+$ efficiently react with CH$_4$ under dehydrogenation, reaction 2.[8]

$$Pt_2^+ + CH_4 \rightarrow Pt_2CH_2^+ + H_2 \qquad (2)$$
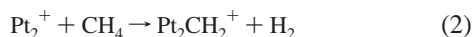
The carbene thus formed, Pt$_2$CH$_2^+$, efficiently reacts with NH$_3$ by elimination of H$_2$ (reaction efficiency $\phi = 0.6$), reaction 3. This behavior seemingly resembles that of the monomer carbene PtCH$_2^+$ where the analogous reaction yields the aminocarbene PtC(H)-NH$_2^+$.[2] However, in contrast to the aminocarbene bound to atomic Pt$^+$, [Pt$_2$,C,H$_3$,N]$^+$ does not dehydrogenate a second NH$_3$ molecule but simply forms the adduct (reaction 4) in a rather inefficient process, presumably assisted by termolecular stabilization.

$$Pt_2CH_2^+ + NH_3 \rightarrow [Pt_2,C,H_3,N]^+ + H_2 \qquad (3)$$

$$[Pt_2,C,H_3,N]^+ + NH_3 \rightarrow [Pt_2,C,H_6,N_2]^+ \qquad (4)$$
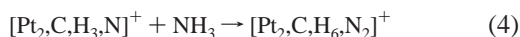
A further distinction emerges upon isotopic labeling. Whereas PtCD$_2^+$ eliminates HD upon reaction with NH$_3$, exclusively D$_2$ is produced in the case of Pt$_2$CD$_2^+$, reaction 3a. Hence, formally the D atoms in Pt$_2$CD$_2^+$ are substituted for NH$_3$. Finally, collision-induced dissociation (CID) of [Pt$_2$,C,H$_3$,N]$^+$ yields Pt$_2$C$^+$ as the only product detected at various collision energies, reaction 5.

$$Pt_2CD_2^+ + NH_3 \rightarrow [Pt_2,C,H_3,N]^+ + D_2 \qquad (3a)$$

$$[Pt_2,C,H_3,N]^+ \rightarrow Pt_2C^+ + NH_3 \qquad (5)$$

Both reactions 3a and 5 do not indicate that C−N bond coupling is accomplished in [Pt$_2$,C,H$_3$,N]$^+$, but rather suggest that this species is a simple adduct of the carbide Pt$_2$C$^+$ and intact NH$_3$, that is, Pt$_2$C$^+\cdot$NH$_3$. As the larger clusters Pt$_n^+$, $n = 3-5$, display a reactivity
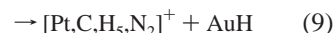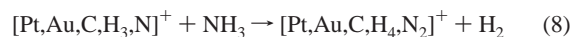
analogous to reactions 3−5, we conclude that small cationic platinum clusters, in marked difference to atomic Pt$^+$, do not mediate C−N coupling between CH$_4$ and NH$_3$. Likewise, Au$_2^+$ fails in this respect because it does not dehydrogenate methane.[9]

A probe of the reactivity of PtAu$^+$ requires a workable gas-phase synthesis of this bimetallic cluster. We found that heteronuclear clusters Pt$_m$Au$_n^+$ can be produced by laser desorption/ionization of a Pt−Au alloy (1:1) and subsequent supersonic expansion. However, a major complication for the reactivity studies with respect to PtAu$^+$ arises from the presence of Pt$_2^+$, which, like Au$_2^+$, is co-generated along with the mixed dimer. Namely, the broad isotope distribution characteristic of Pt leads to massive overlap between PtAu$^+$ and Pt$_2^+$ isotopomers (Figure 1a), e.g. ^{195}Pt^{197}Au$^+$ is sumperimposed by ^{196}Pt$_2^+$ and ^{194}Pt^{198}Pt$^+$. The differences between the exact masses of these ions are far too small for the application of selective ion-ejection techniques. Fortunately, separation is feasible by the different reactivities of Pt$_2^+$ and PtAu$^+$ toward pulsed-in oxygen. Whereas Pt$_2^+$ is efficiently converted to Pt$^+$ concomitant with loss of neutral PtO$_2$, both the PtAu$^+$ and the Au$_2^+$ cation[9] do not react at all. After this chemical separation from Pt$_2^+$ (Figure 1b, <1% isobaric Pt$_2^+$ left compared to PtAu$^+$), the ^{195}Pt^{197}Au$^+$ isotopomer is easily selected by ejection of all remaining ions (Figure 1c).[6] Accordingly, the reactivity of this species can be studied without any interference by other ions.[10]

Similarly to Pt$_2^+$, but unlike Au$_2^+$, PtAu$^+$ efficiently dehydrogenates CH$_4$ ($\phi = 0.3$), reaction 6.

$$PtAu^+ + CH_4 \rightarrow PtAuCH_2^+ + H_2 \qquad (6)$$

The heterometallic carbene PtAuCH$_2^+$ reacts with NH$_3$ under loss of H$_2$, reaction 7, in formal analogy to the corresponding reaction of Pt$_2$CH$_2^+$. The ionic product then undergoes consecutive reactions with a second NH$_3$ molecule, reactions 8 and 9.

$$PtAuCH_2^+ + NH_3 \rightarrow [Pt,Au,C,H_3,N]^+ + H_2 \qquad (7)$$

$$[Pt,Au,C,H_3,N]^+ + NH_3 \rightarrow [Pt,Au,C,H_4,N_2]^+ + H_2 \qquad (8)$$

$$\rightarrow [Pt,C,H_5,N_2]^+ + AuH \qquad (9)$$

The dehydrogenation observed in reaction 8 implies an activation of NH$_3$ that is inconsistent with [Pt,Au,C,H$_3$,N]$^+$ being a simple adduct of a PtAuC$^+$ entity and molecular NH$_3$. Instead, such a complex should only undergo degenerate ligand exchange and, if termolecular stabilization is feasible, association with a second NH$_3$ molecule, as Pt$_2$C$^+\cdot$NH$_3$ does in reaction 4. Behavior analogous to reaction 8, however, is observed for the aminocarbene PtC(H)NH$_2^+$ formed from atomic Pt$^+$ in the presence of CH$_4$ and NH$_3$.[2] This observation is a first indication that the reactivity of PtAu$^+$ resembles that of Pt$^+$ rather than of Pt$_2^+$. Similarly, the second product channel, reaction 9, brings about degradation of the metal core by loss of neutral AuH and, thus, does not agree with a PtAuC$^+\cdot$NH$_3$ structure, either.
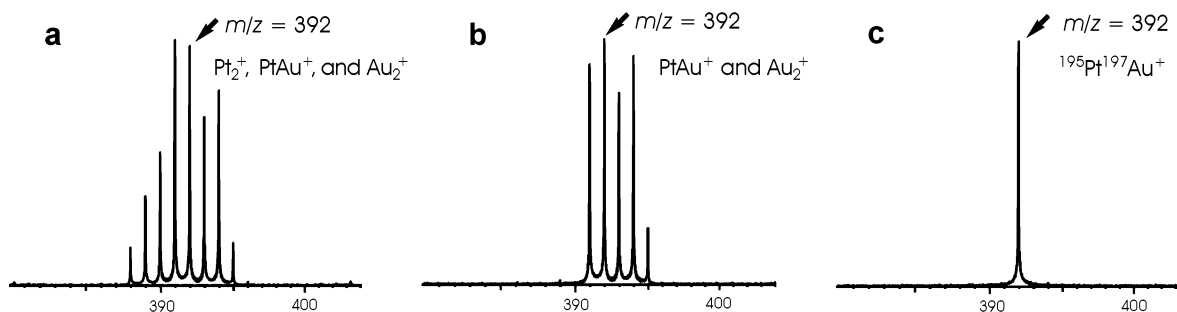
Figure 1. Mass range $m/z = 380-404$ (a) prior to reaction with O_2, (b) after reaction with O_2, and (c) after reaction with O_2 and ion ejection. The m/z values of the different isotopomers with significant abundance are $388-394$ for Pt_2^+, 391, 392, 393, and 395 for $PtAu^+$, and 394 for Au_2^+.

Further mechanistic insight is achieved by labeling. Reaction of $PtAuCD_2^+$ with NH_3 gives a mixture of $[Pt,Au,C,H_3,N]^+$, $[Pt,Au,C,H_2,D,N]^+$, and $[Pt,Au,C,H,D_2,N]^+$ in a ratio 1:1.4 (± 0.2): 1.1 (± 0.2), reactions 7a−c.

$$PtAuCD_2^+ + NH_3 \rightarrow [Pt,Au,C,H_3,N]^+ + D_2 \qquad (7a)$$

$$\rightarrow [Pt,Au,C,H_2,D,N]^+ + HD \qquad (7b)$$

$$\rightarrow [Pt,Au,C,H,D_2,N]^+ + H_2 \qquad (7c)$$

Reactions 7b and c clearly demonstrate activation of NH_3. Once again, $PtAu^+$ behaves differently from Pt_2^+, but similarly to Pt^+. For the latter, only the analogue of HD elimination 7b was observed,[2] however, whereas also losses of D_2 and H_2 occur in the reaction of $PtAuCD_2^+$ and NH_3. This points to an equilibration of all H and D atoms in the course of the reaction. For a completely statistical distribution, a ratio of 1:6:3 would be expected for reactions 7a−c. Experiment finds a much higher fraction of 7a which may be rationalized by some contribution of simple D_2/NH_3 substitution exclusively leading to $PtAuC^+ \cdot NH_3$. This second product channel would correspond to the reactivity of $Pt_2CD_2^+$, suggesting that $PtAu^+$ and Pt_2^+ are related at least in this respect. The higher extent of reaction 7c than predicted by statistics is ascribed to the operation of kinetic isotope effects which are supposed to favor H_2 elimination in reaction 7c compared to losses of HD or D_2.

Finally, CID of $[Pt,Au,C,N,H_3]^+$ yields the fragments $PtAuC^+$ and $[Pt,Au,C,H,N]^+$ in a ratio of about 2:1 for a range of collision energies (at higher energies, occurrence of atomic Au^+ and Pt^+ is also observed), reactions 10 and 11. The dehydrogenation (reaction 11) is clearly inconsistent with a simple adduct $PtAuC^+ \cdot NH_3$. However, partial presence of such a species fragmenting solely according to reaction 10 is possible.

$$[Pt,Au,C,H_3,N]^+ \rightarrow PtAuC^+ + NH_3 \qquad (10)$$

$$\rightarrow [Pt,Au,C,H,N]^+ + H_2 \qquad (11)$$

We conclude that $PtAu^+$, unlike Pt_2^+, does mediate C−N coupling between CH_4 and NH_3. The crucial effect of Au on reactivity can qualitatively be understood by noting that its closed 5d shell does not permit a strong interaction with the carbene moiety which, in turn, is available for combination with NH_3. In contrast, the presence of two Pt atoms enhances binding to carbon, resulting in carbide formation rather than C−N coupling. A too-weak interaction between the carbene and the metal core is counterproductive as well, as seen in the case of Au_2^+ that does not effect dehydrogenation of CH_4 at all.

The observed similarities in the reactivities of $PtAu^+$ and Pt^+ further suggest that formation of an aminocarbene may not only occur in the case of Pt^+ but also for $PtAu^+$, thus yielding (PtAu)C-(H)NH_2^+ as a product of C−N coupling. However, a notable difference between $PtAu^+$ and Pt^+ is that only the former effects equilibration of the hydrogen atoms provided by the carbene fragment and NH_3.

In conclusion, our experiments indicate that $PtAu^+$ mediates C−N bond coupling of CH_4 and NH_3. This might point to possible potential of Au as cocatalyst in the Degussa process. More generally, $PtAu^+$ can serve as a model for the examination of cooperative effects in bimetallic systems.

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(3) Cationic metal clusters were generated by laser desorption/-ionization with subsequent supersonic expansion[4] and transferred into the cell of a CMS 47X FT-ICR.[5] In the case of Pt_2^+, the most abundant dimer with $m/z = 390$ (corresponding to a mixture of $^{195}Pt_2^+$, $^{194}Pt^{196}Pt^+$, and $^{192}Pt^{198}Pt^+$) was isolated by means of the FERETS ion-ejection protocol,[6] whereas in the case of $PtAu^+$, selection of the $^{195}Pt^{197}Au^+$ isotopomer required further efforts (see text). After thermalization with pulsed-in Ar buffer gas, reactions with the leaked-in substrates (p(substrate) $\approx 10^{-8}$ to 10^{-7} mbar) were studied at variable times. From the decline of the reactant ion and the increase of the product ions, bimolecular rate constants (estimated errors of ± 30 and $\pm 50\%$ for the reactions with CH_4 and NH_3, respectively) were derived on the basis of the pseudo-first-order approximation. To investigate the reactions of the metal carbenes, these were produced by pulsing in CH_4 to the mass-selected and thermalized dimer ions. Indications with respect to the structure of some of the product ions were obtained from collision-induced dissociation (CID) experiments. To this end, the ions of interest were mass-selected, kinetically excited, and fragmented by collisions with Ar gas.

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JA029791Q