C−N Coupling of Methane and Ammonia by Bimetallic Platinum−Gold Cluster Cations

Konrad Koszinowski, Detlef Schröder, and Helmut Schwarz*

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

Received November 21, 2003

Fourier transform ion-cyclotron resonance mass spectrometry is used to investigate the reactivity of mass-selected bimetallic $Pt_mAu_n^+$ clusters ($m + n \leq 4$) with respect to the C−N coupling of methane and ammonia. To this end, the reactions of the heterometallic carbene species $Pt_mAu_nCH_2^+$ with NH_3 as well as those of the bare clusters with CH_3NH_2 are studied. On the basis of these experiments augmented by deuterium labeling studies, structural assignments for the reaction products are proposed. Surprisingly, only the dinuclear carbene $PtAuCH_2^+$ mediates C−N bond formation to presumably afford the aminocarbene complex $PtAuC(H)NH_2^+$, whereas the larger bimetallic carbene clusters mainly yield the carbide species $Pt_mAu_nC^+{\cdot}NH_3$ upon reaction with NH_3. This difference is rationalized by distinct metal−carbene binding energies. While the pure Au_n^+ clusters do not afford C−N coupling either, they undergo degradation reactions with NH_3 and CH_3NH_2 that are subject to pronounced even−odd size effects.

Introduction

Contemporary chemistry heavily exploits transition metals for their outstanding catalytic activity. The attraction of these elements arises to a large extent from their versatility. Because of its unique electronic configuration, each transition metal exhibits a distinct chemical character appropriate for a specific scope of catalytic applications. Given the number of transition metals in the periodic table, a wide variety of catalytic systems emerges that can be further multiplied by tuning surface textures, ligand spheres, etc. Despite these manifold possibilities, however, numerous problems in chemistry still await catalytic realizations such that additional strategies are highly appreciated. One possible approach exploits bimetallic catalysts rather than relying on a single transition metal only.[1] Obviously, the combination of different transition metals greatly increases the number of potentially catalytically active systems and may result in entirely novel reactivity patterns.

Very recently, we have applied the concept of bimetallic catalysis to a gas-phase model of the coupling of methane and ammonia.[2] In industry, this economically important reaction is realized in the Degussa process, which accomplishes the large-scale synthesis of hydrogen cyanide by means of platinum contacts.[3,4] Previous work from our group has shown that atomic Pt^+ can mimic the reactivity of the heterogeneous platinum catalyst by mediating C−N coupling of CH_4 and NH_3 with the carbene species $PtCH_2^+$ as a key intermediate.[5,6] To probe the effects of aggregation, the model system has also been extended to dinuclear and larger platinum clusters Pt_m^+.[7] At first sight, surprisingly, these clusters do not mediate C−N coupling as mononuclear Pt^+ does. However, a more thorough investigation quite plausibly suggests that the strong binding of carbon to the polynuclear metal core prohibits C−N bond formation for $Pt_mCH_2^+$ and NH_3.[2,7] One conceivable way to modify the interaction between carbon and the cluster core may commence by sequential replacement of platinum atom(s) by a second metal. On the basis of previous work on various mononuclear metal carbenes,[6] we considered the combination of Pt with Au promising and could indeed provide compelling evidence for the mediation of C−N bond formation by the bimetallic cluster ion $PtAu^+$.[2]

Obviously, exploring and eventually understanding the behavior of the larger heteronuclear clusters $Pt_mAu_n^+$ is of prime interest as well. Regarding the activation of CH_4 by $Pt_mAu_n^+$ clusters ($m + n \leq 4$), we found a continuous trend in cluster-ion reactivity.[8] Whereas the platinum-rich clusters dehydrogenate CH_4 in analogy to the homonuclear Pt_m^+ ions, the gold-rich clusters proved inert, much like pure Au_n^+ ions; a similar behavior is observed for the degradation reactions of the clusters in the presence of O_2.[8] In the present work, we further address the reactivity of the bimetallic $Pt_mAu_n^+$ clusters ($m + n \leq 4$) and focus on the second step of the C−N coupling process: i.e., the reaction of the corresponding carbene species with NH_3. In this respect, we do not only take into account the

---

[1] Sinfelt, J. H. *Bimetallic Catalysts*; Wiley: New York, 1985.
[2] Koszinowski, K.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **2003**, *125*, 3676.
[3] Hasenberg, D.; Schmidt, L. D. *J. Catal.* **1986**, *97*, 156.
[4] Bockholt, A.; Harding, I. S.; Nix, R. M. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3869.
[5] Aschi, M.; Brönstrup, M.; Diefenbach, M.; Harvey, J. N.; Schröder, D.; Schwarz, H. *Angew. Chem.* **1998**, *110*, 858; *Angew. Chem., Int. Ed.* **1998**, *37*, 829.
[6] Diefenbach, M.; Brönstrup, M.; Aschi, M.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1999**, *121*, 10614.
[7] Koszinowski, K.; Schröder, D.; Schwarz, H. *Organometallics* **2003**, *22*, 3809.
[8] Koszinowski, K.; Schröder, D.; Schwarz, H. *ChemPhysChem* **2003**, *4*, 1233.

10.1021/om0306675 CCC: $27.50
Publication on Web 01/30/2004

$Pt_mAu_nCH_2^+$ ions, which are accessible upon dehydrogenation of CH_4, but also include some less stable gold-rich carbene clusters that have to be generated by other methods. In addition, the reactions of bare $Pt_mAu_n^+$ clusters with NH_3 are considered for obtaining a more complete characterization of these systems. Finally, the reactions of the $Pt_mAu_n^+$ clusters with methylamine are studied as well, as these processes probe alternative entrance channels to the potential-energy surfaces relevant to the reactions of the carbene species with NH_3 and may thus provide complementary information.

Experimental Section

The experiments were performed using a Spectrospin CMS 47X FT-ICR mass spectrometer that has been described in detail before.[9,10] Recently,[11] the instrument has been equipped with a Smalley-type[12] cluster-ion source developed by Bondybey, Niedner-Schatteburg, and co-workers.[13] Briefly, the fundamental of a pulsed Nd:YAG laser ($\lambda = 1064$ nm, Spectron Systems) is focused onto a rotating metal target (pure Pt, pure Au, or a 1:1 alloy for producing Pt_m^+, Au_n^+, or $Pt_mAu_n^+$, respectively). The metal plasma thereby generated is entrained in a synchronized helium pulse and cooled by supersonic expansion so that formation of clusters can occur. 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. The distribution of cluster ions thus produced can be controlled by varying the delays between helium pulse, laser shot, and inlet into the analyzer cell. However, the highest abundances achieved for the clusters are still more than 1 order of magnitude smaller than those of atomic Pt^+ or Au^+.

Whereas ^{197}Au is the only naturally occurring gold isotope, the existence of several Pt isotopes results in a broad distribution of different isotopomers for the Pt-containing clusters; this unfortunate situation is likely to obscure product analyses, especially in isotopic labeling experiments. In the case of the homonuclear Pt_m^+ clusters, mass selection of a single peak and subsequent collisional thermalization is relatively straightforward, as detailed elsewhere.[7,14] For the bimetallic clusters, the situation is more complicated, because of isobaric interferences arising that cannot be eliminated by ion-ejection techniques only. With respect to the dinuclear species, reaction with pulsed-in O_2 in combination with conventional mass selection[15] achieves the desired separation of $PtAu^+$ from Pt_2^+.[2,8] Similar methods can be applied to isolate the gold-rich clusters $PtAu_2^+$ and $PtAu_3^+$. In contrast, Pt_3Au^+ and $Pt_2Au_2^+$ cannot be separated, because of their apparently very similar reactivity toward the various substrates probed. As also the isotopic patterns of these clusters do not differ largely and thus do not allow their facile distinction either, the individual rate constants for their reactions could not be determined. Notwithstanding, the rate constants for the different reactions do not substantially vary for reactant ions with m/z 782−784, although the predicted abundances of Pt_3Au^+ and $Pt_2Au_2^+$ significantly change in this mass range (100:83:54 for Pt_3Au^+ versus 40:79:100 for $Pt_2Au_2^+$).[16] To a first approximation, we therefore assume that the reactions of Pt_3Au^+ and $Pt_2Au_2^+$ with the investigated substrates proceed with similar efficiencies and that the individual rate constants equal the combined values within a factor of 2. The corresponding carbene species $Pt_mAu_nCH_2^+$ are generated upon reaction of the bare metal clusters with pulsed-in CH_4 or other appropriate precursors, as described below. For the reactions of $Pt_3AuCH_2^+$ and $Pt_2Au_2CH_2^+$ with NH_3 and the assignment of a combined rate constant, similar considerations hold, as in the case of the bare $Pt_3Au^+/Pt_2Au_2^+$ clusters.

Table 1. Bimolecular Rate Constants *k* and Efficiencies φ for the Reactions of $Pt_mAu_nCH_2^+$ Clusters with NH_3

products	m	n	$k/10^{-10}$ cm^3 s^{-1}	φ
$CH_2NH_2^+ + Pt_mAu_nH$	1	0	4.3[a]	0.21
	0	1	12.0[a]	0.60
$[Pt_m,Au_n,C,H_3,N]^+ + H_2$	1	0	1.6[a]	0.09
	2	0	9.7[b]	0.49
	1	1	6.0	0.30
	0	2	<0.1	<0.01
	3	0	9.6[b]	0.48
	2	1	8.3	0.42
	1	2	2.2	0.11
	4	0	17.0[b]	0.86
	3	1	11.0[c]	0.54
	2	2		
	1	3	0.3	0.02
$NH_4^+ + Pt_mAu_nCH^+$	1	0	0.3[a]	0.02
$[Pt_m,Au_{n-1},C,H_5,N]^+ + Au$	1	2	5.1	0.25

[a] Taken from ref 6. [b] Taken from ref 7. [c] Combined value for $Pt_3AuCH_2^+$ and $Pt_2Au_2CH_2^+$; see Experimental Section for details.

The mass-selected cluster ions are thermalized by an argon pulse (for details, see ref 7) before exposure to the neutral reactants at $p \approx 3 \times 10^{-9}$ to 10^{-6} mbar. From the decline of the reactant and the evolution of the product ions bimolecular rate constants k are derived on the basis of the pseudo-first-order kinetic approximation. The error of the rate constants reported is estimated at 50%. Reaction efficiencies $\varphi \equiv k/k_{cap}$ are calculated according to capture theory.[17] Consecutive reactions are analyzed by reisolation of the intermediate of interest or by numerical routines.[18,19] In some cases, product ions are subjected to collision-induced dissociation. To this end, the respective ion is mass-selected, kinetically excited, and collided with argon present as buffer gas.

Results and Discussion

Reactions of $Pt_mAu_nCH_2^+$ Clusters with NH_3. As established previously, both $PtCH_2^+$ and $AuCH_2^+$ accomplish efficient coupling between the CH_2 fragment and NH_3 (Table 1).[5,6] In contrast, labeling and collision-induced dissociation (CID) experiments demonstrate that $Pt_2CH_2^+$ as well as the homologous larger clusters only yield carbide species upon exposure to NH_3 (reaction 1).[2,7] Presumably, this process requires additional

$$Pt_mCH_2^+ + NH_3 \rightarrow Pt_mC^+\cdot NH_3 + H_2 \qquad m = 2-5 \quad (1)$$

free valences at the metal core that can interact with the carbon atom after dehydrogenation and thereby stabilize the resulting carbide complexes.

---

[9] Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243.

[10] Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.

[11] Engeser, M.; Weiske, T.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **2003**, *107*, 2855.

[12] Maruyama, S.; Anderson, L. R.; Smalley, R. E. *Rev. Sci. Instrum.* **1990**, *61*, 3686.

[13] Berg, C.; Schindler, T.; Kantlehner, M.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys.* **2000**, *262*, 143.

[14] Koszinowski, K.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **2003**, *107*, 4999.

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

[16] See: http://www.liv.ac.uk/Chemistry/Links/links.html.

[17] Su, T. *J. Chem. Phys.* **1988**, *88*, 4102; **1988**, *89*, 5355.

[18] Mazurek, U.; Schwarz, H. ICR Kinetics; Technische Universität Berlin, 1998.

[19] Mazurek, U. Dissertation, Technische Universität Berlin, D83, 2002.

The analogous reaction of the smallest heteronuclear metal carbene, i.e., $\mathrm{PtAuCH_2^+}$, leads to dehydrogenation as well (reaction 2 with $m = n = 1$).[2] However,

$$\mathrm{Pt}_m\mathrm{Au}_n\mathrm{CH_2}^+ + \mathrm{NH_3} \rightarrow [\mathrm{Pt}_m,\mathrm{Au}_n,\mathrm{C},\mathrm{H_3},\mathrm{N}]^+ + \mathrm{H_2} \tag{2}$$

deuterium labeling reveals significant differences between the reactivities of $\mathrm{PtAuCH_2^+}$ and its homonuclear counterpart $\mathrm{Pt_2CH_2^+}$. Thus, whereas exclusive loss of $\mathrm{D_2}$ occurs in the reaction of $\mathrm{Pt_2CD_2^+}$ with $\mathrm{NH_3}$, the bimetallic cluster $\mathrm{PtAuCD_2^+}$ gives rise to H/D scrambling. Moreover, upon CID only the heteronuclear $[\mathrm{Pt,Au,C,H_3,N}]^+$ product ion eliminates $\mathrm{H_2}$, affording $[\mathrm{Pt,Au,C,H,N}]^+$, while $[\mathrm{Pt_2,C,H_3,N}]^+$ solely loses ammonia. These experiments prove N−H bond activation of ammonia in the case of $\mathrm{PtAu^+}$, thereby strongly indicating the occurrence of C−N coupling. Furthermore, the consecutive processes point to the activation of a second $\mathrm{NH_3}$ molecule (reactions 3 and 4 with a branching ratio (b.r.) of 45:55).

$$[\mathrm{Pt,Au,C,H_3,N}]^+ + \mathrm{NH_3} \rightarrow [\mathrm{Pt,Au,C,H_4,N_2}]^+ + \mathrm{H_2} \tag{3}$$

$$\rightarrow [\mathrm{Pt,C,H_5,N_2}]^+ + \mathrm{AuH} \tag{4}$$

The reactivity of $\mathrm{Au_2CH_2^+}$ has not been examined yet. Unlike the carbenes derived from Pt_m^+ and $\mathrm{PtAu^+}$, $\mathrm{Au_2CH_2^+}$ cannot be produced by reaction of the bare metal cluster with $\mathrm{CH_4}$.[2,8,20] Instead, application of either $\mathrm{CH_3Cl}$ or $\mathrm{CH_3Br}$ proves successful in this respect (reaction 5 with $m = 0$ and $n = 2$).

$$\mathrm{Pt}_m\mathrm{Au}_n^+ + \mathrm{CH_3X} \rightarrow \mathrm{Pt}_m\mathrm{Au}_n\mathrm{CH_2}^+ + \mathrm{HX} \qquad \mathrm{X} = \mathrm{Cl, Br} \tag{5}$$

Except for a very low tendency toward adduct formation, $\mathrm{Au_2CH_2^+}$ does not react with $\mathrm{NH_3}$ ($\varphi \leq 5 \times 10^{-3}$). This finding is somewhat surprising, because the previous results suggested an inverse correlation between the binding energy of the metal−carbene bond, $D(\mathrm{M^+{-}CH_2})$, and its reactivity in terms of C−N coupling. In analogy to the mononuclear systems, where the relation $D(\mathrm{Au^+{-}CH_2}) \leq 373 \pm 3 < D(\mathrm{Pt^+{-}CH_2}) = 463 \pm 3$ kJ mol^{-1} is well established,[21,22] one expects a decrease in $D(\mathrm{M^+{-}CH_2})$ when going from $\mathrm{Pt_2CH_2^+}$ via $\mathrm{PtAuCH_2^+}$ to $\mathrm{Au_2CH_2^+}$. The parallel drop in the reactivities of the dinuclear $\mathrm{M_2^+}$ cations toward $\mathrm{CH_4}$ is fully consistent with the assumption that filling up the metals' d shells weakens the binding to the $\mathrm{CH_2}$ fragment and, thus, lowers the thermodynamic driving force for dehydrogenation of $\mathrm{CH_4}$.[8,23] However, the decreased interaction with the metal core obviously does not sufficiently activate the carbene moiety in $\mathrm{Au_2CH_2^+}$ for a coupling reaction with $\mathrm{NH_3}$. Less surprisingly, the formation of carbide complexes as observed in the case of $\mathrm{Pt_2CH_2^+}$ (reaction 1) does not occur either for $\mathrm{Au_2CH_2^+}$. As mentioned above, such a process is believed to require a strong binding between the carbon atom and the metal core.

With respect to the trinuclear clusters, $\mathrm{Pt_3CH_2^+}$ behaves in perfect analogy to its smaller congener $\mathrm{Pt_2CH_2^+}$.[2,7] Similarly, the Pt-rich bimetallic cluster $\mathrm{Pt_2AuCH_2^+}$ efficiently loses $\mathrm{H_2}$ upon exposure to $\mathrm{NH_3}$ (Table 1; reaction 2 with $m = 2$ and $n = 1$). This observation alone does not suffice for a distinction of the two different reactivity patterns identified so far: i.e., carbide generation versus C−N coupling. However, both types of reactivities can be distinguished by considering the consecutive reactions of the primary products formed. Whereas the C−N coupling products are assumed to activate a second molecule of $\mathrm{NH_3}$ in analogy to reaction 3, the carbide complexes simply add a further $\mathrm{NH_3}$ molecule.[2,7] The observed reactivity of the trinuclear $[\mathrm{Pt_2,Au,C,H_3,N}]^+$ cluster corresponds to the latter pathway such that a $\mathrm{Pt_2AuC^+{\cdot}NH_3}$ structure seems likely. This assignment is further supported by CID experiments of the mass-selected $\mathrm{NH_3}$ adduct that result in facile loss of ammonia without any indication of its activation. Besides simple $\mathrm{NH_3}$ elimination (reaction 6 with $m = 2$ and $n = 1$), additional loss of an Au atom occurs upon CID (reaction 7), where the neutral

$$[\mathrm{Pt}_m,\mathrm{Au}_n,\mathrm{C},\mathrm{H_3},\mathrm{N}]^+ \rightarrow \mathrm{Pt}_m\mathrm{Au}_n\mathrm{C}^+ + \mathrm{NH_3} \tag{6}$$

$$[\mathrm{Pt_2,Au,C,H_3,N}]^+ \rightarrow \mathrm{Pt_2C^+} + [\mathrm{Au,H_3,N}] \tag{7}$$

species might either correspond to $\mathrm{Au(NH_3)}$ or to bare Au concomitant with $\mathrm{NH_3}$. Given the appreciable binding energy of neutral $\mathrm{Au(NH_3)}$, $D_\mathrm{e}(\mathrm{Au{-}NH_3}) = 76 \pm 6$ kJ mol^{-1} according to ab initio calculations,[24] the formation of the bound complex appears somewhat more probable, although it is entropically disfavored in comparison to the separated species. The replacement of a metal atom by $\mathrm{NH_3}$ does not have a counterpart in the case of the homonuclear Pt clusters and thus points to the weaker binding of the gold atom in the cluster.

Further evidence for the formation of a carbide species in the $\mathrm{Pt_2AuCH_2^+/NH_3}$ system is provided by labeling experiments. Upon reaction with $\mathrm{NH_3}$, $\mathrm{Pt_2AuCD_2^+}$ exclusively loses $\mathrm{D_2}$ (reaction 2a with $m = 2$ and $n = 1$), thereby ruling out the occurrence of N−H bond activation required for C−N coupling.

$$\mathrm{Pt}_m\mathrm{Au}_n\mathrm{CD_2}^+ + \mathrm{NH_3} \rightarrow [\mathrm{Pt}_m,\mathrm{Au}_n,\mathrm{C},\mathrm{H_3},\mathrm{N}]^+ + \mathrm{D_2} \tag{2a}$$

In the case of the Au-rich trinuclear system $\mathrm{PtAu_2^+}$, the carbene cluster can no longer be generated by dehydrogenation of $\mathrm{CH_4}$. Instead, as for the mononuclear $\mathrm{Au^+}$ ion[25] and the $\mathrm{Au_2^+}$ cluster (see above), treatment with $\mathrm{CH_3Cl}$ or $\mathrm{CH_3Br}$ affords the desired carbene complex $\mathrm{PtAu_2CH_2^+}$ (reaction 5 with $m = 1$ and $n = 2$). Because $\mathrm{Pt_2Au^+}$ undergoes the same reaction, however, a mass separation of the overlapping isotope distributions of cluster ions is impossible. On the basis of the isotopomers' predicted abundances, the m/z 604 ion was mass-selected prior to exposure to $\mathrm{NH_3}$ in order to maximize the $\mathrm{PtAu_2^+/Pt_2Au^+}$ ratio. The actual composition of this peak was probed by reaction with $\mathrm{CH_4}$,

---

[20] Cox, D. M.; Brickman, R.; Creegan, K.; Kaldor, A. *Z. Phys. D* **1991**, *19*, 353.

[21] Aguirre, F.; Husband, J.; Thompson, C. J.; Metz, R. B. *Chem. Phys. Lett.* **2000**, *318*, 466.

[22] Zhang, X.-G.; Liyanage, R.; Armentrout, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 5563.

[23] Achatz, U.; Berg, C.; Joos, B. S.; Beyer, M. K.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **2000**, *320*, 53.

[24] Lambropoulos, N. A.; Reimers, J. R.; Hush, N. S. *J. Chem. Phys.* **2002**, *116*, 10277.

[25] Chowdhury, A. K.; Wilkins, C. L. *J. Am. Chem. Soc.* **1987**, *109*, 5336.

which discriminates between the two species;[8,26] a constant $PtAu_2^+/Pt_2Au^+$ ratio of 60:40 (±5%) was found throughout the experiments. Treatment of the m/z 604 ion with NH_3 brings about losses of H_2 (reaction 2 with $m = 1$ and $n = 2$) and Au (reaction 8). As the latter

$$PtAu_2CH_2^+ + NH_3 \rightarrow [Pt,Au,C,H_5,N]^+ + Au \quad (8)$$

process does not take place for $Pt_2AuCH_2^+$, it can be unambiguously attributed to $PtAu_2CH_2^+$, whereas dehydrogenation apparently occurs for both $PtAu_2CH_2^+$ and $Pt_2AuCH_2^+$. Taking into account the $PtAu_2^+/Pt_2Au^+$ ratio determined above, an efficiency $\varphi = 0.36$ and branching ratios of 30 and 70% for H_2 and Au elimination, respectively, can thus be derived for pure $PtAu_2^+$. As shown below, substitution of one Au atom by a nucleophilic reagent is quite a common reaction type for Au-rich clusters. Apparently, this process does not involve the carbene fragment and is therefore irrelevant as far as C−N bond formation is concerned.

With regard to dehydrogenation (reaction 2 with $m = 1$ and $n = 2$), the most interesting question again is whether this reaction involves activation of NH_3. With $PtAu_2CD_2^+$, only D_2 is lost upon interaction with NH_3, thus strongly suggesting a carbide structure for the product ion. Accordingly, $PtAu_2CH_2^+$ behaves similarly to $Pt_2AuCH_2^+$ and $Pt_3CH_2^+$ but differs from $PtAuCH_2^+$. However, the predominance of Au loss compared to dehydrogenation reflects a lowered tendency toward carbide formation for $PtAu_2CH_2^+$, which is in agreement with the expected weaker interaction of the Au-rich metal core and carbon. Despite this weaker binding, the carbene fragment in $PtAu_2CH_2^+$ is obviously not available for a coupling reaction with NH_3, thus resembling the situation encountered for $Au_2CH_2^+$. While a comparison with the reactivity of the trinuclear $Au_3CH_2^+$ cluster would be desirable, unfortunately no practicable gas-phase synthesis for this ion was found, as the reactions of Au_3^+ with CH_4, CH_3Cl, CH_3Br, and CH_3I, respectively, do not yield the desired $Au_3CH_2^+$ ion.

The reactions of the tetranuclear clusters do not show significantly new features. Much like $Pt_4CH_2^+$,[2,7] the bimetallic clusters $Pt_3AuCH_2^+$ and $Pt_2Au_2CH_2^+$ (see Experimental Section) efficiently undergo dehydrogenation in their reactions with NH_3. Labeling experiments again indicate the formation of carbide complexes (reaction 2a). The same holds true for the reaction of $PtAu_3CH_2^+$, although this species shows a considerably decreased reaction efficiency compared to its Pt-rich counterparts (Table 1). Presumably, the lower rate constant derived for the dehydrogenation of $PtAu_3CH_2^+$ reflects a less favorable thermochemistry in terms of a weaker interaction between the carbon atom and the electronically more saturated Au-rich metal core. In contrast to its smaller congener $PtAu_2CH_2^+$, cluster degradation analogous to reaction 8 does not occur for $PtAu_3CH_2^+$, thus pointing to distinct stabilities of the different clusters. In conclusion, all bimetallic $Pt_mAu_nCH_2^+$ clusters, except for $PtAuCH_2^+$, behave similarly in that they do not mediate C−N bond formation in the presence of ammonia. Quite clearly, $PtAuCH_2^+$ must have an electronic structure which distinguishes this cluster from all other bimetallic $Pt_mAu_nCH_2^+$ species, and computational studies, though very demanding, are indicated to shed light on this system.

Table 2. Apparent and Bimolecular Rate Constants k and Efficiencies φ for the Reactions of $Pt_mAu_n^+$ Clusters with NH_3

products	m	n	k/cm^3 s^{-1}	φ
$Pt_mAu_nNH_3^+$	1	0	5.0×10^{-13} [a,b]	3.0×10^{-4}
	0	1	3.6×10^{-14} [a]	2.0×10^{-5}
	3	0	5.4×10^{-12} [a,c]	3.0×10^{-3}
	2	1	5.2×10^{-12} [a]	3.0×10^{-3}
	1	2	$\leq 10^{-12}$ [a]	$\leq 10^{-3}$
	0	3	$\leq 10^{-12}$[a]	$\leq 10^{-3}$
	4	0	2.3×10^{-11} [a,c]	0.012
	3	1	3.0×10^{-11} [a,d]	0.015
	2	2		
	1	3	1.0×10^{-11} [a]	5.0×10^{-3}
$Pt_mAu_nNH^+ + H_2$	2	0	5.4×10^{-10} [c]	0.27
$Pt_mAu_{n-1}NH_3^+ + Au$	1	1	2.8×10^{-10}	0.14
	0	2	6.0×10^{-10}	0.30
	0	4	8.8×10^{-10}	0.46
$Pt_mAu_{n-3}NH_3^+ + Au_3$	0	4	2.2×10^{-10}	0.12

[a] Apparent rate constants for $p(NH_3) \approx 10^{-7}$−10^{-6} mbar. [b] Taken from ref 6. [c] Taken from ref 14. [d] Combined value for Pt_3Au^+ and $Pt_2Au_2^+$; see Experimental Section for details.

Reactions of $Pt_mAu_n^+$ Clusters with NH_3. With the exception of Pt_2^+, the homonuclear Pt_m^+ clusters simply add NH_3, where the efficiencies of these association reactions strongly increase with cluster size mostly because of lifetime effects (Table 2).[14] Besides the addition of further NH_3 in consecutive reactions, also H_2 elimination takes place for $m \geq 4$ once a certain degree of ligation y is reached (reaction 9).[14] In the case of dinuclear Pt_2^+, already the primary reaction affords activation of NH_3 (reaction 10).[14]

$$Pt_mN_yH_{3y}^+ + NH_3 \rightarrow Pt_mN_{y+1}H_{3y+1}^+ + H_2 \qquad m \geq 4 \quad (9)$$

$$Pt_2^+ + NH_3 \rightarrow Pt_2NH^+ + H_2 \quad (10)$$

For the reactions of homonuclear Au_n^+ clusters with NH_3, two different types can be distinguished. Whereas slow association occurs for $n = 1, 3$,[27] efficient cluster degradation takes place for $n = 2, 4$ (reaction 11) (Table

$$Au_n^+ + NH_3 \rightarrow Au_{n-1}NH_3^+ + Au \quad (11)$$

$$Au_4^+ + NH_3 \rightarrow AuNH_3^+ + Au_3 \quad (12)$$

2). In the case of the tetramer, a second degradation process brings about loss of Au_3 (20% br) (reaction 12). Given the much lower IE of the gold trimer, IE(Au_3) = 7.50 eV, compared to IE(Au) = 9.23 eV,[28,29] the charge distribution observed for the products of this reaction channel might appear surprising. Yet, $AuNH_3^+ + Au_3$ still is lower in energy than the alternative $AuNH_3 + Au_3^+$ asymptote because of the high bond-dissociation

---

[26] The relative difference between the exact masses of both ions, $\Delta m/m \approx 2$ ppm, is too small for their distinction under standard conditions.

[27] Irion, M. P.; Schnabel, P.; Selinger, A. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1291.

[28] Jackschath, C.; Rabin, I.; Schulze, W. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1200.

[29] See: http://webbook.nist.gov/.

energy of the cationic gold−ammonia complex, $D(\mathrm{Au^+{-}NH_3}) = 297 \pm 30$ kJ mol^{-1} versus $D(\mathrm{Au{-}NH_3}) = 76 \pm 6$ kJ mol^{-1} (note that the most stable combination corresponding to $\mathrm{Au_3NH_3^+ + Au}$ is realized in reaction 11 with $n = 4$).[30,31] Essentially, relativistic effects account for the high stabilization of $\mathrm{Au^+}$ by ammonia and other electron-donating ligands.[32,33]

The fact that only $\mathrm{Au_2^+}$ and $\mathrm{Au_4^+}$ undergo cluster degradation, whereas $\mathrm{Au_3^+}$ is inert toward $\mathrm{NH_3}$ in this respect, points to a pronounced even−odd alternation, well-known for coinage-metal clusters in general[34] and for gold-cluster ions in particular.[35−37] Having a $5d^{10}6s^1$ electron configuration, each Au atom added to the ionic cluster provides a single valence electron that is available for intracluster binding. Because electron pairing is energetically favorable, clusters with even numbers of valence electrons, i.e., odd n for the cationic clusters, are more stable, as demonstrated by a comparison of the bond-dissociation energies $D_0(\mathrm{Au}_n^+{-}\mathrm{Au})$.[38,39]

Interestingly, the primary product for reaction with $n = 4$, $\mathrm{Au_3NH_3^+}$, is subject to a second degradation process (reaction 13) although the metal core has an even number of valence electrons and thus should bear an enhanced stability. Possibly, the $\mathrm{NH_3}$ ligand transfers an appreciable amount of electron density to the metal core and thereby constitutes a substantial perturbation to the simple even−odd alternation scheme such that it no longer adequately describes the cluster's electronic situation. Moreover, occurrence of reaction 13 might be attributed to the particular stability of the $\mathrm{Au(NH_3)_2^+}$ cation, which has previously been observed in the gas phase as well as in condensed matter (for the related case of $\mathrm{AuNH_3^+}$, see above);[40,41] The anticipated loss of neutral $\mathrm{Au_2}$ in reaction 13 (expulsion of two separate Au atoms would be hardly feasible thermochemically) equals the main dissociation channel for kinetically excited bare Au_n^+ cluster ions with odd values of n.[38]

$$\mathrm{Au_3NH_3^+ + NH_3 \rightarrow Au(NH_3)_2^+ + Au_2} \qquad (13)$$

Let us now address the reactions of the heterometallic $\mathrm{Pt}_m\mathrm{Au}_n^+$ clusters with $\mathrm{NH_3}$ in order to examine whether these species show continuous trends as a function of composition. $\mathrm{PtAu^+}$, as their smallest representative, reacts with $\mathrm{NH_3}$ under cluster degradation in analogy to $\mathrm{Au_2^+}$ (reaction 14). Interestingly, the larger bimetallic cluster ions do not undergo corresponding degradation reactions but simply add $\mathrm{NH_3}$, similarly to the homonuclear Pt_m^+ ions (reaction 15). In the case of $\mathrm{PtAu_2^+}$, the absence of degradation processes is particularly unexpected, because such a reaction occurs for the corresponding carbene species (reaction 8). Apparently, the carbene ligand destabilizes the metal's core and thus makes the substitution of an Au atom by $\mathrm{NH_3}$ possible. Note that this ligand effect resembles the one observed for $\mathrm{Au_3^+/Au_3NH_3^+}$, where the bare cluster is also inert and only the ligated system undergoes fragmentation.

$$\mathrm{PtAu^+ + NH_3 \rightarrow PtNH_3^+ + Au} \qquad (14)$$

$$\mathrm{Pt}_m\mathrm{Au}_n^+ + \mathrm{NH_3} \rightarrow \mathrm{Pt}_m\mathrm{Au}_n\mathrm{NH_3^+} \qquad (15)$$

The efficiencies of the association reactions exhibit a marked dependence on cluster composition (Table 2). Whereas the reactions of $\mathrm{Pt_2Au^+}$, $\mathrm{Pt_3Au^+}$, and $\mathrm{Pt_2Au_2^+}$ proceed with rates almost identical with those of the Pt_m^+ ions of equal cluster size, the Au-rich species show a significantly decreased reactivity. This trend is fully consistent with the behavior of the bimetallic clusters toward $\mathrm{CH_4}$ and $\mathrm{O_2}$.[8] Accordingly, the lower reactivities of the Au-rich clusters can be attributed to their increased electronic saturation, which diminishes the interactions with the substrate. The close similarity between the Pt-rich $\mathrm{Pt}_m\mathrm{Au}_n^+$ and the homonuclear Pt_m^+ cluster ions is also evident from the consecutive reactions. For $\mathrm{Pt_3Au^+/Pt_2Au_2^+}$ (see Experimental Section), two $\mathrm{NH_3}$ molecules are added first, while dehydrogenation occurs in the reaction with a third molecule. This behavior is analogous to that observed for the larger Pt_m^+ clusters (reaction 9).[14]

Reactions of $\mathrm{Pt}_m\mathrm{Au}_n^+$ Clusters with $\mathrm{CH_3NH_2}$. Whereas the reactions between the carbene clusters and $\mathrm{NH_3}$ directly probe C−N bond formation, an alternative approach for a better understanding of this reaction arises from consideration of the corresponding reverse processes. To this end, the reactions of the bare cluster ions with methylamine as a prototypical C−N coupling product are studied. Usage of $\mathrm{CH_3NH_2}$ appears particularly appropriate, because the combination with the $\mathrm{Pt}_m\mathrm{Au}_n^+$ clusters leads to exactly the same elemental compositions as those of the $\mathrm{Pt}_m\mathrm{Au}_n\mathrm{CH_2^+/NH_3}$ systems. A comparison of the reactivities evolving for the two different entrance channels might therefore help to assess the energetic and structural requirements of C−N coupling. A second aspect concerns the size-specific degradation of Au_n^+ clusters observed with $\mathrm{NH_3}$. Given the similarities between $\mathrm{NH_3}$ and $\mathrm{CH_3NH_2}$, the latter reagent is thought to induce cluster degradation as well.

So far, only the reactions of mononuclear $\mathrm{Pt^+}$ with $\mathrm{CH_3NH_2}$ have been investigated.[5,6] The predominant process (80% br) affords hydride abstraction and thus transfers the positive charge to the organic fragment (reaction 16 with $m = 1$ and $n = 0$) (Table 3). Clearly,

$$\mathrm{Pt}_m\mathrm{Au}_n^+ + \mathrm{CH_3NH_2} \rightarrow \mathrm{CH_2NH_2^+} + \mathrm{Pt}_m\mathrm{Au}_n\mathrm{H} \qquad (16)$$

$$\rightarrow [\mathrm{Pt}_m,\mathrm{Au}_n,\mathrm{C},\mathrm{H}_3,\mathrm{N}]^+ + \mathrm{H_2} \qquad (17)$$

$$\rightarrow [\mathrm{Pt}_m,\mathrm{Au}_n,\mathrm{C},\mathrm{H},\mathrm{N}]^+ + 2\mathrm{H_2} \qquad (18)$$

---

(30) Schröder, D.; Schwarz, H.; Hrušák, J.; Pyykkö, P. *Inorg. Chem.* **1998**, *37*, 624.

(31) Lambropoulos, N. A.; Reimers, J. R.; Hush, N. S. *J. Chem. Phys.* **2002**, *116*, 10277.

(32) Schwarz, H. *Angew. Chem.* **2003**, *115*, 4580; *Angew. Chem., Int. Ed.* **2003**, *42*, 4442.

(33) Schröder, D.; Diefenbach, M.; Schwarz, H.; Schier, A.; Schmidbaur, H. In *Relativistic Effects in Heavy-Element Chemistry and Physics*; Hess, B. A., Ed.; Wiley: Chichester, U.K., 2002; p 245.

(34) Alonso, J. A. *Chem. Rev.* **2000**, *100*, 637.

(35) Häkkinen, H.; Landman, U. *Phys. Rev. B* **2000**, *62*, R2287.

(36) Salisbury, B. E.; Wallace, W. T.; Whetten, R. L. *Chem. Phys.* **2000**, *262*, 131.

(37) Mills, G.; Gordon, M. S.; Metiu, H. *Chem. Phys. Lett.* **2002**, *359*, 493.

(38) Becker, S.; Dietrich, G.; Hasse, H.-U.; Klisch, N.; Kluge, H.-J.; Kreisle, D.; Krückeberg, S.; Lindinger, M.; Lützenkirchen, K.; Schweikhard, L.; Weidele, H.; Ziegler, J. *Z. Phys. D* **1994**, *30*, 341.

(39) Gilb, S.; Weis, P.; Furche, F.; Ahlrichs, R.; Kappes, M. M. *J. Chem. Phys.* **2002**, *116*, 4094.

(40) Schröder, D.; Hrušák, J.; Hertwig, R. H.; Koch, W.; Schwerdtfeger, P.; Schwarz, H. *Organometallics* **1995**, *14*, 312.

(41) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1995**, 319.

Table 3. Bimolecular Rate Constants k and Efficiencies φ for the Reactions of $Pt_mAu_n^+$ Clusters with Methylamine

products	m	n	$k/10^{-10}\ cm^3\ s^{-1}$	φ
$CH_2NH_2^+ + Pt_mAu_nH$	1	0	7.1	0.46
	0	1	7.3	0.47
	2	0	2.0	0.13
	1	1	3.3	0.22
	0	2	5.0	0.33
$[Pt_m,Au_n,C,H_5,N]^+$	0	3	1.4[a]	0.10
$[Pt_m,Au_n,C,H_3,N]^+ + H_2$	1	0	0.52	0.03
	2	0	0.50	0.03
	1	1	0.73	0.05
	1	2	8.0	0.54
	0	3	2.1	0.14
$[Pt_m,Au_n,C,H,N]^+ + 2H_2$	1	0	0.95	0.06
	2	0	7.5	0.50
	1	1	3.3	0.22
	3	0	14.0	0.92
	2	1	8.0	0.54
	4	0	11.0	0.68
	3	1	7.6[b]	0.52
	2	2		
	1	3	7.6	0.52
$[Pt_m,Au_{n-1},C,H_5,N]^+ + Au$	0	2	1.2	0.08
	0	4	8.2	0.56

[a] Apparent rate constant for $p(NH_3) \approx 10^{-8}$ mbar. [b] Combined value for Pt_3Au^+ and $Pt_2Au_2^+$; see Experimental Section for details.

the high ionization energy of atomic Pt (IE(Pt) = 9.0 eV)[29] favors this transformation, in analogy to the reaction of $PtCH_2^+$ with NH_3, which yields the same products (see above). In addition, single and double dehydrogenation occur (reactions 17 and 18 with $m = 1$ and $n = 0$); the former process has its counterpart in the $PtCH_2^+/NH_3$ system as well.[5,6] In contrast, exposure of Au^+ to CH_3NH_2 exclusively results in hydride transfer according to reaction 16 with $m = 0$ and $n = 1$, which is ascribed to the even higher IE of Au in comparison to Pt (IE(Au) = 9.23 eV).[29] Remarkably, also the reaction of $AuCH_2^+$ with NH_3 solely produces protonated formimine concomitant with neutral AuH.

The higher tendency of gold toward hydride abstraction is also evident in the case of the dinuclear clusters. Both the branching ratio and the efficiency of reaction 16 increase when going from Pt_2^+ via $PtAu^+$ to Au_2^+ (Table 3). In comparison to mononuclear Pt^+ and Au^+, however, the fraction of hydride transfer is reduced for the dinuclear clusters, in accordance with their presumably lower IE values. Whereas $Pt_2CH_2^+$ and $PtAuCH_2^+$ only lose a single H_2 molecule upon reaction with NH_3, mainly double dehydrogenation takes place for the systems Pt_2^+/CH_3NH_2 and $PtAu^+/CH_3NH_2$. One possible explanation for this difference relies on energetic arguments. Being more basic than NH_3, CH_3NH_2 should liberate more energy from the interaction with the metal ion that is available as internal energy for surpassing putative barriers associated with H_2 elimination. Provided the validity of this hypothesis, external energy input to $[Pt,Au,C,H_3,N]^+$ originating from reaction 2 should induce further dehydrogenation. Indeed, the heteronuclear cluster exhibits the expected loss of H_2 upon CID, whereas its homonuclear $[Pt_2,C,H_3,N]^+$ counterpart exclusively eliminates NH_3, which is in accordance with its inferred $Pt_2C^+\cdot NH_3$ structure.[2,7]

Although this finding itself already strongly suggested C−N linkage in $[Pt,Au,C,H_3,N]^+$,[2] the comparison with the present experiments employing CH_3NH_2 adds further confirmation to this interpretation. Probably, the $PtAuCH_2^+/NH_3$ and $PtAu^+/CH_3NH_2$ routes both lead to the same species $[Pt,Au,C,H_3,N]^+$, thus allowing conclusions with respect to the structure of this ion. In the case of mononuclear Pt^+, labeling experiments have proven a selective 1,1-elimination of H_2 from the methyl group in CH_3NH_2.[5] This behavior is consistent with the high reactivity of Pt^+ toward CH_4 and its failure to dehydrogenate NH_3. Because $PtAu^+$, like the larger Pt-rich bimetallic clusters, also discriminates between CH_4 and NH_3, this ion should selectively attack the methyl group in CH_3NH_2 as well. Direct support for this assumption is provided by isotopic labeling. Upon treatment with CD_3NH_2, $PtAu^+$ yields $CD_2NH_2^+$ (reaction 16a with $m = n = 1$) and $[Pt,Au,C,H,N]^+$ (reaction 18a with $m = n = 1$) (single dehydrogenation according to reaction 17

$$Pt_mAu_n^{\ +} + CD_3NH_2 \rightarrow CD_2NH_2^{\ +} + Pt_mAu_nD \quad (16a)$$

$$\rightarrow [Pt_m,Au_n,C,H,N]^+ + D_2 + HD \quad (18a)$$

does not occur to an appreciable extent). The latter process most probably involves the transient aminocarbene complex $PtAuC(D)NH_2^+$, which undergoes a fast 1,2-dehydrogenation. Apparently, the $PtAuC(D)NH_2^+$ ion corresponds to the C−N-coupled species common to both the $PtAuCD_2^+/NH_3$ and $PtAu^+/CD_3NH_2$ routes. Note that C−N bond formation mediated by mononuclear Pt^+ involves an analogous structure.[5,6]

Another remarkable point concerns the consecutive processes observed in the $PtAu^+/CH_3NH_2$ system. Both primary dehydrogenation products react with a further CH_3NH_2 molecule under elimination of AuH (reactions 19 and 20). Given the isolobal relation between AuH

$$[Pt,Au,C,H_3,N]^+ + CH_3NH_2 \rightarrow [Pt,C_2,H_7,N_2]^+ + AuH \quad (19)$$

$$[Pt,Au,C,H,N]^+ + CH_3NH_2 \rightarrow [Pt,C_2,H_5,N_2]^+ + AuH \quad (20)$$

and H_2, these processes are best understood as aura analogues of ordinary dehydrogenation reactions.[33] Interestingly, a similar consecutive process occurs between $[Pt,Au,C,H_3,N]^+$ and NH_3 (reaction 4). This parallel in reactivity once more supports the conclusion that identical $[Pt,Au,C,H_3,N]^+$ species evolve from $PtAuCH_2^+/NH_3$ on one hand and $PtAu^+/CH_3NH_2$ on the other.

In contrast to Pt_2^+ and $PtAu^+$, Au_2^+ does not dehydrogenate CH_3NH_2, which is consistent with the inertness of Au_2^+ toward CH_4. Instead, CH_3NH_2 substitutes one Au atom and thus probably leads to the complex of Au^+ with an intact methylamine ligand, $AuCH_3NH_2^+$ (reaction 21 with $n = 2$). This process parallels the NH_3-

$$Au_n^{\ +} + CH_3NH_2 \rightarrow Au_{n-1}CH_3NH_2^{\ +} + Au \quad (21)$$

induced cluster degradation (reaction 11) and thus points to the similarity between these two substrates.

The analogy between the reactivities of CH_3NH_2 and NH_3 also holds for the larger clusters studied. Whereas Au_3^+ does not undergo the substitution according to reaction 21, this process represents the exclusive primary reaction channel in the case of $n = 4$. Apparently, the even−odd alternation already inferred from the reactions with NH_3 is quite a general feature of the reactivity of small cationic gold clusters. In addition, distinct similarities are also observed for the consecutive processes of the $Au_3NH_3^+/Au_3CH_3NH_2^+$ clusters. In both cases, the reaction with a second substrate molecule leads to expulsion of neutral Au_2 (reaction 13 versus reaction 22).

$$Au_3CH_3NH_2^+ + CH_3NH_2 \rightarrow Au(CH_3NH_2)_2^+ + Au_2 \tag{22}$$

The larger Pt_m^+ and $Pt_mAu_n^+$ clusters exclusively undergo dehydrogenation processes with CH_3NH_2. Whereas $PtAu_2^+$ only affords single dehydrogenation (reaction 17 with $m = 1$ and $n = 2$), all other clusters eliminate two molecules of H_2 (reaction 18). The fact that even the Au-rich clusters achieve dehydrogenation of CH_3NH_2 points to the activating effect of the amino group compared to nonsubstituted CH_4. Moreover, the high interaction energy between the cationic clusters and the dipolar amine is expected to further facilitate dehydrogenation. Although this enhanced reactivity of the substrate results in a leveling effect, some differences in the reaction patterns of the $Pt_mAu_n^+$ clusters still remain visible: namely, for the trinuclear systems. As soon as Au predominates in the clusters' elemental composition, merely single dehydrogenation occurs. This finding is consistent with the previous results and the general picture of reactivity dampening by valence saturation. In addition to H_2 elimination, homonuclear Au_3^+ simply adds CH_3NH_2 (40% br for $p(CH_3NH_2) \approx 10^{-8}$ mbar), which further emphasizes the rather poor potential of pure cationic gold clusters with respect to bond activation.

For all homonuclear Pt_m^+ and bimetallic $Pt_mAu_n^+$ clusters studied, the dehydrogenation reactions proceed with high efficiencies (Table 3). This situation contrasts with the behavior of Pt_m^+ toward CH_4, where the tetramer reacts exceptionally slowly;[14,23] apparently, the lower energetic demands for CH_3NH_2 dehydrogenation largely level differences in the clusters' reactivities. Moreover, the reactions do not stop after dehydrogenation of the first substrate molecule but involve up to four further CH_3NH_2 units. For the last steps of these reaction sequences, saturation effects manifest themselves in the change from double to single dehydrogenation. The relatively large uptake of substrate molecules observed is consistent with the prevalence of dative rather than covalent bonds.

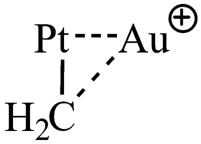
Conclusions

In view of the finding that both Pt^+ and $PtAu^+$ afford coupling of CH_4 and NH_3, one might ask if the specific electronic and structural features of the metal center are really essential for the reaction's success. The failure of the homologous larger clusters to mediate C−N bond formation clearly gives an affirmative answer to this question. Instead, the predominant reactions between ammonia and the bimetallic $Pt_mAu_nCH_2^+$ clusters with $m + n \geq 3$ lead to carbide complexes in which NH_3 serves just as a spectator ligand. Thus, the larger heteronuclear carbenes much resemble the homonuclear $Pt_mCH_2^+$ species that also yield carbide structures upon reaction with ammonia.[2,7] A closer inspection reveals an important difference between the reactivities of the Pt-rich and the Au-rich carbenes, however. Whereas the former, like the homonuclear $Pt_mCH_2^+$ clusters, are efficiently transformed to carbide species in the presence of NH_3, the latter exhibit a strongly decreased tendency toward dehydrogenation (Table 1). Apparently, the Au-rich clusters cannot fully stabilize the highly unsaturated carbon atom such that its formation is significantly hindered. The experimental results suggest that the presence of at least two Pt atoms in the cluster is necessary for facile carbide generation. This finding nicely agrees with the situation of the homonuclear carbenes $Pt_mCH_2^+$, whose reactions with NH_3 exclusively yield the carbide species for $m \geq 2$. In these cases, the enhanced stabilities of polynuclear carbide clusters could also be directly shown by energy-dependent CID of $Pt_mCH_2^+$.[7] Most probably, the stronger interaction of the carbon atom with Pt_m^+ and Pt_mAu^+ ($m \geq 2$) required for carbide formation involves a multicenter bonding situation.

With regard to the intended C−N coupling, a dilemma evolves from the observed trends in reactivity. Whereas a high platinum content on one hand is needed to dehydrogenate CH_4 in the first step, the presence of two or more Pt atoms in the cluster on the other hand results in an unfavorably strong metal−carbon interaction. As a consequence of this stronger binding, the Pt-rich carbenes are no longer activated for coupling with NH_3. These opposing demands for the overall process of C−N bond formation are only fulfilled for Pt^+ and $PtAu^+$, which are distinguished from all other $Pt_mAu_n^+$ ions by especially well-balanced metal−carbene interactions. Whereas the metal−carbene binding energy thus can be considered as the prime factor controlling the clusters' reactivities toward NH_3, other effects appear to be important as well. In particular, the failure of $Au_2CH_2^+$, $PtAu_2CH_2^+$, and $PtAu_3CH_2^+$ to mediate C−N coupling points to the operation of such specific electronic or structural effects, because these relatively weakly bound carbenes are expected to be reactive from a merely energetic point of view. This finding highlights the unique position of $PtAu^+$ among the bimetallic $Pt_mAu_n^+$ cluster ions.

Further insight is gained from the application of CH_3NH_2. Specifically, these experiments point to the aminocarbene structure $PtAuC(H)NH_2^+$ for the product of C−N bond formation between $PtAuCH_2^+$ and NH_3. Apparently, the reaction pathway strongly resembles that of the $PtCH_2^+/NH_3$ system, where the reaction intermediates as well as the final aminocarbene complex could also be characterized by quantum-chemical methods.[6] This similarity is not necessarily expected a priori, because the addition of an Au atom with its $5d^{10}6s^1$ valence-electron configuration is thought to severely perturb the electronic situation of Pt^+. One borderline case would be the complete transfer of gold's single 6s electron to Pt. Although this charge distribution is disfavored by the metals' IE values and thus unlikely

Chart 1



for bare $PtAu^+$ (ab initio calculations predict an equal partitioning of the positive charge),[42] it appears more probable for the $PtAuCH_2^+$ species, because the resulting $5d^96s^1$ configuration of Pt would be well suited to form a double bond with the CH_2 fragment. The $PtCH_2$ entity then could coordinate to the Au^+ center and stabilize it by the transfer of electron density (Chart 1); a similar situation is found in the complexes of Au^+ with other electron-donating ligands (see above).[32] The Au atom is also likely to actively participate in the coupling reaction of $PtAuCH_2^+$ with NH_3. In analogy to the theoretical results obtained for the reaction of mononuclear $PtCH_2^+$ with NH_3,[6] strong metal−hydrogen interactions are also assumed in the $PtAuCH_2^+/NH_3$ system to account for the hydrogen rearrangements clearly visible upon labeling. Because of atomic gold's high affinity for H ($D_0(\text{Au−H}) = 300$ kJ mol^{-1}),[43] its involvement in these H shifts appears probable. The consecutive loss of AuH (reaction 4) can be regarded as direct evidence for such processes.

In addition to their relevance to the question of C−N coupling, the reactions of the bare $Pt_mAu_nCH_2^+$ clusters with NH_3 and CH_3NH_2 display some further interesting aspects. Despite the leveling effect caused by the rather high reactivity of CH_3NH_2, one observes an inverse correlation between the tendency toward bond activation and the gold content of the clusters. Similarly, the efficiencies for the addition of NH_3 to the clusters decrease as a function of Au content. These findings agree with previous results obtained for the $Pt_mAu_n^+$/CH_4 and $Pt_mAu_n^+/O_2$ systems.[8] In all these cases, a gradual increase of the Au/Pt ratio appears to saturate the clusters' open valences, thereby weakening the interaction with the neutral substrates and attenuating the reactivity. For the Au-rich bimetallic and especially the homonuclear gold clusters, cluster degradation constitutes an additional type of reaction. Here, the basic substrates NH_3 and CH_3NH_2 replace Au atoms in substitution reactions. For the homonuclear Au_n^+ ions, these processes distinctly depend on the cluster size and follow a simple even−odd rule that reflects the influence of electronic effects on the stabilities of the clusters. Ligation of the clusters appears to suspend the even−odd alternation and to modify the reactivities in a less evident manner. Although this finding is not directly relevant to the problem of C−N coupling, it demonstrates how a seemingly minor extension of the system can lead to a drastic increase in complexity.

In conclusion, the metal−carbene interaction energy turns out to be the key parameter with respect to the coupling of CH_4 and NH_3 by bimetallic $Pt_mAu_n^+$ clusters. As a result of the contrary energetic requirements for the primary CH_4 activation on one hand and the consecutive reactions of the resulting carbenes with NH_3 on the other, $PtAu^+$ is found to be the only cluster capable of C−N coupling. Although this example shows the possible utility of bimetallic catalysis in the case of CH_4 functionalization, it also points to the crucial importance of a well-adjusted catalyst composition for achieving an optimum reactivity.

Acknowledgment. Financial support by Degussa AG, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie is gratefully acknowledged. K.K. particularly thanks the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie for a Kekulé scholarship. This paper is dedicated with admiration and in friendship to Professor Yitzhak Apeloig, TECHNION Haifa, on the occasion of his 60th birthday.

OM0306675

---

(42) Dai, D.; Balasubramanian, K. *J. Chem. Phys.* **1994**, *100*, 4401.
(43) Huber, H. P.; Herzberg, G. *Constants of Diatomic Molecules*; van Nostrand-Reinhold: New York, 1979.