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A Gas-Phase Model for the Pt⁺-Catalyzed Coupling of Methane and Ammonia^{**}

Massimiliano Aschi, Mark Brönstrup, Martin Diefenbach, Jeremy N. Harvey, Detlef Schröder,* and Helmut Schwarz*

Dedicated to Professor Heribert Offermanns on the occasion of his 60th birthday

The activation of methane has been referred to as one of the central challenges in contemporary chemical research.^[1] In addition to various academic aspects, methane activation is of

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. M. A. acknowledges support from the C.N.R. (Italy), and M. B. thanks the Fonds der Chemischen Industrie for a Kekulé scholarship. We thank P. E. M. Siegbahn for providing us with a basis set for platinum. We are indebted to Degussa AG for having brought this important topic to our attention. eminent industrial importance. One economically attractive process is the coupling of ammonia and methane according to reaction (1) to afford hydrogen cyanide, a valuable feedstock for chemical synthesis. Reaction (1) is, however, endother-

 $CH_4 + NH_3 \rightarrow HCN + 3H_2 \tag{1}$

mic^[2] by 61 kcal mol⁻¹ and the thermochemical equilibrium must be shifted to the right by appropriate means. Two concepts have been pursued in the chemical industry,^[3] both of which rely on platinum catalysts.^[4] In the Degussa process, reaction (1) is performed at elevated temperatures (ca. 1500 K), while in the Andrussow synthesis of HCN, molecular oxygen is added to shift the energy balance by formation of water rather than molecular hydrogen.

Details of the reaction mechanism of the Pt-catalyzed coupling of methane and ammonia remain uncertain.^[3] Gasphase studies can complement catalyst research by providing information about the elementary steps of bond activation and formation as well as the characterization of possible reaction intermediates. Here, we describe the reactions of atomic platinum cations with methane and ammonia examined using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry.^[5–7]

As has been described previously,^[8, 9] bare platinum cations dehydrogenate methane to afford the platinum carbene cation [PtCH₂]⁺ with an apparent rate constant of $k = 8.2 \times 10^{-10}$ cm³molecule⁻¹s⁻¹.^[9a] Subsequently, [PtCH₂]⁺ reacts with an excess of methane to form [PtC₂H₄]⁺ and higher [PtC_nH_m]⁺ ions, but the associated rate constants are small as compared to that of reaction (2).^[9a]

 $Pt^{+} + CH_4 \rightarrow [PtCH_2]^{+} + H_2$ ⁽²⁾

$$Pt^+ + NH_3 \rightarrow [Pt(NH_3)]^+$$
(3)

$$\mathbf{Pt}^{+} + \mathbf{NH}_{3} \not\rightarrow [\mathbf{PtNH}]^{+} + \mathbf{H}_{2} \tag{4}$$

When Pt⁺ is allowed to interact with ammonia under FTICR conditions ($p \approx 10^{-8}$ mbar) only adducts such as [Pt(NH₃)]⁺ and subsequently [Pt(NH₃)₂]⁺ form. The association reaction (3) proceeds quite slowly ($k \approx 5 \times 10^{-13}$ cm³molecule⁻¹s⁻¹), even though B3LYP calculations predict an appreciable Pt⁺–NH₃ binding energy of 74 kcalmol⁻¹.^[10, 11] Further, although dehydrogenation of ammonia to yield the NH fragment is less endothermic (101 kcalmol⁻¹) than that of methane to afford methylene (111 kcalmol⁻¹).^[2] formation of [PtNH]⁺ by means of reaction (4) is not observed. While this result may be attributed to kinetic barriers, the B3LYP calculations suggest that reaction (4) is endothermic by 17 kcalmol⁻¹, and thus its nonoccurrence is a consequence of a thermodynamic restriction.

Mass-selected [PtCH₂]⁺ reacts rapidly with ammonia ($k = 6.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) to form three different product ions according to reactions (5a-c) in a ratio of 70:25:5.

$$[PtCH_2]^+ + NH_3 \rightarrow CH_2NH_2^+ + [PtH]$$
(5a)

$$[PtCH_2]^+ + NH_3 \rightarrow [Pt, C, N, H_3]^+ + H_2$$
(5b)

$$PtCH_2]^+ + NH_3 \rightarrow NH_4^+ + [PtCH]$$
(5c)

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Reaction (5c) represents a simple proton transfer from [PtCH₂]⁺ to the ammonia base and will not be discussed further. Instead, we will focus on the formation of the iminium ion in reaction (5a), which clearly indicates the coupling of methane and ammonia concomitant with C-N bond formation. The assignment of the iminium structure to the ionic product of reaction (5a) is further supported by the finding that $[PtCD_2]^+$ reacts with ammonia to yield neutral [PtH] and $CD_2NH_2^+$; the latter undergoes proton but not deuteron transfer in its subsequent reaction with ammonia to yield NH_{4}^{+} . The combination of reactions (2) and (5 a) together with deprotonation and dehydrogenation steps constitutes a route for the generation of HCN, which is summarized in Sequence 1. In this sequence platinum mediates the activation of methane and its coupling with ammonia, but does not intervene in the final steps to yield hydrogen cyanide. Notably, the dehydrogenation step (6d) in Sequence 1 is almost thermoneutral (0.3 kcalmol⁻¹),^[2] thus it may readily occur at the elevated temperatures possibly needed to overcome kinetic barriers.^[12]

Sequence 1

 $Pt^+ + CH_4 \rightarrow [PtCH_2]^+ + H_2$ (6 a)

 $[PtCH_2]^+ + NH_3 \rightarrow CH_2NH_2^+ + [PtH]$ (6b)

 $CH_2NH_2^+ + NH_3 \rightarrow NH_4^+ + CH_2NH \tag{6c}$

 $CH_2NH \rightarrow HCN + H_2$ (6d)

$$[PtH] + NH_4^+ \rightarrow Pt^+ + NH_3 + H_2 \tag{6e}$$

$$CH_4 + NH_3 \rightarrow HCN + 3 H_2 \tag{1}$$

Let us now address the side reaction (5b) leading to the organometallic species [Pt,C,N,H₃]⁺, for which two connectivities are considered. Formation of the formimine complex $[PtN(H)(CH_2)]^+$ (1) would imply that both hydrogen atoms of the molecular hydrogen in reaction (5b) are cleaved from the ammonia molecule in a 1,1-elimination. However, in the reaction of $[PtCD_2]^+$ with ammonia only HD is lost in this channel,^[13] suggesting the occurrence of a 1,2-elimination formally leading to the aminocarbene complex $[PtC(D)(NH_2)]^+$ (2). With respect to the structural assignment of the $[Pt,C,N,H_3]^+$ ion, the subsequent ion/molecule reactions are quite revealing. [Pt,C,N,H₃]⁺ reacts with ammonia in yet another dehydrogenation step to afford $[Pt,C,N_2,H_4]^+$, and when $[PtCD_2]^+$ is used as the initial reactant, all the deuterium label is lost in the dehydrogenation steps to afford $[Pt,C,N_2,H_4]^+$ exclusively. These results imply substitution of the hydrogen (deuterium) atoms of the carbene, and the proposed sequence of reactions (7a) and (7b) lends strong support to structure 2.

 $[PtCD_2]^+ + NH_3 \rightarrow [PtC(D)(NH_2)]^+ + HD$ (7 a)

$$[PtC(D)(NH_2)]^+ + NH_3 \rightarrow [PtC(NH_2)_2] + HD$$
(7b)

The results of the B3LYP calculations are in accord with this assignment: the formation of 2 is approximately

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17 kcalmol⁻¹ more favorable than that of **1** and 33 kcal mol⁻¹ more favorable than that of a η^2 -bridged formimine complex, and also the second dehydrogenation to yield the diamino-carbene complex [PtC(NH₂)₂]⁺ (**3**) is exothermic (Scheme 1).



Scheme 1. Geometries (bond lengths [Å] and angles $[^{\circ}]$) of $[PtCH_2]^+$ and 1-3 (optimized at the B3LYP/6-31 + G* level) and relative energies for the reaction with ammonia (obtained at the B3LYP/6-311 + G**//B3LYP/6-31 + G* level of theory).

We stress, however, that the current theoretical results are only qualitative since the barriers en route to the products remain unknown. Nevertheless, complexes 2 and 3 formed in the reactions of $[PtCH_2]^+$ with ammonia are unprecedented gas-phase analogues to the metal complexes of Arduengotype^[14] aminocarbenes.^[15, 16]

Can the aminocarbene complex 2 also contribute to the formation of hydrogen cyanide in the coupling of methane and ammonia? To address this question we subjected massselected [Pt,C,N,H₃]⁺ to collisional activation. Dehydrogenation predominates to yield [Pt,C,N,H]+ along with small amounts of Pt⁺ and [C,N,H₃]⁺ fragment ions. B3LYP calculations predict the formation of $[Pt(CNH)]^+$ (28 kcalmol⁻¹) and $[Pt(NCH)]^+$ (41 kcal mol⁻¹) to be the least endothermic processes, but at present we cannot assess the barriers associated with dehydrogenation of [Pt,C,N,H₃]⁺. To further probe this aspect experimentally, we studied the reaction of bare platinum cations with methylamine.^[17] Here, single (10%) and double (10%) dehydrogenation are observed, giving [Pt,C,N,H₃]⁺ and [Pt,C,N,H]⁺, respectively, along with predominating hydride transfer to yield CH₂NH⁺₂ and neutral [PtH] (80%).

In perfect analogy to the Pt⁺/CH₄/NH₃ system, only D₂, D₂+HD, and [PtD] are lost as neutral fragments when CD₃NH₂ is used as a neutral reagent. Apparently the fact that the entrance energy of the reactants is somewhat higher for the Pt⁺/CH₃NH₂ couple ($\Sigma \Delta H^{\circ} = 328 \text{ kcal mol}^{-1}$)^[2] than for the [PtCH₂]⁺/NH₃ system ($\Sigma \Delta H^{\circ} = 303 \text{ kcal mol}^{-1}$)^[2, 9b, 18] is sufficient to surmount the barriers associated with double dehydrogenation to afford [Pt,C,N,H]⁺. Further, the formation of [Pt,C,N,H]⁺ rather than [Pt,C,N,D]⁺ from Pt⁺/CD₃NH₂ implies an intermediate complex with isonitrile coordination. Combination of reactions (2) and (6b) with a dehydrogenation and a desorption step suggests an additional route for the formation of hydrogen cyanide (Sequence 2).

Sequence 2

 $\mathbf{Pt}^{+} + \mathbf{CH}_{4} \rightarrow [\mathbf{PtCH}_{2}]^{+} + \mathbf{H}_{2}$ (8 a)

 $[PtCH_2]^+ + NH_3 \rightarrow [Pt,C,N,H_3]^+ + H_2 \tag{8b}$

 $[Pt,C,N,H_3]^+ \rightarrow [Pt,C,N,H]^+ + H_2$ (8c)

$$[Pt,C,N,H]^+ \rightarrow Pt^+ + HCN \tag{8d}$$

$$CH_4 + NH_3 \rightarrow HCN + 3 H_2 \tag{1}$$

Finally, let us extrapolate these results towards a working model for the heterogeneous catalysis of the methane/ ammonia coupling according to reaction (1). In the first step an active platinum center brings about the dehydrogenation of methane to yield a surface-bound carbene intermediate (Scheme 2).^[19] Next, ammonia approaches the carbon center



Scheme 2. Proposed mechanism for the platinum-catalyzed methane/ammonia coupling. Note that the isomerization HNC \rightarrow HCN in the lower route may be facilitated by acid-base catalysis.

with subsequent C-N bond formation. This can either lead to gaseous formimine, which is then dehydrogenated to give HCN in the gas phase, or to a surface-bound aminocarbene, which may decompose to yield HCN at elevated temperatures. Thus, we suggest two independent routes for the formation of hydrogen cyanide, one of which occurs entirely on the surface and the other is terminated in the gas phase. Common to both pathways is the initial activation of methane at platinum. The possible existence of two parallel pathways for the formation of HCN may result in rather complex dependencies of the product yields on pressure and temperature. Currently, we are further exploring the reaction mechanism and the effect of oxygen as an additional reactant on the elementary steps, and we are attempting to design a catalytic routine for the gas-phase process under FTICR conditions.^[9, 20]

> Received: November 3, 1997 [Z11117IE] German version: *Angew. Chem.* **1998**, *110*, 858–861

Keywords: ammonia • gas-phase chemistry • hydrogen cyanide • methane • platinum

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$CH_2NH + NH_2^- \rightarrow CH_2N^- + NH_3$	(9a)
$(\Delta H = 15 \text{ kcal mol}^{-1})$	
$CH_2N^- + NH_3 \rightarrow HCN + H_2 + NH_2$	(9b)
$(\Delta H = -15 \text{ kcal mol}^{-1})$	
An acid-catalyzed sequence like that in reaction (10) is also conceiv-	
able.	
$CH_2NH + NH_4^+ {\rightarrow} HCNH^+ + H_2 + NH_3$	(10 a)
$(\Delta H = 32 \text{ kcal mol}^{-1})$	
$HCNH^+ + NH_3 \rightarrow HCN + NH_4^+$	(10b)
$(\Delta H = -32 \text{ kcal mol}^{-1})$	
$(\Delta H = +32 \text{ kcal mol}^{-1})$	
$HCNH^+ + NH_3 \rightarrow HCN + NH_4^+$	(10b)
$(\Delta H = -32 \text{ cal mol}^{-1})$	

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Yttrate-Mediated Ligand Transfer and Direct Synthesis as a Route to Amidopalladium Complexes**

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In the wide range of applications of palladium compounds,^[1] amidometal complexes^[2] have played only a secondary role to date.^[3] Only a few examples of this reactive class of compounds have been reported.^[3, 4] This could be due to difficulties in the synthesis or to the instability of these compounds which arise from the "unfortunate" combination of a soft metal with the hard amido ligand.^[5] The development of new synthetic routes could help solve this problem. We report here on an yttrate-mediated ligand transfer as well as the direct synthesis as efficient routes to amido complexes of late transition metals.

The in situ reaction of lithiated 4-methyl-2-(trimethylsilylamino)pyridine (TMS-ApH) with dry YCl₃ in ether in the presence of pyridine gave the colorless yttrate complex 1 in good yields [Eq. (a)].



Aminopyridinato complexes of the early transition metals are rare,^[6] and compounds with Group 3 metals, as well as the corresponding lanthanide complexes, have not yet been reported. The two sets of signals observed for the aminopyridinato ligands in the ¹H NMR spectrum of **1** (see Table 1) is explained by coordination to lithium. This was confirmed by X-ray structural analysis^[7] (Figure 1). The lithium atom is sterically shielded and has trigonal planar coordination (sum of the angles 360°).^[8] Because of the bridging function of the amido nitrogen atom, the Y-N_{pyridine} bond in the Li-coordinated TMS-Ap ligands is significantly shorter than the Y-N_{amido} bond. The yttrium-nitrogen bond lengths of the other two aminopyridinato ligands are equally long and indicate a delocalized bonding mode.^[9] In the reaction of 1 with ZrCl₄ the complexed lithium is displaced by a ZrCl₃ unit to form the extremely unstable Y-Zr heterobimetallic complex 2, which is also colorless [Eq. (b)]. Complex 2 acts as an intermediate in

[**] This work was supported by the Max-Planck-Gesellschaft and by the Fonds der Chemischen Industrie. We thank Prof. Rosenthal for his support.

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