A Gas-Phase Model for the Pt \(^{\dagger}\) -Catalyzed Coupling of Methane and Ammonia**

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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 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, endothermic: \(\text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + \text{H}_2\) (1)

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,\(^{[2]}\) both of which rely on platinum catalysts.\(^{[3]}\) In the Degussa process, reaction (1) is performed at elevated temperatures (ca. 1500 K), while in the Andrussov 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.\(^{[4]}\) Gas-phase 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.\(^{[5]}\)

As has been described previously,\(^{[8]}\) bare platinum cations dehydrogenate methane to afford the platinum carbene \([\text{PtCH}_2]^+\) with an apparent rate constant of \(k = 8.2 \times 10^{-10} \text{cm}^3\text{ molecule}^{-1} \text{s}^{-1}\)\(^{[8]}\) Subsequently, \([\text{PtCH}_2]^+\) reacts with an excess of methane to form \([\text{PtC}_2\text{H}_4]^+\) and higher \([\text{PtC}_n\text{H}_{2n-2}]^+\) ions, but the associated rate constants are small as compared to that of reaction (2).\(^{[9]}\)

\[
\begin{align*}
\text{Pt}^+ + \text{CH}_4 &\rightarrow [\text{PtCH}_2]^+ + \text{H}_2 \\
\text{Pt}^+ + \text{NH}_3 &\rightarrow [\text{Pt(NH)}]^+ \\
\text{Pt}^+ + \text{NH}_3 &\rightarrow [\text{PtN}H]^+ + \text{H}_2
\end{align*}
\]

When \(\text{Pt}^+\) is allowed to interact with ammonia under FTICR conditions \((p \approx 10^{-8} \text{mbar})\) only adducts such as \([\text{Pt(NH)}]^+\) and subsequently \([\text{Pt(NH)}]^+\) form. The association reaction (3) proceeds quite slowly \((k \approx 5 \times 10^{-13} \text{cm}^3\text{ molecule}^{-1} \text{s}^{-1})\), even though B3LYP calculations predict an appreciable \(\text{Pt}^+ + \text{NH}_3\) binding energy of 74 kcal mol\(^{-1}\)\(^{[10, 11]}\) Further, although dehydrogenation of ammonia to yield the NH fragment is less endothermic (101 kcal mol\(^{-1}\)) than that of methane to afford methylene \((111 \text{ kcal mol}^{-1})\),\(^{[2]}\) formation of \([\text{PtNH}]^+\) 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 kcal mol\(^{-1}\), and thus its non-occurrence is a consequence of a thermodynamic restriction.

Mass-selected \([\text{PtCH}_2]^+\) reacts rapidly with ammonia \((k = 6.2 \times 10^{-20} \text{cm}^3\text{ molecule}^{-1} \text{s}^{-1})\) to form three different product ions according to reactions (5a–c) in a ratio of 70:25:5:

\[
\begin{align*}
[\text{PtCH}_2]^+ + \text{NH}_3 &\rightarrow [\text{CH}_2\text{NH}_2]^+ + [\text{PtH}] \\
[\text{PtCH}_2]^+ + \text{NH}_3 &\rightarrow [\text{PtC}_2\text{N}_2]^+ + \text{H}_2 \\
[\text{PtCH}_2]^+ + \text{NH}_3 &\rightarrow [\text{PtCH}]^+ \\
\end{align*}
\]
Reaction (5c) represents a simple proton transfer from [PtCH_3]^+ 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_3NH_2; the latter undergoes proton but not deuterium transfer in its subsequent reaction with ammonia to yield NH_3. The combination of reactions (2) and (5a) 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 kcal mol^-1), thus it may readily occur at the elevated temperatures possibly needed to overcome kinetic barriers.

Sequence 1

\[
\begin{align*}
\text{Pt} + \text{CH}_4 &\rightarrow \text{[PtCH}_3]^+ + \text{H}_2 \\
\text{[PtCH}_3]^+ + \text{NH}_3 &\rightarrow \text{CH}_2\text{NH}_2 + \text{[PtH]} \\
\text{CH}_2\text{NH}_2 + \text{NH}_3 &\rightarrow \text{NH}_3 + \text{CH}_3\text{NH} \\
\text{PtH} + \text{NH}_3 &\rightarrow \text{Pt}^+ + \text{NH}_3 + \text{H}_2 \\
\text{CH}_4 + \text{NH}_3 &\rightarrow \text{CH}_2\text{NH}_2 + 3 \text{H}_2 
\end{align*}
\]

Let us now address the side reaction (5b) leading to the organometallic species [Pt,C,N,H_3]^+, for which two connectivities are considered. Formation of the formimine complex [Pt(NH)(CH_3)]^+ ([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, 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,H_3]^+ reacts with ammonia in yet another dehydrogenation step to afford [Pt,C,N_2,H_3]^+, 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_3]^+ exclusively. These results imply substitution of the hydrogen (deuterium) atoms of the carbone, and the proposed sequence of reactions (7a) and (7b) lends strong support to structure 2.

\[
\begin{align*}
\text{[PtCD}_2]^+ + \text{NH}_3 &\rightarrow \text{[PtC(D)(NH}_2)]^+ + \text{HD} \\
\text{[PtC(D)(NH}_2)]^+ + \text{NH}_3 &\rightarrow \text{[PtC(NH}_2)]^+ + \text{HD} 
\end{align*}
\]

The results of the B3LYP calculations are in accord with this assignment: the formation of 2 is approximately 17 kcal mol^-1 more favorable than that of 1 and 33 kcal mol^-1 more favorable than that of a π^* bridged formimine complex, and also the second dehydrogenation to yield the dianimocarbene complex [PtC(NH_2)_2]^+ (3) is exothermic (Scheme 1).

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_3]^+ with ammonia are unprecedented gas-phase analogues to the metal complexes of Arduengo-type^14 aminocarbenes. 

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 mass-selected [Pt,C,N,H_3]^+ to collisional activation. Dehydrogenation predominates to yield [Pt,C,N,H]^+ along with small amounts of Pt^t and [C,N,H]^+ fragment ions. B3LYP calculations predict the formation of [Pt(CNH)]^+ (28 kcal mol^-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,H]^+. To further probe this aspect experimentally, we studied the reaction of bare platinum cations with methylamine. Here, single (10%) and double (10%) dehydrogenation are observed, giving [Pt,C,N,H]^+ and [Pt,C,N,H]^+, respectively, along with predominating hydride transfer to yield CH_2NH_2 and neutral [PtH] (80%).

In perfect analogy to the Pt/CH_3/NH_3 system, only D_2, D_2 + HD, and Pt(D) are lost as neutral fragments when CD_3NH_2 is used as a neutral reagent. Apparently the fact that the entrance energy of the reactants is somewhat higher for the Pt/CH_3/NH_2 couple (∑ΔH^E = 328 kcal mol^-1) than for the [PtCH_3]^+ /NH_3 system (∑ΔH^E = 303 kcal mol^-1)^22, 9b, 18c is sufficient to surmount the barriers associated with double
dehydrogenation to afford \([\text{Pt,C,N,H}]^+\). Further, the formation of \([\text{Pt,C,N,H}]^+\) rather than \([\text{Pt,C,N,D}]^+\) from \(\text{Pt}^+/\text{CD}_2\text{NH}\) 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

\[
\begin{align*}
\text{Pt}^+ + \text{CH}_4 &\rightarrow [\text{PtCH}_2]^+ + \text{H}_2 \quad (8a) \\
[\text{PtCH}_2]^+ + \text{NH}_3 &\rightarrow [\text{Pt,C,N,H}]^+ + \text{H}_2 \quad (8b) \\
[\text{Pt,C,N,H}]^+ &\rightarrow [\text{Pt,C,N,H}]^+ + \text{H}_2 \quad (8c) \\
[\text{Pt,C,N,H}]^- &\rightarrow \text{Pt}^+ + \text{H}_2 \quad (8d)
\end{align*}
\]

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 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.[20]

Keywords: ammonia \cdot gas-phase chemistry \cdot hydrogen cyanide \cdot methane \cdot platinum

[5] The experiments were performed with a Spectrospin CMS 47X FTICR mass spectrometer, which has been described previously.[20] In brief, Pt⁺ ions were generated by laser ionization of a platinum target in the external ion source and transferred to the analyzer cell, which was located within a superconducting magnet (705 T). Prior to the ion/molecule reactions the Pt⁷⁺ isotope was mass-selected by double-resonance techniques and thermalized with pulsed-in argon buffer gas. The reactions were studied at room temperature. Then, Pt⁺ was reacted with ammonia, which was leaked in at pressures between 0.5 and 10 × 10⁻⁶ mbar. In the same manner, [PtCH₂]^+ was produced from Pt⁺ and pulsed-in methane, mass-selected, and reacted with NH₃; similarly, the reactivity of subsequent product ions was examined. A complete analysis of the kinetic and thermochemical data including the secondary reactions as well as additional experiments will be published elsewhere.

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

[10] The Pt⁺/CH₃/NIH potential energy surface was characterized en gros at the B3LYP level. Nonmetallic atoms were calculated with a 6-31+G* basis set, whereas a LANL2DZ basis set was used for platinum. The 60 platinum core electrons were treated with the corresponding valence basis set for platinum.[9 c] Details of these and further calculations with the larger 6-311G(d,p) basis set will be published elsewhere.


[12] At the B3LYP level of theory, the barrier associated with the unimolecular dehydrogenation of CH₃NH to yield HCN is substantial (93 kcal mol⁻¹), but is likely to be lowered significantly by bimolecular acid–base reactions which exhibit low barriers. Reaction (9) is such a base-catalyzed process.
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] amidmetal 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-(trimethylsilyl-amino)pyridine (TMS-ApH) with dry YCl3 in ether in the presence of pyridine gave the colorless yttrate complex 1 in good yields [Eq. (a)].

\[
\begin{align*}
\text{CH}_2\text{NH} + \text{H}_2\text{N} &\rightarrow \text{CH}_2\text{N} + \text{NH}_3 & \text{(9a)} \\
\text{CH}_3\text{N} + \text{NH}_3 &\rightarrow \text{HCN} + \text{H}_2 + \text{NH}_2 & \text{(9b)}
\end{align*}
\]

An acid-catalyzed sequence like that in reaction (10) is also conceivable.

\[
\begin{align*}
\text{CH}_2\text{NH} + \text{H}_2\text{N} &\rightarrow \text{HCN} + \text{H}_2 + \text{NH}_2 & \text{(10a)} \\
\text{HCN} + \text{NH}_3 &\rightarrow \text{HCNH} + \text{NH}_2 & \text{(10b)}
\end{align*}
\]


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°).[9] Because of the bridging function of the amido nitrogen atom, the Y−Npyridine bond in the Li-coordinated TMS-AP ligands is significantly shorter than the Y−Naquo; 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 ZrCl4 unit to form the extremely unstable Y-Zr heterobimetallic complex 2, which is also colorless [Eq. (b)]. Complex 2 acts as an intermediate in...