HCN-Synthesis from Methane and Ammonia:
Mechanisms of Pt^{+}-Mediated C–N Coupling

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The Pt^{+}-mediated coupling of methane and ammonia has been studied both experimentally and computationally. This system serves as a model for the DEGUSSA process for the industrial production of the valuable feedstock hydrogen cyanide. Mass spectrometric studies demonstrate that C–N bond formation is catalysed efficiently by Pt^{+}. Details of the experimentally observed reaction channels have been explored computationally using the B3LYP hybrid DFT/HF functional. In the first reaction step, Pt^{+} dehydrogenates CH_4 to yield $PtCH_2^{+}$; in contrast, dehydrogenation of ammonia by Pt^{+} is endothermic and does not occur experimentally. Starting from $PtCH_2^{+}$ and NH_3, C–N bond formation, which constitutes the crucial step in making HCN from CH_4 and NH_3, is achieved via two independent pathways. The major pathway is found to be exothermic by 23 kcal mol^{-1} and yields neutral PtH and $CH_2NH_2^{+}$. The second pathway involves a dehydrogenation to yield the aminocarbene complex $PtC(H)NH_2^{+}$ ($\Delta_r H = -36$ kcal mol^{-1}); dehydrogenation of $PtC(H)NH_2^{+}$ to $PtCNH^{+}$ is exothermic with respect to $PtCH_2^{+} + NH_3$ ($\Delta_r H = -8$ kcal mol^{-1}), but hindered by kinetic barriers. A comparison of Pt^{+} with other transition metal cations (Fe^{+}, Co^{+}, Rh^{+}, W^{+}, Os^{+}, Ir^{+}, and Au^{+}) shows that Pt^{+} is unique with respect to its ability to activate one equivalent of CH_4 *and* to mediate C–N-bond coupling.