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The Metal Is the Kinetic Site of Protonation of (Diimine)Pt Dimethyl Complexes

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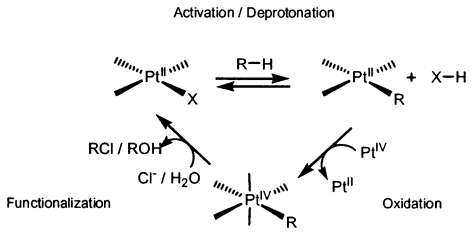
The development of methods for direct, selective oxidation of methane to value-added products continues to pose a major challenge to chemists.[1] Thirty years ago, Shilov and co-workers reported the catalytic conversion of methane to methanol and chloromethane by aqueous Pt salts.[1e,2] Since then, the classical Shilov system as well as model systems have been the subject of detailed investigations. The accumulated evidence suggests that three major steps, each of which gives rise to intriguing mechanistic possibilities, constitute the catalytic system (Scheme 1).[1d]

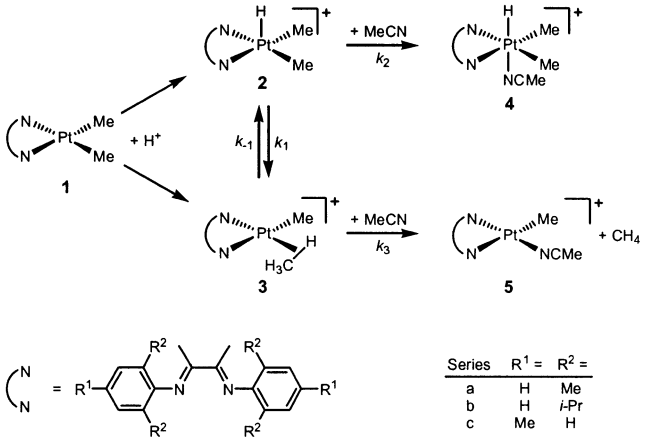
Experimental[3] and theoretical[3d,4] studies of relevant Pt systems have focused mostly on the initial C−H activation step, which is considered to yield a Pt(IV) hydridoalkyl species by oxidative addition of R−H. H/D scrambling between labeled hydride and methyl ligands during alkane elimination imply the intermediacy of (as yet unobserved) Pt(II) σ-alkane complexes, as well as their facile interconversion with Pt(IV) hydridoalkyl species.[3c−d,5] The mechanism requires the loss of a proton as X−H, but it has not been firmly established whether the deprotonation occurs from the Pt(IV) hydridoalkyl or the Pt(II) σ-alkane complex. Experimentally, these reactions have been investigated through the microscopic reverse of the C−H activation, that is, protonation of Pt(II) alkyl precursors. Hydridoalkyl Pt(IV) species have been observed during low-temperature protonations,[3a,d,5a−c,6] and it has been asserted that the metal must be the preferred site of protonation. However, the observation of such hydrides only identifies the *thermodynamic* site of protonation. It is still possible that these hydrides are preceded by unobserved *kinetic* products that rapidly rearrange to the observed hydrides. We now present evidence that at least under the applied conditions (vide infra), it is the metal center of Pt(II) dialkyl complexes that is the kinetically preferred site of protonation.

The strategy that has been applied to probe this issue is delineated in Scheme 2. Initial protonation of the Pt(II) dimethyl complex **1** produces a five-coordinate[7] Pt(IV) hydridomethyl complex **2** by metal protonation or a Pt(II) σ-methane complex **3** by protonation at a methyl ligand. It is well established[5] that species such as **2** and **3** undergo facile interconversion. Intermediate **2** is irreversibly (vide infra) trapped by MeCN to produce the observed **4**. The σ complex **3** is also irreversibly trapped by MeCN by associative displacement[8] of the methane ligand to give Pt(II) complex **5**. Both trapping processes are intermolecular and should exhibit first-order dependencies on [MeCN], whereas the intramolecular interconversion between **2** and **3** is [MeCN] independent. This results in a diagnostic dependence of the **5**:**4** product ratio on [MeCN], depending on the relative magnitudes of the rate constants k_1, k_{-1}, k_2, and k_3. If k_1 and k_{-1} are rapid compared to k_2[MeCN] and k_3[MeCN], the **5**:**4** ratio will be independent of [MeCN] and also independent of the identity of the protonation site. The Curtin−Hammett principle applies,[9] and the product ratio will only depend on the relative magnitudes of k_2 and k_3. On the other hand, if k_1 and k_{-1} are very slow compared to k_2[MeCN] and k_3[MeCN], the **5**:**4** ratio will reflect the relative occurrence of Pt versus methyl protonation but will still be independent of [MeCN]. Finally, if the interconversion between **2** and **3** and trapping by MeCN occur at comparable rates, the **5**:**4** ratio will be [MeCN]-dependent: If initial protonation occurs at Pt to give **2**, an increase of [MeCN] will trap **2** more efficiently, inhibiting the interconversion of **2** to **3**. Increasing [MeCN] therefore decreases the **5**:**4** ratio. In contrast, initial protonation at a methyl group to give **3** will cause the **5**:**4** ratio to increase with increasing [MeCN].

Scheme 1



Scheme 2



A series of experiments has been conducted in which (diimine)-$PtMe_2$ complexes **1a**−**c** were protonated with ca. 4 equiv[10] of $HBF_4 \cdot Et_2O$ in CD_2Cl_2 at −78 °C in the presence of variable amounts of MeCN-d_3.[11−13] The products **4** and **5** were readily observed by ^{1}H NMR at this temperature, and the **5**:**4** product ratios were obtained by integration of selected ^{1}H NMR signals.[14] Figure 1 summarizes the results, expressed as the yield of **5** relative to the combined yields of **4** and **5**, as a function of [MeCN] in the 0.03−5.5 M range. It can be immediately seen that for all three series, the relative yield of **5** decreases with increasing [MeCN]. *This result is consistent with initial protonation occurring exclusively or mostly at Pt.*[15]

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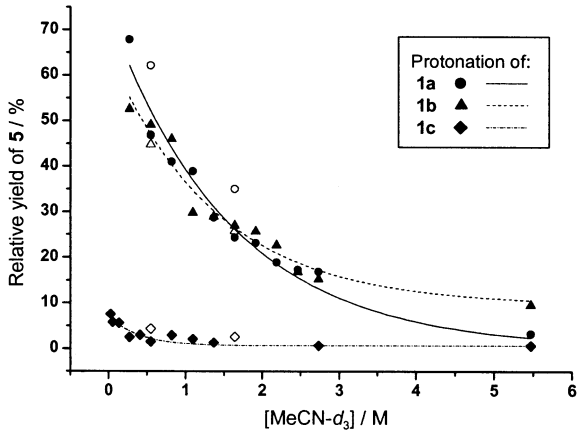

Figure 1. Relative yield of **5** (= [**5**]/([**5**]+[**4**]) resulting from protonation of **1a**−**c** with HBF_4·Et_2O. Filled symbols represent experiments conducted at −78 °C, whereas open symbols derive from protonations at −40 °C.

The *N*-aryl groups of the diimine are oriented more or less perpendicularly with respect to the coordination plane in **1**.[3f,i] Bulky 2,6-substituents exert a significant steric hindrance of the empty apical coordination site in **2**. The three complexes **1a**−**c** qualitatively show the same response to increasing [MeCN], but significant quantitative differences may be understood in terms of these steric effects. Complex **1c**, unsubstituted in the 2,6-positions, is effectively trapped after protonation at very low [MeCN]—the relative yield of **4c** through efficient trapping of **2c** is greater than 95% even at 0.1 M MeCN. For **2a**, which is 2,6-dimethyl-substituted, trapping is less efficient, and ca. 5 M MeCN is required to achieve a 95% trapping yield of **4a**. Finally, for **1b**, with the much bulkier isopropyl substituents, trapping as **4b** is only 90% efficient even at this concentration.[16]

In conclusion, we have shown that protonation of a series of (diimine)$PtMe_2$ complexes occurs preferentially at Pt as opposed to at a methyl ligand. The principle of microscopic reversibility then dictates that the deprotonation step in the general Shilov mechanism must occur from the Pt(IV) hydridomethyl, rather than the Pt(II) σ-methane, species. We anticipate that the competitive trapping technique described herein will be useful for further mechanistic studies and provide further insight into how the site of protonation/deprotonation may depend on metal complex structure, solvent, identity of acid, and other experimental parameters.

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Supporting Information Available: NMR data for **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Excess acid is used to ensure complete consumption of **1**. The protonation occurs irreversibly under these conditions: Protonation of **1a**-d_6 with HBF_4·Et_2O leads to the formation of CD_3H but not CD_2H_2, CDH_3, or CH_4 as judged by ^1H NMR.

(11) A solution of **1a**−**c** (ca. 3 mg, 5−8 μmol) in CD_2Cl_2 (400 μL) in an NMR tube was layered with CD_2Cl_2 (100 μL). (Careful layering was used to prevent premature mixing of **1** and acid). The contents were cooled to −78 °C and layered with a solution of HBF_4·Et_2O (3 μL) in a mixture of MeCN-d_3 (x μL) and CD_2Cl_2 (200 − x μL.; x = 0−200 μL). The tube was capped, kept at −78 °C, and shaken to mix the reactants *immediately* before transfer to a precooled NMR probe. A pale, homogeneous yellow solution was immediately obtained. Particular care was taken to minimize any heating of the sample. The product distributions at −40 °C are not very different from those at −78 °C, suggesting that unintentional heating did not perturb the results.

(12) The observed **5**:**4** product yields and ratios were unchanged after 2 h at −78 °C, indicating that **2** is irreversibly trapped by MeCN (otherwise, more **5** should be formed over time). Heating resulted in elimination of methane from **4**, yielding more **5**.

(13) Compounds **1** and **5** have been previously described (see refs 3h,i). ^1H NMR data for **4**: (**a**) δ −22.38 ($^2J_{Pt-H}$ = 1563 Hz); (**b**) δ −22.66 ($^2J_{Pt-H}$ = 1571 Hz); (**c**) δ −22.90 ($^2J_{Pt-H}$ = 1547 Hz). Additional NMR data for **4** are given in the Supporting Information.

(14) Due to extensive signal overlap, relative yields were consistently determined from the integral of the CH_4 signal at δ 0.20 and the combined Pt−CH_3 signals of **4** and **5**. In cases where relative yields of **4** and **5** could be determined from nonoverlapping diimine ligand signals, the results were identical within experimental uncertainties.

(15) In contrast, for $CpW(CO)_2(PMe_3)H$, protonation at the hydride ligand (yielding an η^2-H_2 complex) precedes dihydride formation. Papish, E. T.; Rix, F. C.; Spetseris, N.; Norton, J. R.; Williams, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 12235.

(16) We cannot rule out that the steric effect is caused by protonation at methyl as a *minor* reaction pathway.

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