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Five-Coordinate Platinum(IV) Complex as a Precursor to a Novel Pt(II) Olefin Hydride Complex for Alkane Activation

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Some of the most promising approaches to the selective functionalization of alkanes involve platinum catalysts.[1] Significant recent progress has been made in the development of catalytic systems for alkane oxidation,[2] as well as in the understanding of the mechanisms of these platinum(II/IV) based systems.[3,4] Mechanistic studies have shown that virtually all C−C and C−H reductive elimination reactions to form alkanes from six-coordinate Pt(IV) complexes involve prior dissociation of a ligand to form five-coordinate Pt(IV) intermediates.[4,5] Conversely, the oxidative addition of C−H bonds to Pt(II) must (by the principle of microscopic reversibility) involve either a three-coordinate Pt(II) intermediate, formed by dissociation of a ligand from square-planar Pt(II), or an associative substitution step[3d] in which hydrocarbon replaces a weakly bound ligand. Coordination of hydrocarbon within the Pt(II) square plane appears to be a key factor for C−H activation at Pt(II).[6] In Shilov's classic system, aquation of $PtCl_4^{2-}$ occurs to generate a reactive species that has a good leaving group.[2c,d] More recently, Pt(II) complexes with labile solvento ligands or weakly bound anionic ligands have been found to activate hydrocarbon C−H bonds.[3a−g] A Lewis acid has also been used to remove a strongly bound anionic ligand for this purpose.[3h] Thus, all Pt(II)-based C−H bond activation reactions have required that a platinum-bonded ligand leaves. Herein we describe a different approach: olefin insertion can create the open site and allow for selective alkane activation under mild conditions.

Recently, we reported the isolation and structural characterization of the five-coordinate platinum(IV) alkyl complex (nacnac)$PtMe_3$ (**1**), nacnac$^-$ = $[\{(o\text{-}^iPr_2C_6H_3)NC(CH_3)\}_2CH]^-$.[7] This study provided the first physical model for the five-coordinate alkyl intermediates proposed in alkane reductive elimination reactions from Pt(IV) complexes.[7,8] We now report that thermolysis of **1** in C_6D_6 at 150 °C in the dark produces within 10 min ethane (the organic product of C−C reductive elimination), methane, and a novel Pt(II) complex.[9] The ^1H NMR spectrum of this new complex exhibits the CH_3 and the CH signals of the ligand backbone as well as the aryl protons of the ligand. However, isopropyl hydrogens of the ligand are not observed in the ^1H NMR spectrum. Crystallization of the product allowed the identification of this species as the olefin(deuterido)platinum(II) complex **2**-d_{27} (Figure 1, relevant parameters in the legend).[10] The isopropyl groups, the isopropenyl group, and the metal hydride position in this compound are completely deuterated. If the reaction is instead carried out in C_6H_6, the analogous olefin(hydrido)platinum(II) complex **2**, unambiguously characterized by NMR spectroscopy, is formed.[11]

A straightforward mechanism is proposed for the formation of **2** (left side of Scheme 1). The five-coordinate Pt(IV) complex **1** undergoes reductive elimination of ethane to generate the Pt(II) intermediate (nacnac)PtMe. This three-coordinate Pt(II) species should be highly reactive toward oxidative addition of C−H bonds.

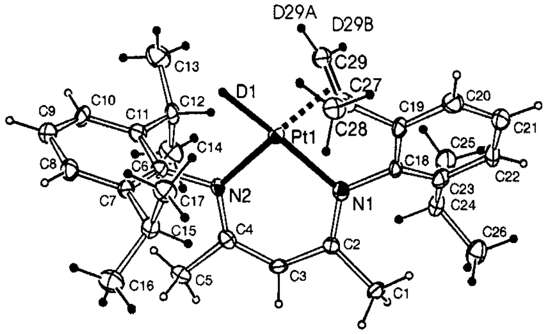

Figure 1. Thermal ellipsoid plot for **2**-d_{27}: heavy atoms as 30% probability envelopes, ^1H as white spheres, ^2H as dark spheres of arbitrary radius. Selected distances and angles (Å, deg; centroid $\boldsymbol{X}$ defined halfway between C27 and C29): Pt1−N1, 2.089(4); Pt1−N2, 2.011(4); Pt1−D1, 1.66(5); Pt1−C27, 2.152(6); Pt1−C29, 2.128(6); Pt1−$\boldsymbol{X}$, 2.023(6); N1−Pt1−N2, 92.4(2); N2−Pt1−D1, 87.0(2); N1−Pt1−$\boldsymbol{X}$, 90.3(2); torsion angle N1−Pt1−$\boldsymbol{X}$−C27, 55.5(1) (olefin roughly halfway between coplanar and perpendicular to the ligand plane); interplanar angle {C29−D29A−D29B}/{C27−C28−C19}, 50(4).

The nearby isopropyl groups are subject to C−H oxidative addition at either the methyl or methine positions to generate ("NNC")-PtMe(H). Since ("NNC")PtMe(H) are five-coordinate Pt(IV) alkyl hydride species, rapid C−H reductive elimination of methane occurs to produce ("NNC")Pt. β-Hydride elimination from ("NNC")Pt then generates the olefin hydride species **2**. This reaction should be facile since an open site exists on the metal cis to the cyclometalated ligand bearing β-hydrogens. This mechanism is in agreement with the methane product detected; when the thermolysis is conducted in C_6D_6, CH_4 with only a minor amount of CH_3D (<5%) is formed.

The incorporation of deuterium into the isopropyl groups shows that a species capable of C−H activation is generated. Activation of C_6D_6 is expected to occur via one of the three-coordinate Pt(II) intermediates, (nacnac)PtMe or ("NNC")Pt. The lack of significant amounts of CH_3D in C_6D_6 argues against the involvement of the former species. Shown on the right side of Scheme 1 is the proposed mechanism. Oxidative addition of a C−D bond of C_6D_6 to ("NNC")Pt generates the five-coordinate Pt(IV) deuteride species ("NNC")PtR(D) (R = C_6D_5).[12] Then, while C−D reductive elimination of C_6D_6 to regenerate the three-coordinate species of the type ("NNC")Pt is nonproductive, C−D elimination of the isopropyl group produces the three-coordinate Pt(II) species (nacnac-d_1)PtR. Oxidative addition of a C−H bond of one of the isopropyl groups then produces ("NNC"-d_1)PtR(H). C−H reductive elimination of the C_6D_5−H solvent molecule occurs and is followed by oxidative addition of another R−D solvent molecule. Repetition of this sequence (at least 26 more times) leads to the product **2**-d_{27}.

Since only **2**-d_{27} (and no **2**) is observed upon thermolysis of **1** in C_6D_6, the oxidative addition of C_6D_6 to ("NNC")Pt must either be much faster than β-hydride elimination or β-hydride elimination to form **2** must be reversible. There is strong literature precedent

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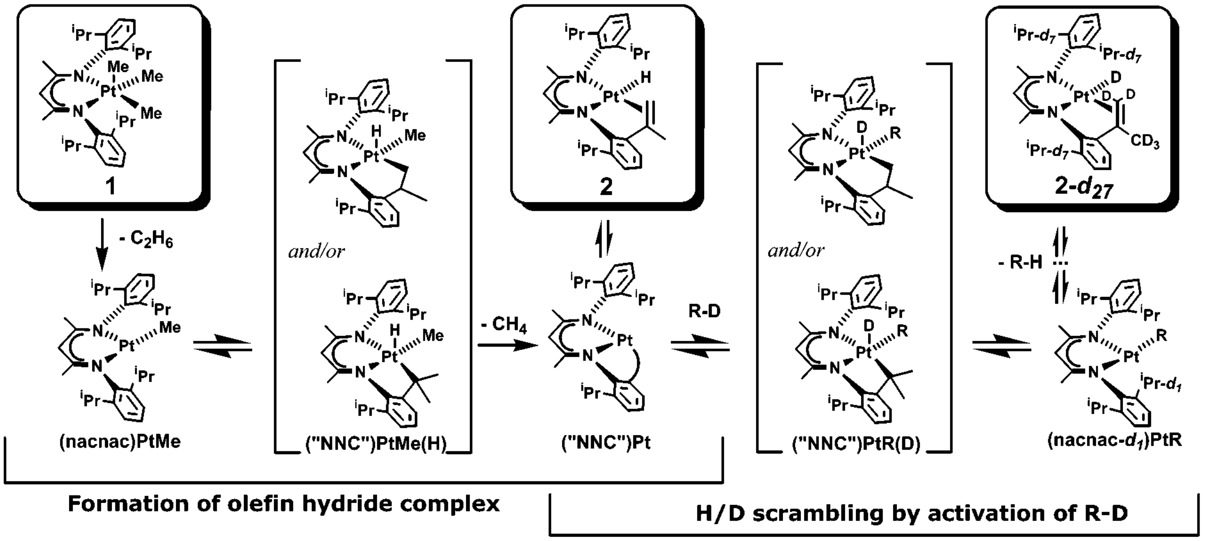
Scheme 1



in support of the latter; several cationic alkene hydride complexes of Pt(II) with phosphine ligands have been observed to undergo reversible olefin insertion/β-hydride elimination.[13] There appears to be only a small energy difference with a low activation barrier between the Pt(II) alkene hydride complex and the Pt(II) alkyl with a C−H agostic interaction.[13,14]

If β-hydride elimination from ("NNC")Pt to form **2** is reversible, the deuteration of **2** should not depend on an in situ preparation from **1**. Isolated samples of **2** should be capable of activating hydrocarbon C−D bonds. Indeed, heating of **2** in C_6D_6 to 85 °C for 16 h led to the formation of **2**-d_{27}. Even more remarkable is that **2** is also able to activate alkane C−H bonds under mild conditions. Deuterium incorporation (ca. 50%) into the positions shown for **2**-d_{27} in Scheme 1 was observed when **2** was heated in pentane-d_{12} to 85 °C for 18 h. After 62 h, deuteration at these positions was virtually complete.[15] The regioselectivity of the alkane H/D exchange was determined by heating **2**-d_{27} in pentane-h_{12} wherein the formation of **2** and partially deuterated pentane was observed. Deuteration of the primary positions of pentane was favored over that of the secondary positions by a statistically corrected factor of ca. 6 (determined by ^{2}H NMR).[16]

In summary, thermolysis of a five-coordinate platinum(IV) complex has led to the formation of an olefin(hydrido)platinum(II) complex, where the olefin moiety is part of a nacnac-type ligand. This complex activates alkanes by a novel mechanism; olefin insertion into the Pt−H bond opens a coordination site at Pt(II) allowing alkane coordination and C−H oxidative addition. Experiments to apply this promising alkane activation concept to the functionalization of alkanes are underway in our laboratories. It is important in this respect that the desirable selectivity for terminal C−H bonds, typical for Pt(II)-based systems,[1] was also observed in H/D exchange reactions with this olefin(hydrido)platinum(II) complex.[16]

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Supporting Information Available: Synthetic procedures and NMR spectral data for **2** and **2**-d_{27} (PDF); X-ray crystallographic data for **2**-d_{27} (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The yield of **2**-d_{27} is 50−60%. As a soluble side product, free ligand nacnac-H is formed in ca. 5% yield.
(10) **2**-d_{27}: $C_{29}H_{13}D_{27}N_2Pt$, MW = 638.88, clear yellow-brown prism; monoclinic, space group $P2_1/c$, $T = 130(2)$ K, $a = 8.7950(4)$ Å, $b = 26.0160(14)$ Å, $c = 11.6170(6)$ Å, $\beta = 102.853(3)°$, $Z = 4$, $R_1 = 0.0421$, $wR_2 = 0.0781$. GOF (F^2) = 0.716.
(11) NMR data are given in the Supporting Information.
(12) Both isomers must be accessible, since scrambling occurs into isopropyl CH and CH_3 positions.
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(15) Additionally, significant deuteration at the CH_3 positions of the ligand backbone was observed, as indicated by appearance of CH_2D (1:1:1) triplets along with small peaks due to double-deuteration (CHD_2, quintets). This process is slow and apparently an intermolecular reaction; if free ligand nacnac-H is present in the sample, partial deuteration of analogous positions on the free ligand takes place.
(16) This selectivity may stem from the initial activation step or from possible subsequent reactions (C−H reductive coupling/oxidative cleavage or reversible β-H elimination) which could isomerize the alkyl to the thermodynamically favored terminal position.

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