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Facile Dehydrogenation of Ethers and Alkanes with a β-Diiminate Pt Fragment

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Many transition metal complexes activate C−H bonds of alkanes, but few lead to functionalized products.[1] Recent successes use d^8 transition metals for catalytic dehydrogenation of alkanes,[2] including their use in alkane metathesis.[2f] Progress in dehydrogenation of functionalized hydrocarbons has lagged behind alkane dehydrogenation,[3] and reports of C−H activation of ethers by d^8 metals are rare in comparison to alkane activation reactions.[4]

We report herein Pt complexes that dehydrogenate diethyl ether, THF, and alkanes, with dehydrogenation of ethers kinetically favored relative to dehydrogenation of alkanes.

Recently, β-diiminate (nacnac) ligands with bulky *ortho*-substituents on the *N*-phenyl groups have become popular due to both their ease of synthesis and their ability to shield the metal center. Goldberg has used this type of ligand to stabilize five-coordinate Pt(IV) trimethyl species.[5a] Thermolysis of these complexes results in reductive elimination of ethane and dehydrogenation of either the *ortho*-substituent or the alkane solvent.[5b,c,6]

Hypothesizing that a (nacnac)Pt(olefin)(H) species with simple *N*-phenyl rings would facilitate associative olefin displacement, we attempted to synthesize a monomethyl Pt(II) species capable of C−H activation that would not require the use of bulky substituents on the ligand for stability. Note that thermolysis at 85 °C of *p*-Cl or *p*-OMe (nacnac)Pt(Me)(SMe_2) in benzene has been shown to form (nacnac)Pt(Ph)(SMe_2).[7a]

The targeted monomethyl Pt(II) species was formed by stirring Li(nacnac) with (Me)(Cl)Pt(SMe_2)$_2$ followed by addition of L (CO or ethylene), yielding (nacnac)Pt(Me)(L) **1** (L = C_2H_4 **1a**, CO **1b**).[7] Both **1a** and **1b** were crystallographically characterized (**1a** is shown in Figure 1).[8] Although the bound ethylene in **1a** is static at room temperature, olefin rotation can be observed at higher temperature by ^{1}H NMR and reflects a barrier of 16.7 kcal/mol.

The crystal structures indicate that the metal is indeed more exposed than that in related structures with *ortho*-substituents on the nacnac phenyl rings. Although we had the (nacnac)Pt^{II}(Me) framework in place, our efforts to isolate sp^3 C−H activation products by displacing L either photolytically or thermally failed. In spite of the high CO stretching frequency of **1b** (2065 cm^{-1}, CH_2Cl_2), complexes **1a,b** were inert under the conditions we explored.

We turned to a one-pot method for generating a (nacnac)Pt^{II} species capable of C−H activation. The neutral β-enamineimine ligand (nacnacH) has an acidic proton available to react with $Me_4Pt_2(\mu\text{-}SMe_2)_2$ to form CH_4 and generate a reactive Pt(II) methyl fragment. Stirring these reagents in diethyl ether did not yield (nacnac)Pt(L)(Me) (L = SMe_2, OEt_2),[9,10] but rather the downstream dehydrogenation product (nacnac)Pt(H)(ethyl vinyl ether), **2a**, was isolated (Scheme 1). Reaction with $CH_3CD_2OCH_2CH_3$ yields a mixture of CH_4 and CH_3D as well as both (nacnac)Pt(H)($C_4H_6D_2O$) (**2a**) and (nacnac)Pt(H)(C_4H_7DO) (**2a-*d*₁**), indicating that the α-C is the site of initial C−H activation. Accordingly, no Pt−D product was observed in this experiment. The other reported product of dehydrogenation of diethyl ether with platinum, [(TMEDA)Pt(ethyl vinyl ether)(H)]$^+$, isomerizes over time to the Fischer-type carbene.[4e,f]

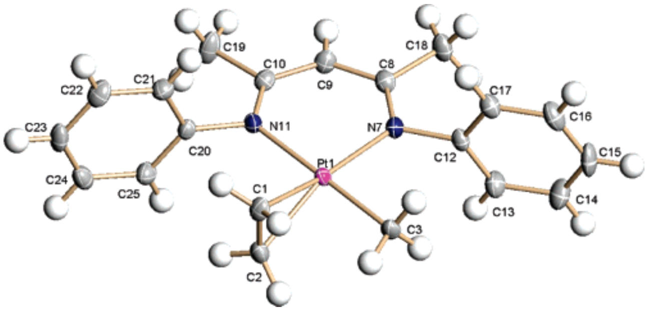
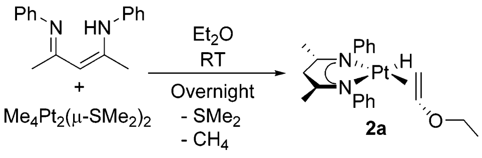


Figure 1. X-ray structure of (nacnac)Pt(Me)(ethylene) **1a**. Thermal ellipsoids at 30%.

Scheme 1. Dehydrogenation of Et_2O



Conducting the reaction in THF led to the formation of the 2,3-dihydrofuran adduct with the double bond adjacent to the oxygen in (nacnac)Pt(H)(2,3-dihydrofuran) (**2b**). Metal hydride complexes of 2,3-dihydrofuran have been elusive, but here dehydrogenation of THF leads to an olefin adduct rather than to the isomeric heteroatom carbene.

Reaction of nacnacH and $Me_4Pt_2(\mu\text{-}SMe_2)_2$ in *n*-pentane solvent yielded (nacnac)Pt(H)(1-pentene), **2c**. Only the 1-pentene isomer adduct was observed.[11] Acyclic alkanes yield only terminal olefins, indicating a preference for terminal C−H bonds in alkanes. This is in contrast to ethers which favor activation of the C−H bond adjacent to oxygen. The differing pathways are likely due to coordination through oxygen preceding C−H activation.

Competition experiments in which mixtures of two solvents were used displayed a kinetic preference for activation of ethers over alkanes. Diethyl ether is favored 3.9:1 over pentane, Et_2O is favored 1.2:1 over THF, and *n*-pentane is favored 3.2:1 over cyclopentane. The kinetic preference for ethers is compatible with a mechanism involving associative displacement of methane from (nacnac)Pt(CH_3)(CH_4). Presumably ether binds more quickly than pentane to form the unobserved intermediate (nacnac)Pt(Me)(OEt_2) which then undergoes intramolecular C−H activation at the α position. A similar intramolecular C−H activation of ether was observed by Bercaw in (TMEDA)Pt(Me)(OEt_2).[4f] Our results also show that straight chain alkanes are favored over cyclic alkanes. However, no similar effect favoring primary C−H activation is seen in ethers, no doubt reflecting their ability to initially bind through oxygen.

Kinetic isotope effects were determined using 1:1 ratios of protio and deutero substrates. Diethyl ether and THF both yielded k_H/k_D values of 2.2(1), while for pentane, the k_H/k_D ratio was 3.8(4). The

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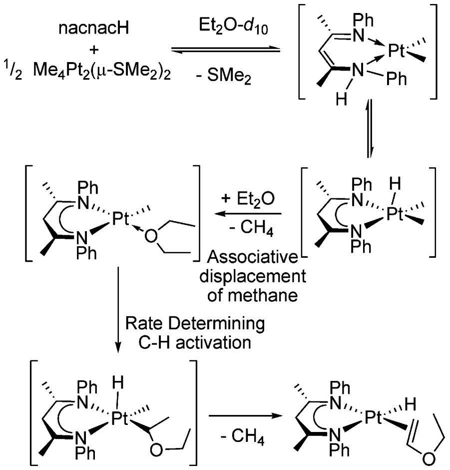
Scheme 2. Proposed Mechanism for Et_2O Dehydrogenation



significantly lower value for the ethers is consistent with initial coordination through oxygen followed by rate-limiting C−H activation at the α position (Scheme 2). The use of $CH_3CD_2OCH_2CH_3$ also yielded an intramolecular KIE of 2.2(1). Rate-limiting C−H activation may explain the preference for terminal activation of alkanes. Several d^8 systems have been found to favor *coordination* of secondary C−H bonds,[12] though *activation* of primary C−H bonds is favored.[13]

Transfer dehydrogenations of Et_2O, THF, and *n*-pentane using *t*-butyl ethylene (TBE) as a hydrogen acceptor were attempted using a catalytic amount of (nacnac)Pt(H)(TBE) (**2d**).[14] Formation of free olefin product (ethyl vinyl ether, 2,3-dihydrofuran, and pentenes, respectively) and *t*-butyl ethane (TBA) was observed with (nacnac)Pt(H)(TBE) as the only Pt species visible by NMR.[15] A 7:1 ratio of TBE to **2d** in diethyl ether yielded 1.3 turnovers (19% yield) after 120 h at 50 °C. Similar conditions in THF yielded 1.1 turnovers. The low yields are due to catalyst decomposition over the course of the reaction. This is a rare example of catalytic dehydrogenation with Pt and the first reported transfer dehydrogenation of Et_2O.

Hydride migration appears to be the rate-limiting step since olefin exchange is facile. Equilibrium binding ratios were measured for the olefins from worst to first: ethyl vinyl ether, neohexene, cyclopentene, 2,3-dihydrofuran, *n*-pentene, ethylene: 1:1.8:2.1:4.35:7.0:58. Addition of olefin to the platinum hydride species results in a rapid shift to the equilibrium concentration of bound olefin. The ethylene complex (nacnac)Pt(H)(C_2H_4) (**2e**) displays rapid olefin rotation at room temperature, with a barrier to rotation of only 9.2 kcal/mol determined by low-temperature ^1H NMR. This is 7.5 kcal/mol lower than the corresponding ethylene rotation barrier in the methyl complex and indicates a much less sterically hindered metal center which helps to explain why ligand exchange is rapid. The facile olefin exchange is in stark contrast to the *ortho*-substituted nacnac complexes reported by Goldberg; they underwent rapid hydride migration but failed to undergo efficient olefin exchange.[5c]

In conclusion, simple ethers and alkanes undergo facile activation by reaction with nacnacH and $Me_4Pt_2(\mu\text{-}SMe_2)_2$. Activation of ethers is kinetically favored due to the associative displacement of methane, but activation of the α C−H bond is rate-limiting as demonstrated by the kinetic isotope effect. Selectivity for ether activation facilitates its dehydrogenation using an alkyl hydrogen acceptor. The lack of bulky *ortho*-substituents on the nacnac nitrogens exposes the metal center to associative olefin exchange and allows transfer dehydrogenation to occur. Resistance to hydride migration and thermal instability limits the utility of this catalyst for transfer dehydrogenation.[16]

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Supporting Information Available: Experimental details for the synthesis of complexes **1a,b** and **2a**−**d**, solvent competition reactions, kinetic isotope effect studies, transfer dehydrogenation reactions, and crystallographic data for **1a,b** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The structure of **1b** is given in the Supporting Information.

(9) Products of this nature are observed from the reaction of 2-(*N*-arylimino)-pyrrole and $Me_4Pt_2(\mu\text{-}SMe_2)_2$ in: Iverson, C. N.; Carter, C. A. G.; Baker, R. T.; Scollard, J. D.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 12674.

(10) A little (nacnac)Pt(Me)(SMe_2) is formed as a byproduct.

(11) Pentene isomers were observed after 48 h at 50 °C.

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(14) Compound **2d** was synthesized by adding excess TBE to **2c**.

(15) Olefins and TBA observed by ^1H NMR and GC.

(16) Decomposition occurs rapidly above 60 °C.

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