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C-H Bond Activation of Arenes by a Transient η^2-Cyclopropene Niobium Complex

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Understanding mechanisms by which transition-metal complexes activate hydrocarbon C−H bonds is of utmost importance if the design of well-defined catalysts for the selective functionalization of such strong and inert bonds is to be achieved.[1] Late transition-metal complexes usually cleave a C−H bond by oxidative addition[2] or electrophilic activation.[3] σ-Bond metathesis pathways were recently disclosed in arene C−H activation by Ru−X (X = OR, NHPh) and Ir−OMe bonds.[4] High valent, early transition-metal complexes activate C−H bonds via σ-bond metathesis[5] or 1,2-addition across M=N,[6] M=C,[7] and, more recently, M≡C bonds.[8] The reactive species are generated by 1,2-H or α-H abstraction reactions from alkylamido, dialkyl, or alkylalkylidene species, respectively. β-H abstraction from a high valent β-H containing dialkyl complex to yield an alkene complex and an alkane is pervasive in organometallic chemistry,[9] but it is rarely reversible, that is, it rarely leads to *inter*molecular activation of unreactive C−H bonds.[10] C−H bond activation may occur when an intermediate benzyne complex is generated, that is, from a phenyl precursor.[7d,11] We report herein synthetic, structural and mechanistic studies on the *room temperature* C−H bond activation of arenes by a transient η^2-cyclopropene niobium complex generated from a cyclopropylmethyl complex via a β-H abstraction reaction.

Treatment of the α-C−C agostic cyclopropyl complex[12] Tp^{Me2}-NbCl(*c*-C_3H_5)(MeC≡CMe) (**1**) [Tp^{Me2} = hydrotris(3,5-dimethyl)-pyrazolylborate] with LiMe yields the methylcyclopropyl complex Tp^{Me2}NbMe(*c*-C_3H_5)(MeC≡CMe) (**2**).[13] Key NMR parameters are ^{1}H signals at δ 1.23 (s, Nb*Me*) and 1.49 (m, Nb-α-C*H*) and ^{13}C signals at δ 48.7 (q, $^1J_{CH}$ 119 Hz, Nb*Me*) and 62.6 (d, $^1J_{CH}$ 139 Hz, Nb-α-*C*H). Diastereotopic Hβs and Hβ's on the *c*-C_3H_5 ring are also observed, as are Cβ (δ 20.3, t, $^1J_{CH}$ 160 Hz) and Cβ' (δ 11.5, t, $^1J_{CH}$ 156 Hz). There is no α- or β-C−H agostic interaction, and evidence for/against an α-C−C agostic interaction is lacking.

In benzene solution *at room temperature*, **2** undergoes two successive transformations (Scheme 1). In a first, faster step ($t_{1/2}$ ≈ 7 h), **2** and C_6H_6 are cleanly converted to the phenyl cyclopropyl complex Tp^{Me2}NbPh(*c*-C_3H_5)(MeC≡CMe) (**3**) and CH_4 (^{1}H NMR). Total conversion to the diphenyl complex Tp^{Me2}NbPh$_2$(MeC≡CMe) (**4**) and *c*-C_3H_6 is more conveniently achieved after 48 h at 50 °C. When toluene is used instead of benzene, ditolyl Tp^{Me2}Nb(C_6H_4-Me)$_2$(MeC≡CMe) (**5**) is obtained as a mixture of regioisomers (^{1}H and ^{13}C NMR). Under these thermodynamic conditions, no benzyl complex is observed.[14] The X-ray crystal structure of the di-*p*-tolyl complex (Figure 1) reveals Nb−C_{tolyl} bonds of 2.223(4) and 2.228-(5) Å.

There is no evidence for any agostic interaction in **3**, whether C−H or C−C. **3** (X-ray crystal structure, Figure 1) has a slightly longer Nb−C_{Ph} [2.254(4) Å] bond than **5** and a longer Nb−C_α with the cyclopropyl ring [2.196(4) Å] than that in **1** [2.159(3) Å]. The C−C bond lengths within the C3 ring are virtually equal [C(5)−C(6), 1.509(5); C(5)−C(7), 1.523(6); C(6)−C(7), 1.482(6) Å]. For

Scheme 1

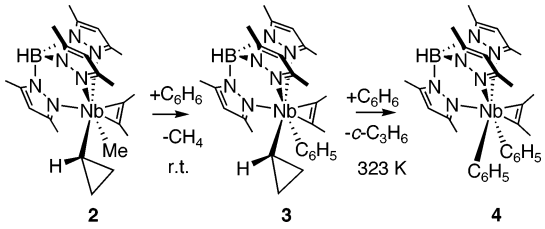
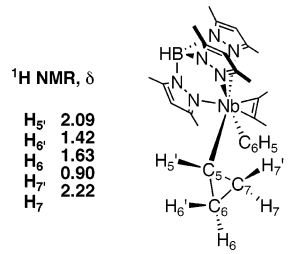


Chart 1. NMR Data for **3** (C_6D_6, 283 K)



mechanistic purposes (see below), full assignments of all protons and carbons of the cyclopropyl ring in **3** have been obtained through ^{1}H and ^{13}C NMR with HSQC and ROESY sequences (Chart 1). $^1J_{\alpha\text{-C}-\text{H}}$ of 142 Hz and $^1J_{\beta\text{-C}-\text{H}}$ of 159 Hz confirm the absence of any C−H agostic interaction.

These transformations realize two successive C−H bond activations of arenes, the first one occurring under unexpectedly mild conditions. This first reaction is totally selective: the Nb−Me bond is more reactive than the Nb−*c*-C_3H_5 bond.[6c,15] We consequently concentrated on the mechanism of this first reaction.

To understand the mechanism by which a C−H bond of benzene is activated during the conversion of **2** to **3**, we conducted kinetic studies. The disappearance of **2** was monitored by ^{1}H NMR in C_6D_{12} in the presence of C_6H_6 (5−15 equiv). The reaction is first-order in **2** and zero-order in C_6H_6 with $k = (2.93 \pm 0.05) \times 10^{-5}$ s^{-1} (303 K). Temperature-dependent studies (303−323 K) lead to activation parameters $\Delta H^\ddagger = 99 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = -6 \pm 10$ J K^{-1} mol^{-1}. Reaction of **2** with C_6D_6 in place of C_6H_6 yielded an insignificant isotope effect k_H/k_D (1.0 at 303 K). Here CH_4 was the only observed isotopomer of methane (^{1}H, ^{2}H, and ^{13}C{^{1}H} NMR). The data provide evidence for an intramolecular rate-determining CH_4 loss from **2** that generates an intermediate **A**. **A** then rapidly activates a C−H bond of C_6H_6 to give **3**. Note that heating **2** at 303 K in C_6D_{12} in the absence of benzene leads to extensive decomposition.

Evidence for the nature of intermediate **A** was obtained from careful monitoring of the reaction of **2** with C_6D_6. Thanks to the full assignments described in Chart 1, ^{1}H, ^{2}H, and ^{13}C NMR all indicate that, kinetically, incorporation of a single deuterium atom in **3-*d*$_6$** occurred selectively at either of the two Cβ at positions

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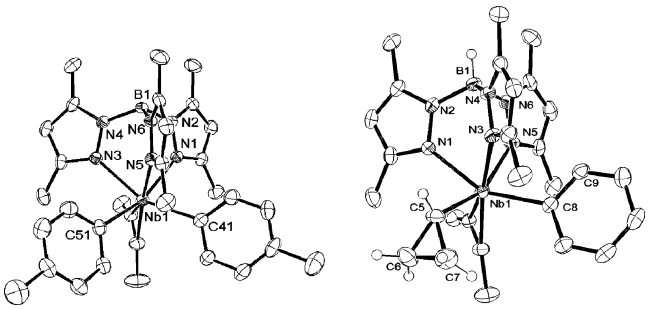
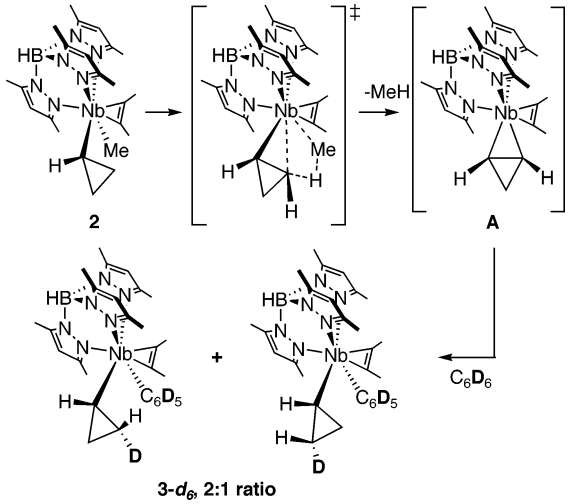


Figure 1. The molecular structures of complex **5** (left) and complex **3** (right).

Scheme 2



H/D_6 or H/D_7, that is, on the same enantioface of the cyclopropyl ring as niobium (Scheme 2). There is a slight ca. 2:1 preference for one of the two stereoisomers as shown. Indeed, after 3 h of thermolysis at 323 K, a $^{13}C\{^1H\}$ NMR spectrum at 293 K showed C6 as a singlet at δ 22.38 originating from a *C*H_2 group and, assigned to a *C*HD group, as a very broad featureless signal at higher field (δ 22.11) that narrowed upon ^2H decoupling. Associated C7 resonances, that is, *C*HD (δ 12.56) and *C*H_2 (δ 12.73), respectively, were also observed. ^2H NMR cyclopropyl resonances were only those for $^2H6$ and $^2H7$, and H6 and H7 resonances integrated for less than one H in the ^1H NMR spectrum. This conclusively establishes that **A** is an unsaturated η^2-cyclopropene complex generated from **2** by a β-H or 1,3-abstraction of CH_4. A CH/CD bond of C_6H_6/C_6D_6 then rapidly adds across a Nb−C bond of **A** in a stereospecific 1,3-fashion (Scheme 2). Very similar activation parameters to those for α-H abstraction reactions militate for a similar four-center transition state.[6−8]

The intermolecular C−H bond activation of benzene occurs under very mild conditions via a rare 1,3-H addition on an unsaturated η^2-cyclopropene intermediate generated by a β-H abstraction reaction from **2**. The more common α-H abstraction mechanism[6−8] that would yield a cyclopropylidene intermediate is not followed. Methylcyclopropyl zirconocene loses methane, but the resulting η^2-cyclopropene complex fails to activate C−H bonds of arenes.[16] Thus both the accessibility and stability of small ring cycloolefin complexes[17] might be the key to understanding the different pathways available to these early transition-metal complexes. This idea will be addressed in the near future since we have in hands a family of cycloalkyl complexes with ring size ranging from 3 to 6 carbon atoms.[12,18]

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Supporting Information Available: Details of synthesis and characterization of new complexes **2**−**5**, kinetic data (conversion of **2** to **3**), relevant NMR spectra, and crystallographic data for **3** and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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