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Does Methane Bind to d^0 $(^tBu_3SiNH)_2Zr{=}NSi^tBu_3$ Prior to C—H Bond Activation? An Inter vs Intramolecular Isotope Effect Study

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According to recent solution and gas-phase investigations, alkane complexes precede C–H bond activation via oxidative addition.[1–6] Evidence for weak adducts has been obtained primarily for d^8 complexes (e.g., Cp^*ML, M = Rh, Ir; L = PR_3, CO), where dipole–dipole interactions may be used to rationalize $L_nM\cdots RH$ bonding.[1–3] In contrast, metal–alkane bonding has not been implicated in C–H activations mediated by d^0 metal centers where oxidative addition is prohibited,[7] although its existence is supported by calculations.[8] σ-Bond metatheses (e.g., Cp^*_2MR; M = Sc, Lu)[9–13] and 1,2-RH-addition/elimination pathways involving metal imido (e.g., transient $X_{3-n}M({=}NSi^tBu_3)_n$, X = $HNSi^tBu_3$, M = Zr, $n = 1$;[14] M = V,[15] Ta,[6] $n = 2$)[16,17] and other metal–ligand multiple bonds[18] may also involve transient alkane species, since intramolecular agostic bonds are common in d^0 complexes.[19] Inter- vs intramolecular kinetic isotope effects that probe plausible methane adducts of d^0 $(^tBu_3SiNH)_2Zr{=}NSi^tBu_3$[14] are described herein.[3,20]

Elimination of CH_3D from $(^tBu_3SiND)_3ZrCH_3$ (**1**-$(ND)_3$-CH_3), and CD_3H from $(^tBu_3SiNH)_3ZrCD_3$ (**1**-CD_3) occurred in C_6H_6 and C_6D_6 to give $(^tBu_3SiNH)_3ZrC_6H_5$ (**1**-Ph) and **1**-$(ND)_3$-Ph-d_5, respectively, without measureable exchange of amido and methyl sites prior to methane loss. Labeling and kinetic studies, including primary and secondary isotope effects for methane loss (96.6 °C, k_H(**1**-CH_3)/k_D(**1**-$(ND)_3$-CH_3) = 7.3(4); k(**1**-CH_3)/k(**1**-CD_3) = 1.32(8) or 1.10/D), revealed a rate-determining 1,2-elimination mechanism. If a methane complex is an intermediate in the process, *it must succeed the elimination step.*[21]

In the presence of excess methane (≫20 equiv), $(^tBu_3SiNH)_3ZrCy$ (**1**-Cy) was thermolyzed (C_6H_{12} solvent, 95.0 °C) to induce the irreversible 1,2-elimination of cyclohexane (CyH) and generate the presumed transient $(^tBu_3SiNH)_2Zr{=}NSi^tBu_3$ (**2**, Scheme 1). Two pathways are considered for the subsequent 1,2-addition of methane isotopomers to the imido linkage: (1) **2** is scavenged by either CH_4/CD_4 or CH_nD_{4-n} in a one-step (k_3) pathway or (2) trapping of **2** occurs in a two-step (k_1k_2/k_{-1}) process via intermediate $(^tBu_3SiNH)_2{}^tBu_3SiN{=}Zr(CH_nD_{4-n})$ (**2**-CH_nD_{4-n}). The reaction was stopped at ≤20% conversion in order to ensure that the process was pseudo-first-order and uncomplicated by reversible methane addition. An H_2O/THF quench of products **1**-$CH_{n-1}D_{4-n}$ and **1**-(ND)-CH_nD_{3-n} gave CH_nD_{4-n} and $CH_{n+1}D_{3-n}$, reflecting C–H vs C–D bond activations, respectively, which were analyzed by integration of their 400-MHz ^1H NMR spectra.

Data analysis employed a conventional model:[20] (1) z_{-1}/D is the isotope effect on CH_nD_{4-n} binding to **2** (i.e., no specific methane binding orientation is implied); (2) z_{-1}/D is the isotope effect for CH_nD_{4-n} loss from **2**-CH_nD_{4-n}; (3) z_2 and z_3 are the primary isotope effects for C–H vs C–D addition in k_2 and k_3; and (4) z'_2/D and z'_3/D are the α-secondary effects for (H)C–H vs (D)C–H addition in k_2 and k_3 (i.e., all secondary effects are considered equal). In the intermolecular experiment, **2** is competitively scavenged by a set ratio of CH_4/CD_4. The CH_4/CHD_3 ratio from the quench refers to $z_3z'^3_3$ of the smooth addition model or $(z_1/z_{-1})^4z_2z'^3_2$ of the methane intermediate pathway. The intramolecular CH_2D_2 experiment serves as a contradiction; in either the methane intermediate (k_1k_2/k_{-1}) or smooth (k_3) pathway, the CH_2D_2/CH_3D ratio reflects the ratio of primary and α-secondary isotope effects, z_2/z'_2 or z_3/z'_3, respectively. Experiments involving CH_3D and CHD_3 yield analogous ratios upon factoring out statistical prefixes of 3 and 1/3, respectively.

Implicit in the large intermolecular C–H/C–D activation ratios (11.2(17), Table 1) is the rotational partition function quotient, $Q_{rot}(CD_4)/Q_{rot}(CH_4)$, which may approach the gas-phase value of 2.83.[22] A similar factor is absent in the intramolecular isotope effect because the same substrate, CH_nD_{4-n} (n = 1–3), is captured in each C-H and C-D activation event. Factoring out $Q_{rot}(CD_4)/Q_{rot}(CH_4)$ yields an intrinsic intermolecular kinetic isotope effect of 4.0, a value similar to the intramolecular cases (e.g., 5.1(6) for CH_2D_2).

Evidence was sought in order to corroborate the free rotor model for methane in cyclohexane solvent. The isotopic exchange equilibrium in eq 1 pertains to the K_H/K_D (EIE) for **2** + CH_4/CD_4 ⇌ **1**-CH_3/**1**-ND-CD_3; the experimental EIE, ignoring a

$$\underset{\textbf{1}\text{-ND-CH}_3}{(^tBu_3SiNH)_2(^tBu_3SiND)ZrCD_3} + CH_4 \rightleftharpoons \underset{\textbf{1}\text{-CH}_3}{(^tBu_3SiNH)_3ZrCH_3} + CD_4 \qquad (1)$$

statistical factor of 1/3, is 1.2 (i.e., 11.2/(7.3)(1.32)). Cundari's model species ($(H_2N)_3ZrCH_3$, $(H_2N)_2(HDN)ZrCD_3$)[8] permitted

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Scheme 1

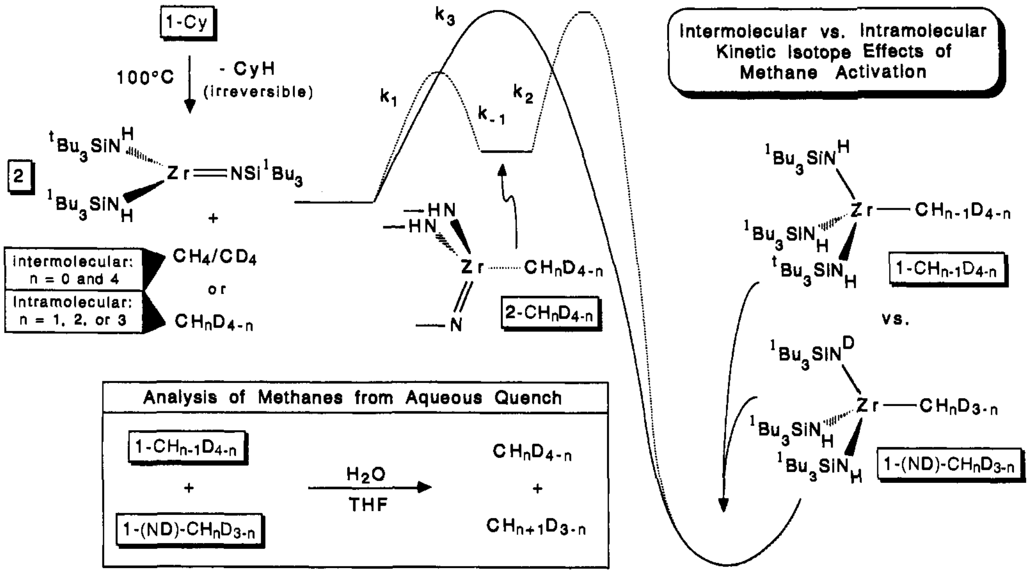

Table 1. Methane Ratios Obtained from Aqueous Quench of **1**-$CH_{n-1}D_{4-n}$/**1**-(ND)-CH_nD_{3-n} Mixtures Obtained According to Scheme 1[a]

	experiment (C*H* vs C*D*)			
	$\frac{r(\mathrm{C}H_4)}{r(\mathrm{C}D_4)}$	$\frac{r(\mathrm{C}H\mathrm{D}_3)}{r(\mathrm{CH}D_3)}$	$\frac{r(\mathrm{C}H_2\mathrm{D}_2)}{r(\mathrm{CH}_2D_2)}$	$\frac{r(\mathrm{C}H_3\mathrm{D})}{r(\mathrm{CH}_3D)}$
trial 1	9.4	6.3[b]	5.7	4.6[c]
trial 2	12.8	6.3[b]	4.6	3.0[c]
trial 3	11.4	5.7[b]	4.9	4.3[c]
trial 4				3.7[c]
trial 5				3.0[c]
av	11.2(17)	6.1(3)[b]	5.1(6)	3.7(7)[c]
		KIE predictions		
k_3 pathway	$z_3z'^3_3$	$(1/3)z_3/z'_3$	z_3/z'_3	$(3)z_3/z'_3$
k_1k_2/k_{-1} pathway	$(z_1/z_{-1})^4z_2z'^3_2$	$(1/3)z_2/z'_2$	z_2/z'_2	$(3)z_2/z'_2$

[a] Methane ratios obtained at ≤20% conversion to limit the role of reversible methane addition. [b] The statistical prefix of (1/3) has been factored out. [c] The statistical prefix of (3) has been factored out.

a rough statistical mechanics calculation of the EIE, as described recently by Goldman *et al.* for methane addition to Vaska's complex.[23] Including $Q_{\mathrm{rot}}(CD_4)/Q_{\mathrm{rot}}(CH_4) = 2.83$ and assuming $\{Q_{\mathrm{tr}}(\mathbf{1}\text{-}CH_3)Q_{\mathrm{tr}}(CD_4)/Q_{\mathrm{tr}}(\mathbf{1}\text{-ND-}CD_3)Q_{\mathrm{tr}}(CH_4)\} \sim 1$ in solution (gas phase, 1.40),[23] the calculated EIE value is 1.2, a value somewhat fortuitous given the crude models; however, CH_4 and CD_4 clearly approximate slightly hindered free rotors in cyclohexane.[22]

The intermolecular/intramolecular C–H vs C–D activation ratio for the k_3 pathway corresponds to $(z_3z'^3_3)/(z_3/z'_3)$ or z'^4_3, neglecting statistical factors; factoring out $Q_{\mathrm{rot}}(CD_4)/Q_{\mathrm{rot}}(CH_4)$ and using the CH_2D_2 intramolecular numbers, $z'^4_3 \geq 4.0/5.1 = 0.78$ or $z'_3 \geq 0.94$. If the k_1k_2/k_{-1} sequence is similarly scrutinized, the intermolecular/intramolecular C–H vs C–D activation ratio is $(z_1/z_{-1})^4z'^4_2 \gtrsim 0.78$, reflecting the product of methane binding and α-secondary effects. Since relatively small α-secondary isotope effects (∼1.0) are expected for the activation step,[24] methane binding is not sufficiently strong to be evident in this study. Although both mechanisms are still plausible, Occam's razor favors the *smooth activation pathway*, despite calculational results which place an η^2-CH_4 complex ∼9 kcal/mol lower in enthalpy than **2** and CH_4.[8] The CHD_3, CH_2D_2, and CH_3D intramolecular ratios are statistically different within 95% confidence (ANOVA test),[25] hence a more complicated model of the reaction pathway (e.g., differing α-secondary KIE's) may prove necessary for a full understanding of the C–H/D activation process.

Late and early metal systems share an important common feature: a metal center electrophilic enough to polarize the C–H bond, rendering it susceptible to cleavage.[6] A plausible difference concerns the position of alkane complexes along the reaction coordinate and the strength of this interaction.[26] These experimental results reemphasize[24] the need to thoroughly analyze, and augment via calculation, interpretations of kinetic and equilibrium isotope effects, especially those pertaining to small (e.g., H_2/D_2, CH_4/CD_4) or "flat" (e.g., C_6H_6/C_6D_6, C_2H_4/C_2D_4) substrates.[22]

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Supplementary Material Available: Experimental details: methane scavenging procedures, ^{1}H NMR spectral aquisition parameters and representative spectrum, a brief kinetics analysis, and results of the ANOVA test (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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