Energetics of C—H Bond Activation and Ethylene Binding to d^0 Transient (silox)$_2$Ti=NSi^{t}Bu$_3$

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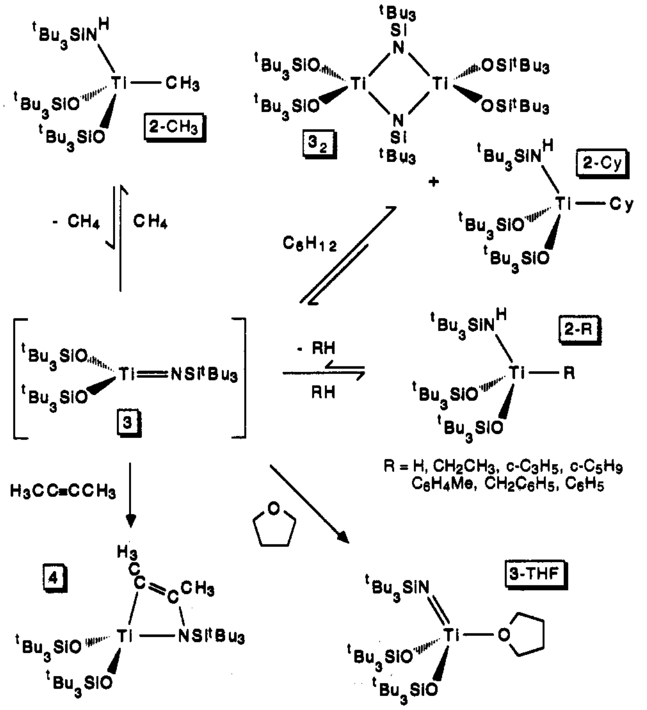
Received September 13, 1993

Current interest in the reactivity of early transition metal–ligand multiple bonds,[1] specifically those of metal–imido complexes,[2] has centered around the 1,2-addition of various substrates to the M=N bond.[3–13] Transient, electrophilic group 4 (e.g., Cp$_2$Zr=NR,[3–6] (^{t}Bu$_3$SiNH)$_2$Zr=NSi^{t}Bu$_3$,[7] (^{t}Bu$_3$SiNH)XTi=NSi^{t}Bu$_3$)[8] and 5 (e.g., (^{t}Bu$_3$SiNH)M(=NSi^{t}Bu$_3$)$_2$, M = Ta,[9] V)[10,11] complexes containing imido functionalities have exhibited intriguing alkane[7,9,11] and arene activations[3–11] of theoretical interest,[16] 2 + 2 cycloadditions,[3–6,10,13] catalytic amination of alkynes,[5] and corresponding adduct chemistry.[3–17] Reported herein is a chemically diverse titanium imido system, developed through inclusion of ancillary silox (^{t}Bu$_3$SiO$^-$) ligands.

Chloride (silox)$_2$(^{t}Bu$_3$SiNH)TiCl (**1**)[18] was prepared in 76% yield by sequential, stoichiometric additions of Na(silox) and ^{t}Bu$_3$SiNHLi to TiCl$_4$(THF)$_2$. Alkylation (i.e., RLi, RMgX) of **1** afforded colorless (silox)$_2$(^{t}Bu$_3$SiNH)TiR (**2-R**, R = Me (76%), Et (51%), CH$_2$Ph (yellow, 58%),[18] Vy = CH=CH$_2$ (30%)).[19] 1,2-RH-Elimination from **2-R** in C$_6$D$_6$ gave (silox)$_2$(^{t}Bu$_3$SiND)TiC$_6$D$_5$ (**2-(ND)-C$_6$D$_5$**), but with lower activation energies vis-à-vis (^{t}Bu$_3$SiNH)$_3$ZrR (e.g., R = Me, $\Delta G^{\ddagger}$(25 °C) = 28.0 kcal/mol),[7] presumably due to weaker Ti–C bonds. Activation parameters for rate-determining CH$_4$ loss from **2-Me** (24.8 °C, k_{MeH} = 1.54(10) × 10^{-5} s^{-1}; 24.8–71.3 °C, $\Delta G^{\ddagger}$ = 24.0(1), $\Delta H^{\ddagger}$ = 20.2(12) kcal/mol, $\Delta S^{\ddagger}$ = −12(4) eu) fit the established four-center mechanism.[7–11] Benzene loss from **2-Ph**[18] (24.8 °C, k_{PhH} = 3.33(3) × 10^{-4} s^{-1}, $\Delta G^{\ddagger}$ = 22.2(1) kcal/mol) was again markedly swifter, just as toluene elimination from **2-CH$_2$Ph** proved slowest (24.8 °C, k_{BzH} = 8.6(6) × 10^{-7} s^{-1}, $\Delta G^{\ddagger}$ = 25.7(1) kcal/mol).

Scheme 1



Scheme 1 illustrates the generation and diverse reactivity of putative three-coordinate (silox)$_2$Ti=NSi^{t}Bu$_3$ (**3**). Thermolysis of (silox)$_2$(^{t}Bu$_3$SiNH)TiR (e.g., **2-CH$_3$**) in cyclohexane afforded a mixture of **2-Cy** and [(silox)$_2$TiNSi^{t}Bu$_3$]$_n$, formulated on steric grounds as a dimer (n = 2), **3$_2$**.[19] Secondary C–H bond activation of cyclo-C$_6$H$_{12}$ solvent, unobserved in previous Ti, Zr, and Ta imido systems, was barely competitive with dimerization of **3**; more hindered bonds (e.g., CMe$_4$, HCMe$_3$) were inert. Dihydrogen (3 atm, 60 °C) scavenged **3** in cyclohexane to afford a rare terminal hydride complex, (silox)$_2$(^{t}Bu$_3$SiNH)TiH (**2-H**: ^{1}H NMR δ 8.62 (TiH); IR ν(Ti–H/D) = 1645/1185 cm^{-1}),[18] and NMR tube scale experiments indicated that methane, ethane, cyclopropane, cyclopentane, toluene (H–Ar and H–CH$_2$Ph), and benzene all undergo 1,2-RH-addition to **3**.[18,19] In THF, **2-R** was smoothly converted to (silox)$_2$(THF)Ti=NSi^{t}Bu$_3$ (**3-THF**),[18] which did not revert to **2-R** in the presence of excess RH. Similarly, 2 + 2 cycloaddition product (silox)$_2$TiC(Me)=C(Me)NSi^{t}Bu$_3$ (**4**)[18] was irreversibly generated from **2-R** and 2-butyne in cyclohexane.

Equilibria between many of these compounds can be *directly measured*, and when these are combined with kinetic data, standard free energy diagrams for reactant pairs can be composed. Assessment of equilibria (**2-Me** + PhH $\rightleftharpoons$ **2-Ph** + MeH, $\Delta G°$ = 0.84(3) kcal/mol; **2-Me** + PhCH$_3$ $\rightleftharpoons$ **2-CH$_2$Ph** + MeH, $\Delta G°$ = −0.11(2) kcal/mol; **2-Ph** + PhCH$_3$ $\rightleftharpoons$ **2-CH$_2$Ph** + PhH, $\Delta G°$ = −0.96(1) kcal/mol) and kinetic data revealed that benzene C–H bond addition by **3** is kinetically favored ($\Delta\Delta G^{\ddagger}$) by 1.0(1) kcal/mol over CH$_4$ and by 2.6(1) kcal/mol over benzylic activation of toluene; likewise, methane C–H bond capture is favored by 1.6(1) kcal/mol over H–CH$_2$Ph addition.

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[18] Corresponding ^{1}H and ^{13}C{^{1}H} NMR data and satisfactory C, H, and N analyses have been obtained for **1**, **2-R** (R = Me, Et, Bz, Ph, H), **3**, and **4**; %N was low for **2-Me** and **2-H**.

[19] Corresponding ^{1}H and ^{13}C{^{1}H} NMR data have been obtained for **2-R** (R = Vy, Cy (no ^{13}C{^{1}H} NMR spectrum due to low solubility), cyclo-C$_3$H$_5$, cyclo-C$_5$H$_9$), **3$_2$**, and **5**. Prepared via metathesis, **2-Vy** is ~95% pure by NMR.

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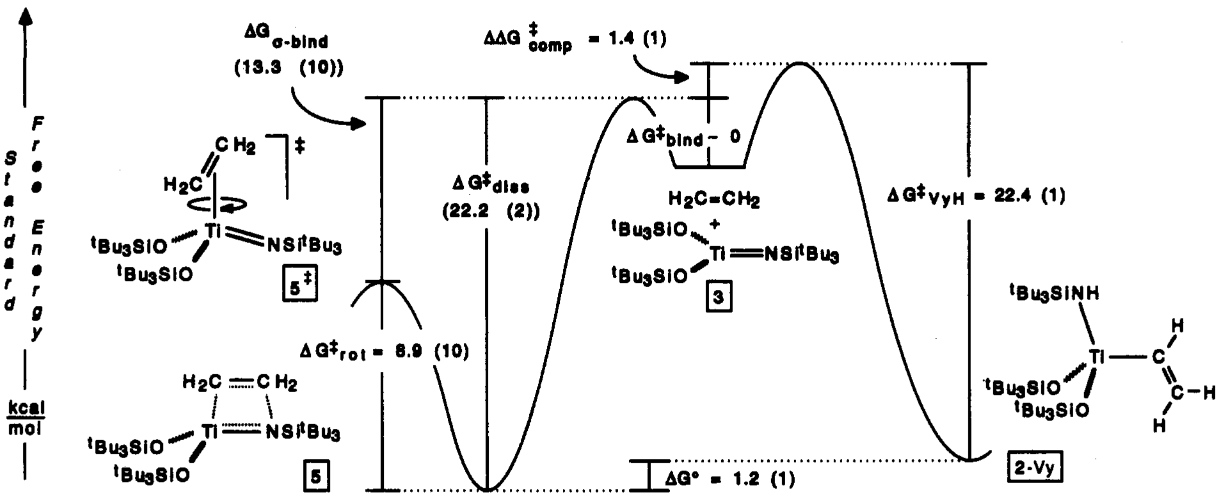

Figure 1. Standard free energy diagram (25 °C) for equilibration of $(\text{silox})_2\overline{\text{TiCH}_2\text{CH}_2\text{N}}\text{Si}^t\text{Bu}_3$ (**5**) and $(\text{silox})_2(^t\text{Bu}_3\text{SiNH})\text{TiCH}{=}\text{CH}_2$ (**2**-Vy) via $(\text{silox})_2\text{Ti}{=}\text{NSi}^t\text{Bu}_3$ (**3**) and ethylene.[21–23] Calculated values are in parentheses.

At early conversion, scavenging of transient $(\text{silox})_2\text{Ti}{=}\text{NSi}^t\text{Bu}_3$ (**3**) by C_2H_4 yielded a ~8:92 ratio ($\Delta\Delta G^{\ddagger}_{\text{comp}} = 1.4(1)$ kcal/mol, Figure 1) of the C–H bond activation product **2**-Vy and azametallacycle $(\text{silox})_2\overline{\text{TiCH}_2\text{CH}_2\text{N}}\text{Si}^t\text{Bu}_3$ (**5**).[19,20] Equilibrium measurements (**5** $\rightleftharpoons$ **2**-Vy, $\Delta G°(25\ °\text{C}) = 1.2(1)$, $\Delta H° = 5.72(11)$ kcal/mol, $\Delta S° = 15.2(3)$ eu), when combined with $\Delta\Delta G^{\ddagger}_{\text{comp}}$ and the $\Delta G^{\ddagger}_{\text{VyH}} = 22.4(1)$ kcal/mol for C_2H_4 elimination from **2**-Vy (25 °C, $k_{\text{VyH}} = 2.39(4) \times 10^{-4}\ \text{s}^{-1}$), allow calculation of $\Delta G^{\ddagger}_{\text{diss}} = 22.2(2)$ kcal/mol for C_2H_4 loss from **5**.[21,22]

^{1}H NMR spectra of **5** revealed a broad singlet at δ 3.09 (20 °C) that split into two methylene multiplets at δ 3.60 and 2.57 when cooled to −130 °C. Line-shape analysis of this fluxional process (C_7D_{14}, −130 °C to 20 °C, $\Delta G^{\ddagger}(25\ °\text{C}) = 8.9(10)$ kcal/mol) revealed a significant enthalpic barrier ($\Delta H^{\ddagger} = 7.9(4)$ kcal/mol) accompanied by a minimal entropic contribution ($\Delta S^{\ddagger} = -3(2)$ eu). The activation parameters were unchanged with 10 equiv of free C_2H_4 present, and no involvement of free olefin was spectroscopically detected below 20 °C, discrediting an associative mechanism. Ethylene rotation equilibrates the methylenes,[6,10] with loss of $d\pi(\text{Ti}{=}\text{N}) \rightarrow p\pi^*(\text{C}{=}\text{C})$ bonding a likely consequence. At the transition state for methylene equilibration, assume the ethylene to be bound solely by a $\pi^b(\text{C}{=}\text{C}) \rightarrow \text{Ti}(d\sigma)$ interaction (e.g., $(\text{silox})_2(\text{H}_2\text{C}{=}\text{CH}_2)\text{Ti}{=}\text{NSi}^t\text{Bu}_3$ ($\mathbf{5}^{\ddagger}$)).[23] As Figure 1 illustrates, if $\Delta G^{\ddagger}_{\text{bind}}$ for the scavenging of C_2H_4 by **3** is ~0 kcal/mol, then the free energy attributed to the purely σ interaction of the ethylene is $\Delta G_{\sigma\text{-bind}} = 13.3$ kcal/mol. An analogous enthalpy diagram (assuming $\Delta S^{\ddagger}_{\text{VyH}} \sim \Delta S^{\ddagger}_{\text{MeH}}$, $\Delta\Delta S^{\ddagger}_{\text{comp}} \sim 0$ kcal/mol) yields an approximate ethylene binding enthalpy: $\Delta H_{\sigma\text{-bind}} = 15.2$ kcal/mol. It is not necessary for $\mathbf{5}^{\ddagger}$ to be on the path toward **5** for these estimates to hold. Given Cundari's calculation of the equivalent $\Delta H^{\ddagger}_{\text{bind}} \sim 4.4$ kcal/mol for CH_4,[16,23] a more reasonable approximation of these values is $\Delta H_{\sigma\text{-bind}} \sim 11$ kcal/mol and $\Delta G_{\sigma\text{-bind}} \sim 9$ kcal/mol. Similar energetics are implicated in the $[(\text{RO})_2\text{XW}{=}\text{CR}_2(\text{olefin})]^+$ (X = halide) complexes of Kress and Osborn.[24]

Despite the small covalent radius of titanium (1.32 Å), the typically linear nature of the M–O–Si linkage has enabled the electrophilic center of $(\text{silox})_2\text{Ti}{=}\text{NSi}^t\text{Bu}_3$ (**3**) to accommodate a wide variety of substrates. A comprehensive investigation of the energetics of C–H bond activation and adduct formation will allow direct comparison with known late metal systems.[25] Such comparisons are imperative if the mechanism(s) by which C–H bonds are broken are to be fully understood. The inference of a significant d^0 Ti–ethylene σ-bond in $\mathbf{5}^{\ddagger}$ lends credence to Cossee–Arlman pathways containing d^0-olefin intermediates (i.e., $L_nM(\eta\text{-}C_2H_4)P$, P is the growing polymer chain).[26] Likewise, the stability and fluxionality of azametallacyclobutane **5** suggest that 2 + 2 (e.g., $L_n\text{Os}{=}\text{O}$ + olefin) complexes are viable intermediates in the dihydroxylation of olefins; recent calculations support this premise.[27]

Acknowledgment. We thank the National Science Foundation and Cornell University for support of this research.

Supplementary Material Available: Experimental details for kinetics measurements and syntheses of **1**, **2**-R (R = Me, Et, CH_2Ph, Vy, Ph, H), **3**-THF, **4**, and **5**, and spectral data of all complexes (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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(21) Initial rate studies of C_2H_4 loss from **5** ($\Delta G^{\ddagger}_{\text{diss}} = 22.1\ (2)$ kcal/mol) corroborate the calculated value.

(22) Alternatively, $\Delta G^{\ddagger}_{\text{diss}}$ describes the conversion of **5** to a σ-bound C_2H_4 complex, $(\text{silox})_2(^t\text{Bu}_3\text{SiN}{=})\text{Ti}(\sigma,\eta^2\text{-H}_2\text{C}{=}\text{CH}_2)$, rather than **3** and free C_2H_4. In either case, the Ti–ethylene $\sigma(\pi^b)$- and π-bonds have been totally broken, thus the energetic estimates are the same.

(23) The transition state for methylene equilibration need not be $\mathbf{5}^{\ddagger}$; this assumption ($\Delta G^{\ddagger}_{\text{rot}} = \Delta G^{\ddagger}$ for methylene equilibration) renders the minimum $\Delta G_{\sigma\text{-bind}}$ and $\Delta H_{\sigma\text{-bind}}$ values.

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