plexes exhibit a rich, controllable, and potentially useful range of chemistry. These studies also suggest that it may be possible to generate elusive isoelectronic Zr=O complexes, which are likely to be even more reactive than their imido analogues. The azametallacyclobutenes **4-6** can be viewed as 1,3-enamine dianion synthons, which raises the possibility of developing applications of this chemistry to organic synthesis through selective insertion of unsaturated molecules into the Zr-N or Zr-C bonds of these complexes. Efforts aimed at achieving these goals are under way.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1a-c**, **2a**, **3b**, **4a-c**, **5bc**, **6b**, **8a-c**, and **9b** and details of the structure determination for complexes **2a** and **9b**, including experimental description, ORTEP drawings showing full atomic numbering and packing in the crystal, crystal and data collection parameters, general temperature factor expressions (B's), positional parameters and their estimated standard deviations, and intramolecular distances and angles (35 pages); tables of observed and calculated structure factors for **2a** and **9a** (24 pages). Ordering information is given on any current masthead page.

Methane and Benzene Activation via Transient $(t\text{-Bu}_3\text{SiNH})_2\text{Zr}{=}\text{NSi-}t\text{-Bu}_3$

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Over the past decade, the activation of carbon-hydrogen bonds by transition-metal complexes has undergone intense investigation,[1] Alkane dehydrogenations,[2] discrete RH oxidative additions,[3] free-radical processes,[4] and σ-bond metatheses[5] comprise most of the reactivity investigated. Reactions of alkanes with multiply bonded functionalities (e.g., $L_nM{=}X$, X = O,[6] NR,[7] CR_2,[8,9] etc.) are rare yet constitute an important class of transformations related to the partial oxidation[10] or functionalization[11] of unactivated C-H bonds. During the course of assessing the utility of $t\text{-Bu}_3\text{SiNH}^-$ as an ancillary ligand related to $t\text{-Bu}_3\text{SiO}^-$ (silox),[12] a mode of *intermolecular* C-H activation involving addition across a transient zirconium imide was discovered.

Treatment of $ZrCl_4$ with 3 equiv of $t\text{-Bu}_3\text{SiNHLi}$, prepared from n-BuLi and $t\text{-Bu}_3\text{SiNH}_2$,[13] resulted in the formation of $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCl}$ (**1**, eq 1)[14] in 88% yield. Alkylation[15] of **1** with appropriate Grignard reagents yielded white crystals of the methyl, phenyl, and cyclohexyl (Cy) derivatives, $(t\text{-Bu}_3\text{SiNH})_3\text{ZrR}$ (R = Me, **2**, 91%;[16] Ph, **3**, 32%;[17] Cy, **4**, 47%;[18] eq 2).[19]

$$ZrCl_4 + 3\,t\text{-Bu}_3\text{SiNHLi} \xrightarrow[-3\text{LiCl}]{\text{Et}_2\text{O}} \underset{\mathbf{1}}{(t\text{-Bu}_3\text{SiNH})_3\text{ZrCl}} \quad (1)$$

$$\underset{\mathbf{1}}{(t\text{-Bu}_3\text{SiNH})_3\text{ZrCl}} + \text{RMgX} \xrightarrow[-\text{MgClX}]{\text{Et}_2\text{O}} (t\text{-Bu}_3\text{SiNH})_3\text{ZrR} \quad (2)$$

R = Me, **2**; Ph, **3**; Cy, **4**

Thermolysis of each alkyl complex (Scheme I) led to C-H bond activation. In benzene solution, $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCH}_3$ (**2**) formed $(t\text{-Bu}_3\text{SiNH})_3\text{ZrPh}$ (**3**) concomitant with the release of CH_4. In C_6D_6, 1.0 equiv of CH_4 was generated, and the rate of reaction was first-order in **2** and zero-order in benzene (>40 equiv) as monitored by ^{1}H NMR spectroscopy. The final product, $(t\text{-Bu}_3\text{SiND})_3\text{ZrC}_6\text{D}_5$ (**3**-$(ND)_3$-d_5), was deuterated in *both* the amido and phenyl positions. When $(t\text{-Bu}_3\text{SiND})_3\text{ZrCH}_3$ (**2**-$(ND)_3$) was heated in C_6H_6, 0.9 equiv of CH_3D (>93% d_1 by NMR) was produced along with **3**. The labeling and kinetics experiments are consistent with a rate-determining abstraction of an amido proton[7] by the methyl group, leading to an intermediate imido complex, $(t\text{-Bu}_3\text{SiNH})_2\text{Zr}{=}\text{NSi-}t\text{-Bu}_3$ (**5**).[20] Subsequent addition

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(14) **1**: ^{1}H NMR (C_6D_6) δ 1.24 (s, t-Bu, 81 H), 4.89 (s, NH, 3 H); ^{13}C{^{1}H} NMR δ 23.32 (SiC), 30.93 (CH_3). Anal. Calcd for $ZrSi_3ClN_3C_{36}H_{84}$: C, 56.15; H, 11.00; N, 5.46. Found: C, 55.91; H, 10.93; N, 5.36.

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(16) **2**: ^{1}H NMR (C_6D_6) δ 0.63 (s, $ZrCH_3$, 3 H), 1.24 (s, t-Bu, 81 H), 4.10 (s, NH, 3 H); ^{13}C{^{1}H} NMR δ 23.24 (SiC), 28.68 (ZrC), 30.92 (CH_3). The pseudo-tetrahedral geometry ascribed to **2** has been confirmed by X-ray structural studies: Harpp, K. S.; Cummins, C. C.; Van Duyne, G. D.; Wolczanski, P. T. Unpublished results.

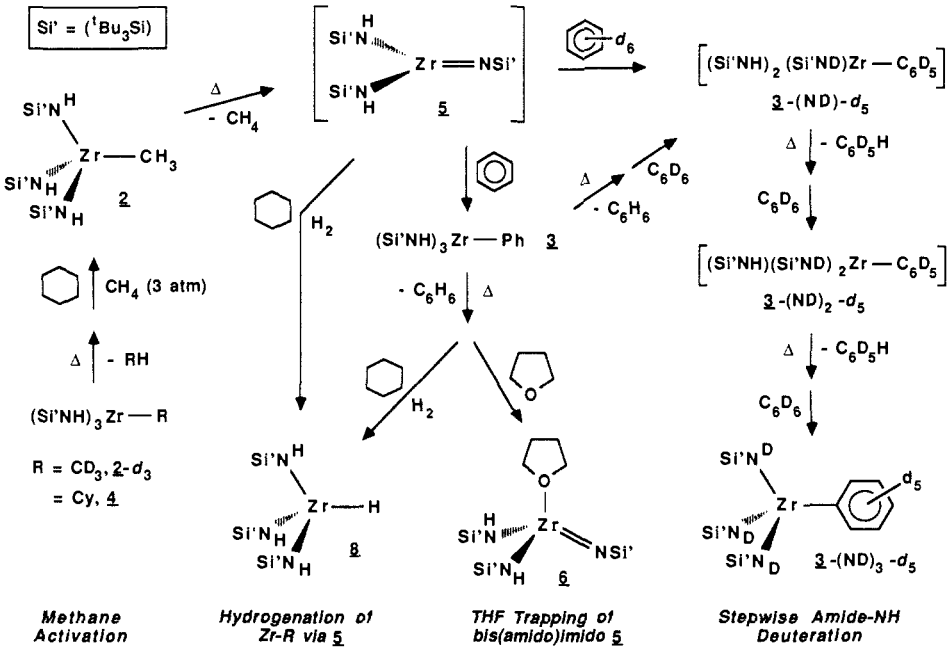
(17) **3**, 59% yield from **2** and C_6H_6 (>95% by ^{1}H NMR): ^{1}H NMR (C_6D_6) δ 1.25 (s, t-Bu, 81 H), 4.50 (s, NH, 3 H), 7.17 (tm, Ph(p), 1 H, ^3J = 7 Hz), 7.31 ("t"m, Ph(m), 2 H, $^3J_{para} = {}^3J_{ortho}$ = 7 Hz), 8.28 (dm, Ph(o), 2 H, ^3J = 7 Hz); ^{13}C{^{1}H} NMR δ 23.68 (SiC), 31.27 (CH_3), 127.18 (Ph), 128.60 (Ph(p)), 138.77 (Ph), 180.29 (Ph(ipso)).

(18) **4**: ^{1}H NMR (C_6D_6) δ 1.26 (s, t-Bu, 81 H), 1.39 (m, Cy, 4 H), 1.90 (m, Cy, 4 H), 2.69 ("d", Cy, 2 H, J = 13 Hz); ^{13}C{^{1}H} NMR δ 23.15 (SiC), 28.03 (δ-Cy), 30.93 (CH_3), 31.05 (γ-Cy), 36.05 (β-Cy), 68.24 (α-Cy).

(19) Combustion analyses of crystalline samples of complexes **2-8** proved unsatisfactory.

0002-7863/88/1510-8731$01.50/0

Scheme I



of a benzene C–H bond across the Zr=N linkage[21] generates the phenyl species **3**. Activation parameters (87.1–127.1 °C) associated with CH_4 extrusion (96.6 °C, $k_{MeH} = 1.06\ (2) \times 10^{-4}\ s^{-1}$) indicate substantial Zr–C bond breaking ($\Delta H^{\ddagger} = 25.9\ (4)$ Kcal/mol) in a relatively constrained transition state ($\Delta S^{\ddagger} = -7\ (1)$ eu). The large k_H/k_D of 7.3 (4) associated with NH vs ND abstraction is similar to those observed for related reactions.[8,22,23] Intermediate **5** was trapped as a THF adduct, $(t\text{-Bu}_3\text{SiNH})_2(\text{THF})\text{Zr=NSi-}t\text{-Bu}_3$ (**6**, >95%, ^{1}H NMR; 81% yield),[24] when the phenyl complex **3** was heated for 45 min in THF.

The intermediacy of bis(amido)imido **5** is also consistent with the deuteration of amido protons during the course of C_6D_6 activation. During the thermolysis of $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCH}_3$ (**2**) in C_6D_6, a single NH resonance of the phenyl derivative was observed (^{1}H NMR) to grow in and then recede. By monitoring this signal, attributed to intermediates $(t\text{-Bu}_3\text{SiNH})_2(t\text{-Bu}_3\text{SiND})\text{ZrC}_6\text{D}_5$ (**3**-(ND)-d_5) and $(t\text{-Bu}_3\text{SiNH})(t\text{-Bu}_3\text{SiND})_2\text{ZrC}_6\text{D}_5$ (**3**-$(\text{ND})_2$-d_5), the rate constant for elimination of C_6D_5H from the latter can be determined (96.6 °C, $k = 7.1 \times 10^{-4}\ s^{-1}$) by using the methane extrusion rate above.[25] Consistent with this observation is the rate of C_6H_6 elimination (96.7 °C, $k_{PhH} = 2.26\ (2) \times 10^{-3}\ s^{-1}$) from $(t\text{-Bu}_3\text{SiNH})_3\text{ZrPh}$ (**3**) in C_6D_6, which is three times faster due to the statistical factor ascribed to the three amido protons.

Cyclohexane served as a useful inert solvent, since its secondary C–H bonds were not attacked, presumably for steric reasons.[6] Extended heating of $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCH}_3$ (**2**) in C_6H_{12} revealed the presence of a cyclometalation product,[26,27] $(t\text{-Bu}_3\text{SiNH})_2\text{ZrN(H)Si-}t\text{-Bu}_2\text{CMe}_2\text{CH}_2$ (**7**),[28] which could be prepared in near quantitative yield via solid-state thermolysis (eq 3). When $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCD}_3$ (**2**-d_3) was heated in C_6D_{12} with

$$(t\text{-Bu}_3\text{SiNH})_3\text{ZrCH}_3 \xrightarrow[\text{solid state}]{\text{2.5 days, 120 °C}} (t\text{-Bu}_3\text{SiNH})_2\text{ZrN(H)Si-}t\text{-Bu}_2\text{CMe}_2\text{CH}_2 + \text{CH}_4 \quad (3)$$

2 **7**

CH_4 (3 atm) present, **2** was generated in addition to CD_3H, indicative of *methane activation* by the transient imido species **5**. In C_6D_{12}, treatment of $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCy}$ (**4**) with methane (3 atm) led to the quantitative formation (^{1}H NMR) of $(t\text{-Bu}_3\text{SiNH})_3\text{ZrCH}_3$ (**2**). Furthermore, the extrusion of CyH from **4** in C_6D_6, leading to **3**-$(\text{ND})_3$-d_5, occurred about ten times faster (96.7 °C, $k_{CyH} = 1.04\ (1) \times 10^{-3}\ s^{-1}$) than the corresponding methane loss from **2**. Considering steric influences, the cyclohexyl complex **4** may be destabilized relative to **2**. Each alkyl species (**2**, **3**, **4** and **7**), when exposed to 3 atm of H_2 in C_6H_{12}, was converted to the hydride $(t\text{-Bu}_3\text{SiNH})_3\text{ZrH}$ (**8**), characterized by a singlet at δ 9.60 in the ^{1}H NMR and a Zr–H stretch at 1553 cm^{-1} (ν(Zr–D) = 1117 cm^{-1}).[29] Hydride **8** again resulted from trapping of the bis(amido)imido (**5**), since D_2 treatment of precursor **2** yielded CH_4 and $(t\text{-Bu}_3\text{SiNH})_2(t\text{-Bu}_3\text{SiND})\text{ZrD}$ (**8**-(ND)-*d*), which exhibited further deuteration of its amido sites upon further heating.

Typically, an early transition-metal imido ligand forms a stable

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(28) **7**: ^{1}H NMR (C_6D_6) δ 1.22 (s, Si-*t*-Bu_2, 18 H), 1.24 (s, Si-*t*-Bu_3, 54 H), 1.42 (s, CH_2, 2 H), 1.57 (s, $C(CH_3)_2$, 6 H), 3.67 (s, NH, 2 H), 3.97 (s, NH, 1 H); ^{13}C{^{1}H} NMR δ 23.13 ($SiC(CH_3)_3$)$_3$, 23.32 ($C(CH_3)_2$), 23.49 ($SiC(CH_3)_3$)$_2$, 30.17 ($SiC(CH_3)_3$)$_2$, 31.04 ($SiC(CH_3)_3$)$_3$, 35.34 ($C(CH_3)_2$), 74.89 (CH_2) (see ref 19).

(29) **8**: ^{1}H NMR (C_6D_6) δ 1.25 (s, *t*-Bu, 81 H), 4.87 (s, NH, 3 H), 9.60 (s, ZrH, 1 H); ^{13}C{^{1}H} NMR δ 22.91 (SiC), 30.84 (CH_3); IR (C_6H_{12}) ν(ZrH/D) = 1553/1117 cm^{-1} (see ref 19).

triple bond.[30] In **5**, pπ–dπ bonds perpendicular to and in the pseudo-trigonal plane are possible, but the latter interaction may be weak due to the disparity in energy between the nitrogen 2p orbital and the Zr dp-hybrid that is characteristically σ*. The resulting electron density on N combined with the electrophilicity of a three-coordinate zirconium center enables the polarization of a C–H bond, rendering it susceptible to activation. Ground-state steric arguments provide an explanation for CyH vs MeH extrusion rates, but the relatively rapid and reversible PhH loss from **3** may be a consequence of transition-state stabilization by the Ph group. Theoretical investigations of **5** and further substrate and mechanistic studies focusing on the relationship of these activations to related heterogeneous processes utilizing metal oxides,[10] such as the ammoxidation of propylene,[31] are ongoing.

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Supplementary Material Available: Synthetic procedures for amido complexes **1–4** and full analytical data (2 pages). Ordering information is given on any current masthead page.

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Isolation and Structure of the Novel Dihydroxamate Siderophore Alcaligin

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Iron is an essential element for the growth of microorganisms. In an oxidative environment, iron exists mainly as colloidal aggregates of ferric hydroxide, which microorganisms cannot take up. Many bacteria, fungi, and phytoplankton living in aerobic environments are known to excrete siderophores to chelate insoluble iron.[1] Siderophores are virtually specific for ferric iron, have low affinity for ferrous iron, and are not produced when iron is available to the microorganisms. Such chelators are generally classified into two main groups from their structures, e.g., secondary hydroxamic acids and catechols.[1]

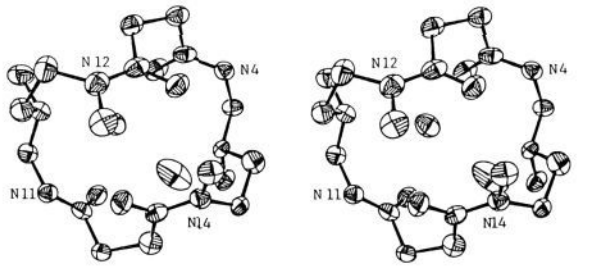

Figure 1. Stereoview of alcaligin. Selected bond lengths (Å) and angles (deg), errors in last digit shown in parentheses. Lengths: O3–C21, 1.235 (7); O9–C18, 1.241 (8); O5–C16, 1.424 (7); O1–N14, 1.383 (6); N4–C18, 1.335 (8); N4–C25, 1.486 (8); N14–C17, 1.346 (7), N14–C13, 1.458 (7). Angles: O2–C17–N14, 121.42 (50); O1–N14–C17, 118.12 (43); C14–C13–C15, 111.34 (45); C25–N4–C18, 121.35 (49); O5–C16–C25, 109.75 (44); O9–C18–N4, 121.17 (59); O3–C21–C30, 119.69 (54); O1–N14–C13, 113.65 (41).

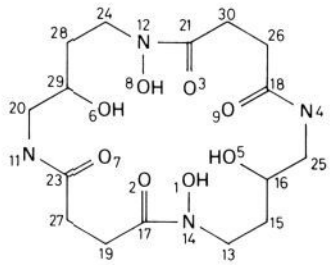

Figure 2. Structure of alcalignin.

Among hundreds of heterotrophic bacteria isolated from sediments of a lagoon near lake Biwa, Japan, a bacterium, *Alcaligenes denitrificans* subsp. *xylosoxydans* KN 3-1, giving a positive reaction for a bioassay for hydroxamate siderophore[3] was selected. *A. denitrificans* KN 3-1 excreted the siderophore into the culture fluid of TTG medium (contained 5 g of Tripticase peptone (BBL), 0.5 g of yeast extract (Difco), and 20 g of glucose (Nakarai) in 1 L of tap water) after its mid-logarithmic growth phase over a 2-week period. The final yield of the siderophore was ca. 1.3 mM in a 10-day-old culture fluid. A siderophore designated alcaligin was isolated and purified from 7- to 10-day-old culture fluid by the following procedure: the culture fluid was applied on Dowex 1×4 (base form) and eluted with 2 M of NaCl. The eluate was adjusted to pH 7, saturated with ammonium sulfate, and extracted with the benzyl alcohol–ether procedure,[4] and gel permeation chromatography on a BioGel P-2 column (2.6 × 90 cm) was performed with aqueous concentrate. The alcaligin fractions detected by adding $FeCl_3$ solution were pooled, and the alcaligin was crystallized from water. The recovery of alcaligin through an overall procedure of isolation was about 20%, corresponding to about 100 mg of alcaligin from 1 L of the culture fluid. Contaminating iron was removed by a treatment with 8-hydroxyquinoline,[5] and the product was recrystallized from water.

The results of FABMS spectrometry[6] and elemental analysis[7] indicated that a crystal of alcaligin contains two molecules of H_2O and leads to an empirical formula of $C_{16}H_{28}N_4O_8 \cdot 2H_2O$. Absorption spectrum of aqueous solutions of alcaligin shows max-

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