

dienone **29** as a 2:1 mixture of diastereomers.¹³ Moreover, the [2 + 2] cycloaddition/electrocyclic ring-opening provides a straightforward method for the preparation of a variety of the previously unknown 2-butadienyl complexes. Specifically, 2-butadienyl carbene complexes of the type **22** would be difficult to prepare by the standard Fischer method since organolithiums of the type **30** would be expected to be unstable with respect to β -elimination at temperatures necessary for addition to group 6 carbonyls. We have found that these complexes will undergo Diels-Alder reactions with highly activated dienophiles (benzoquinone, dimethyl acetylene dicarboxylate, acrolein, maleic anhydride). As revealed by the reaction of complex **22*** with propargyl aldehyde, the regioisomer obtained in these reactions is not the one expected under the influence of an electron-withdrawing group in the 2-position of the diene.¹⁴ Apparently, in diene **22*** the combined effect of the ethoxy and methyl groups dominates over that of the tungsten-carbene functionality in controlling the regiochemistry. This may be for electronic reasons, or perhaps more likely may be due to the combined effect of these groups on the conformation about the diene-carbene carbon bond. Further investigations of the [2 + 2] cycloadditions of chromium and tungsten carbene complexes and the synthetic utility of the organometallic complexes derived therefrom are currently ongoing.

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Supplementary Material Available: Spectral data for all new compounds (8 pages). Ordering information is given on any current masthead page.

(13) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132.

(14) (a) Inukari, T.; Kojima, T. *J. Org. Chem.* **1971**, *36*, 924. (b) Franck-Neumann, M.; Martina, D.; Brion, F. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 864. (c) Bäckvall, J. E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *21*, 6396.

Generation, Alkyne Cycloaddition, Arene C-H Activation, N-H Activation, and Dative Ligand Trapping Reactions of the First Monomeric Imidozirconocene ($\text{Cp}_2\text{Zr}=\text{NR}$) Complexes

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Many metal-oxo ($\text{M}=\text{O}$) and -imido ($\text{M}=\text{NR}$) complexes are known, but in most the $\text{M}=\text{X}$ linkages are notoriously inert. The absence from the literature of monomeric group IV metallocenes of this class ($(\eta^5\text{-C}_5\text{R}_5)_2\text{M}=\text{O}$ and $(\eta^5\text{-C}_5\text{R}_5)_2\text{M}=\text{NR}'$, $\text{M} = \text{Ti, Zr, Hf}$) suggests that if these species could be generated, they might exhibit more extensive chemistry than do oxo and imido complexes that are presently known. We now wish to report the successful generation of imidozirconocene complexes, a study of their chemical reactivity, and the isolation and X-ray structure determination of the monomeric THF-trapped adduct $\text{Cp}_2\text{-(THF)Zr}=\text{N}(t\text{-Bu})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).

The chemistry we have observed is summarized in Scheme I. Our starting material, the zirconocene methyl amide complex **1a**, can be generated by heating Cp_2ZrMe_2 with 1 equiv of 4-*tert*-butylaniline in benzene at 85 °C. This results in loss of 1 equiv

of methane and generation of the zirconocene methyl amide in situ, as observed by ^1H NMR spectrometry. Alternatively, the methyl amides **1a-c** can be prepared in gram quantities by treatment of $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{Cl})^2$ with the lithium salt of the appropriate amine in THF at 25 °C (24 h for **1a** and **1c**; 2.5 h for **1b**). In the case of **1a**, heating the methyl amide at 85 °C for 3 days in benzene leads to elimination of a second equivalent of methane³ and formation of a kelly-green compound that crystallizes from the solution in 70%⁴ yield upon cooling to room temperature. Single crystals suitable for an X-ray diffraction study of **2a** were grown by slow cooling of a toluene solution of the complex from 85 °C to room temperature. The structure shows that **2a** is the bridging imido dimer indicated in Scheme I; an ORTEP drawing is included.⁵ Some atoms in the molecule could not be located precisely due to excessive thermal motion (see Supplementary Material for details). However, the Zr-N-Zr portion of the structure is well-behaved, and, as predicted, the imido bridges are symmetric.⁶ The Zr-N distances of 2.098 (2) and 2.093 (2) Å as well as the N-Zr-N angle of 80.56 (7)° are typical of bridging imido dimers.⁷

It seems likely that **2a** is formed by generation and dimerization of $\text{Cp}_2\text{Zr}=\text{N-Ar}$. This hypothesis was reinforced by the chemistry of the sterically more hindered *tert*-butylamido complex **1b**. In benzene at 85 °C, thermolysis of **1b** does not lead to **2b**, the dimer corresponding to **2a**, but instead gives methane and the phenyl-(amido)zirconocene complex $\text{Cp}_2\text{Zr}(\text{NHCMe}_3)(\text{Ph})$, **3**, isolated in 61% yield⁸ after recrystallization from toluene layered with hexane at -30 °C. In this reaction, the reactive Zr=N linkage apparently induces cleavage of the C-H bond in benzene, leading to the phenyl-substituted product.⁹ Alkynes also serve to trap the imido complex efficiently. In the presence of a number of internal alkynes, heating methyl amides **1a-c** leads to azametallacyclobutene complexes **4a-c**, **5b,c**, and **6b** in good yield.¹⁰ The unsaturated heterometallacycles are intensely colored, possibly due to charge transfer from the azaallyl moiety to the empty orbital on the formally 16-electron zirconium center.¹¹ In the

(2) $\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})$ was prepared by the reaction of Cp_2ZrMe_2 with Cp_2ZrCl_2 . A 0.5 M solution in each reagent in toluene was heated to 130 °C for 35 h. $\text{Cp}_2\text{Zr}(\text{Me})(\text{Cl})$ can be isolated in >90% yield by recrystallization from toluene/hexanes. Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

(3) (a) For a similar reaction, see: (a) Mayer, J. M.; Curtis, L. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651. For α -elimination to generate the isolobal alkylidene complexes, see: (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (c) Gibson, C. P.; Dabbagh, G.; Bertz, S. H. *J. Chem. Soc., Chem. Commun.* **1988**, 603. (d) Bertz, S. H.; Dabbagh, G.; Gibson, C. P. *Organometallics* **1988**, *7*, 563. With analogous complexes having groups with β -hydrogens, β -elimination often occurs at lower temperature; see: (e) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171 and references therein. (f) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(4) Full characterization by spectrometry and elemental analysis has been carried out on all new complexes reported; data are provided as Supplementary Material. All yields are for recrystallized complexes except where noted.

(5) The X-ray diffraction study was carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY). Crystal data for bridging imido dimer **2a**: $P2_1/n$, $V = 2042.9$ (9) Å³, $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) $\mu = 5.3$ cm⁻¹, $d_{\text{calcd}} = 1.36$ g cm⁻³, $a = 13.4185$ (16) Å, $b = 9.3796$ (13) Å, $c = 16.9932$ (23) Å, $\beta = 107.224$ (10)°, $T = 25$ °C, $Z = 2$; the final residuals for 233 variables refined against the 2375 data for which $F^2 > 3\sigma$ (F^2) were $R = 0.0428$, $wR = 0.0689$, and $\text{GOF} = 3.74$. The R value for all 2664 data was 5.30%. Details of the structure determination are provided as Supplementary Material.

(6) Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 357.

(7) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

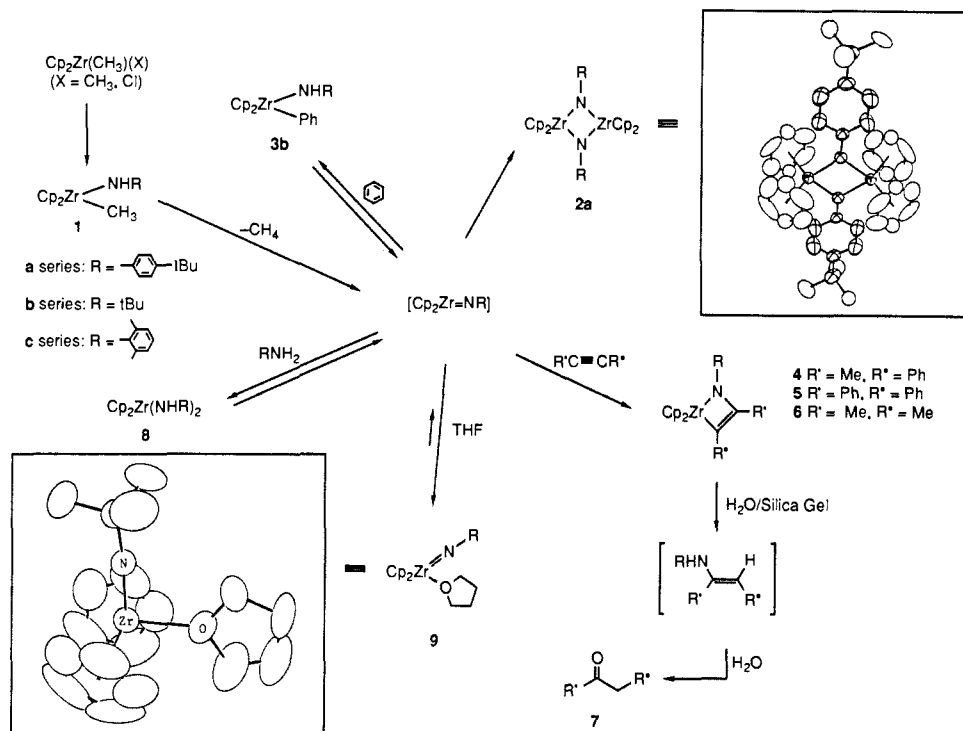
(8) In the reactions involving the alkyl amides all yields are reported as recrystallized yield of the product based on Cp_2ZrMeCl ; the intermediate alkyl amides were not isolated.

(9) Preliminary attempts to activate methane have been unsuccessful. Heating **9** to 95 °C under 18 atm of methane in cyclohexane leads to intractable products. Further efforts toward activation of sp^3 C-H bonds is presently under investigation.

(10) Analogous cycloaddition chemistry has been observed for the iso-electronic titanium methylidene complex $\text{Cp}_2\text{Ti}=\text{CH}_2$; this species does not appear to react with C-H bonds. (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (c) Finch, W. C.; Ansllyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406 and references therein.

(1) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *34*, 155.

Scheme I



reaction of amide complexes **1a–c** with the unsymmetrical alkyne 1-phenyl-1-propyne, only one regioisomer of **4a–c** is observed by ¹H NMR spectrometry in each case. Hydrolysis of these metallacycles on silica gel converted them cleanly to phenylacetone (**7**, R = Me; R'' = Ph), uncontaminated by regioisomer PhCOCH₂CH₃. This establishes the anti-Markovnikov regiochemistry of the imido complex cycloaddition with this alkyne.¹²

Kinetic evidence provided further support for the generation of a discrete transient imido complex intermediate. When phenyl amide **3b** was heated at 85 °C in the presence of 4.5, 7.9, or 17.4 equiv of 1-phenyl-1-propyne in cyclohexane-*d*₁₂, the rate of formation of the metallacycle **4b** was cleanly first order in the concentration of **3b** ($k_{\text{obsd}} = 2.35 \pm 0.2 \times 10^{-5} \text{ s}^{-1}$) but independent of changes in the concentration of alkyne. Thermolysis of methyl amide **1a** was carried out in the absence of added ligand (giving dimer **2a**) as well as in the presence of 1.87, 3.97, and 5.58 equiv of 4-*tert*-butylaniline (leading to bis-amide **8a**) and 4.52, 7.89, and 16.89 equiv of 1-phenyl-1-propyne (giving metallacycle **4a**). All three reactions, followed by ¹H NMR spectrometry at 110 °C, again exhibited first-order behavior in disappearance of **1a** ($k_{\text{obsd}} = 3.8 \pm 0.4 \times 4.81 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$) and were independent of the concentration and nature of the trapping ligand. As a control, the bridging imido dimer **2** was heated at 110 °C with excess 1-phenyl-1-propyne for 3 days, during which time formation of **4a** was *not* observed. Thus the dimer is not an intermediate in the formation of the trapped products. These experiments are all consistent with rate-determining α -elimination of benzene from **3a** and methane from **1a** to form monomeric Cp₂Zr=NR, which is then trapped in a fast step by reaction of the Zr=N linkage with an arene C–H bond, amine N–H bond, or alkyne π -bond. This result also suggests that the conversion of methyl amido complex **1** to bis-amido complex **8** does not proceed by direct transfer of a proton from the incoming amine to the departing methyl group but instead takes place by α -elimination to give Cp₂Zr=NR, followed by N–H activation.

Cp₂Zr=NR can also be trapped to give a simple adduct by using tetrahydrofuran. When **1b** was subjected to thermolysis

in THF, and the solvent was removed under reduced pressure, the monomeric THF solvate **9b** was isolated in 71% yield. Recrystallization of **9b** from toluene/hexanes by liquid diffusion afforded translucent yellow crystals suitable for X-ray analysis.¹³ Interestingly, the structure shows that the imido ligand is essentially linear with a Zr–N–C bond angle of 174.4 (3)°. This indicates that the ligand is acting as a four-electron donor making **9b** formally a 20-electron complex. As a result the Zr–N bond length of 1.826 (4) Å is about 0.13 Å longer⁷ than the average M–N linkage in terminal imido complexes. To our knowledge **7b** is the first monomeric group IV imido complex that has been characterized crystallographically.

Entry into the manifold of chemistry attributable to Cp₂Zr=NR can also be achieved from the bis-amide complexes Cp₂Zr(NHR)₂ (**8**). In analogy to the chemistry of **1b**, heating the bis-amide Cp₂Zr(NHMe)₂ (**8b**) in benzene in the presence of the internal alkyne 1-phenyl-1-propyne leads to elimination of 1 equiv of amine¹⁴ and formation of azametallacyclobutene **4b** in high yield. On a preparative scale thermolysis of **8c** at 110 °C with 4.0 equiv of 1-phenyl-1-propyne for 20 h gave the blue metallacycle **4c** in 86% yield. This indicates that amines, like hydrocarbons, can be eliminated from Zr(IV) complexes.

Very recently Cummins, Baxter, Harpp, and Wolczanski generated and examined the chemistry of an analogous intermediate, (*tert*-Bu₃SiNH)₂Zr=NSi(*tert*-Bu)₃. This species apparently does not undergo metallacyclization with alkynes, but it exhibits higher C–H activation reactivity toward small alkanes (e.g., methane), and it also can be trapped by THF.¹⁵ This seems consistent with the greater degree of coordinative unsaturation (and the larger amount of steric hindrance needed to achieve it) of the three-coordinate system. The combined observations of our group and Wolczanski's indicate that imidozirconium com-

(13) Crystal data for monomeric imido complex **9b**: *Pnma*, $V = 1867.7$ (8) Å³, Mo K α ($\lambda = 0.71073$ Å) $\mu = 5.8 \text{ cm}^{-1}$, $d_{\text{calcd}} = 1.30 \text{ g cm}^{-3}$, $a = 17.341$ (3) Å, $b = 11.5520$ (12) Å, $c = 9.3231$ (13) Å, $T = 25$ °C, $Z = 4$; the final residuals for 109 variables refined against the 933 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0427$, $wR = 0.0587$, and $\text{GOF} = 1.92$. The R value for all 1290 data was 6.90%. Details of the structure determination are provided as Supplementary Material.

(14) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251.

(15) Cummins, C. C.; Baxter, S. M.; Harpp, K. S.; Wolczanski, P. T., following paper in this issue.

(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(12) The possibility that compounds **4–6** exist as imido-alkyne adducts has been ruled out by an X-ray diffraction study of **5c**, which has confirmed its azametallacyclobutene structure. Full details of the structural study will be published at a later date.

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 metatheses⁵ 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.)

(1) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel Publishing Co: Dordrecht, 1984. (c) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902-908. (d) Halpern, J. In *Fundamental Research in Homogeneous Catalysis*; Shilov, A. E., Ed.; Gordon and Breach: New York, 1986; Vol. 1, p 393.

(2) (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243-1244. (b) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1283-1284. (c) Crabtree, R. H.; Cemou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 6994-7001. (d) Burk, M. J.; Crabtree, R. H. *Ibid.* **1987**, *109*, 8025-8032.

(3) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929-3939. (b) McGhee, W. D.; Bergman, R. G. *Ibid.* **1988**, *110*, 4346-4262. (c) Jones, W. D.; Feher, F. J. *Ibid.* **1985**, *107*, 620-631. (d) Jones, W. D.; Feher, F. J. *Ibid.* **1984**, *106*, 1650-1653. (e) Chanchal, K. G.; Graham, W. A. G. *Ibid.* **1987**, *109*, 4726-4727. (f) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723-3725. (g) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1950-1958. (h) Cooper, N. J.; Green, M. L. H.; Mahtab, R. *Ibid.* **1979**, 1557-1562. (i) Chetcuti, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 942-943. (j) Hackett, M.; Whitesides, G. M. *Ibid.* **1988**, *110*, 1449-1462.

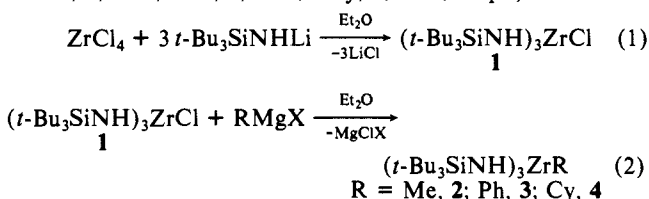
(4) (a) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941-7944. (b) Brown, S. H.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1987**, 970-971.

(5) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51-56. (c) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425-437. (d) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *Ibid.* **1987**, *109*, 203-219.

(6) Cook, B. R.; Reinart, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281-7286, and references therein.

are rare yet constitute an important class of transformations related to the partial oxidation¹⁰ or functionalization¹¹ 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 $n\text{-BuLi}$ and $t\text{-Bu}_3\text{SiNH}_2$,¹³ resulted in the formation of $(t\text{-Bu}_3\text{SiNH})_3ZrCl$ (**1**, eq 1)¹⁴ in 88% yield. Alkylation¹⁵ of **1** with appropriate Grignard reagents yielded white crystals of the methyl, phenyl, and cyclohexyl (Cy) derivatives, $(t\text{-Bu}_3\text{SiNH})_3ZrR$ ($R = \text{Me}$, **2**, 91%;¹⁶ Ph, **3**, 32%;¹⁷ Cy, **4**, 47%;¹⁸ eq 2).¹⁹



Thermolysis of each alkyl complex (Scheme I) led to C-H bond activation. In benzene solution, $(t\text{-Bu}_3\text{SiNH})_3ZrCH_3$ (**2**) formed $(t\text{-Bu}_3\text{SiNH})_3ZrPh$ (**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 1H NMR spectroscopy. The final product, $(t\text{-Bu}_3SiND)_3ZrC_6D_5$ (**3**-(ND) $_3$ - d_5), was deuterated in *both* the amido and phenyl positions. When $(t\text{-Bu}_3SiND)_3ZrCH_3$ (**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 proton⁷ by the methyl group, leading to an intermediate imido complex, $(t\text{-Bu}_3SiNH)_2Zr=NSi-t\text{-Bu}_3$ (**5**).²⁰ Subsequent addition

(7) P. J. Walsh, F. J. Hollander, and R. G. Bergman have recently shown that $Cp_2Zr(NHR)X$ ($X = \text{Me}$, NHR) complexes thermally activate arenes via transient $Cp_2Zr=NR$ species that can be trapped as THF adducts, add alkynes or undergo dimerization. See: *Abstracts of the Third Chemical Congress of North America*, INOR No. 490, Toronto, Canada, 1988 and the preceding paper in this issue.

(8) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629-1634.

(9) Chamberlain, L. R.; Rothwell, I. P.; Huffmann, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502-1509.

(10) (a) Labinger, J. A.; Ott, K. *J. Phys. Chem.* **1987**, *91*, 2682-2684. (b) Sofranko, J. A.; Leonard, J. J.; Jones, C. A. *J. Catal.* **1987**, *103*, 302-310. (c) Ito, T.; Wang, J.-S.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 5062-5068. (d) Ekstrom, A.; Lapszewicz, J. A. *Ibid.* **1988**, *110*, 5226-5228. (e) DeBoy, J. M.; Hicks, R. F. *J. Chem. Soc., Chem. Commun.* **1988**, 982-984.

(11) (a) Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725-733. (b) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109-8111.

(12) (a) Neithamer, D. R.; Pärkányi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421-4423. (b) Toreki, R.; LaPointe, R. E.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 7558-7560, and references therein.

(13) Nowakowski, P. M.; Sommer, L. H. *J. Organomet. Chem.* **1979**, *179*, 95-103. $t\text{-Bu}_3\text{SiNHLi}$ is actually a trimer according to an X-ray structural investigation: Galiano-Roth, A. S.; Collum, D. B.; Cummins, C. C.; Wolczanski, P. T. Unpublished results. 1H NMR (C_6D_6) δ -1.99 (s, NH, 1 H), 1.15 (s, $t\text{-Bu}$, 27 H).

(14) **1**: 1H NMR (C_6D_6) δ 1.24 (s, $t\text{-Bu}$, 81 H), 4.89 (s, NH, 3 H); $^{13}C\{^1H\}$ 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.

(15) For similar complexes, see: Anderson, R. A. *Inorg. Chem.* **1979**, *18*, 1724-1725.

(16) **2**: 1H NMR (C_6D_6) δ 0.63 (s, $ZrCH_3$, 3 H), 1.24 (s, $t\text{-Bu}$, 81 H), 4.10 (s, NH, 3 H); $^{13}C\{^1H\}$ 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 Duyn, G. D.; Wolczanski, P. T. Unpublished results.

(17) **3**, 59% yield from **2** and C_6H_6 (>95% by 1H NMR): 1H NMR (C_6D_6) δ 1.25 (s, $t\text{-Bu}$, 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, $^3J_{ortho} = 7$ Hz), 8.28 (dm, Ph(o), 2 H, $^3J = 7$ Hz); $^{13}C\{^1H\}$ 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**: 1H NMR (C_6D_6) δ 1.26 (s, $t\text{-Bu}$, 81 H), 1.39 (m, Cy, 4 H), 1.90 (m, Cy, 4 H), 2.69 ("d", Cy, 2 H, $J = 13$ Hz); $^{13}C\{^1H\}$ NMR δ 23.15 (SiC), 28.03 ($\delta\text{-Cy}$), 30.93 ($\gamma\text{-Cy}$), 31.05 ($\gamma\text{-Cy}$), 36.05 ($\beta\text{-Cy}$), 68.24 ($\alpha\text{-Cy}$).

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