Organometallics **2004,** *23,* 6166−6175

Terminal Zirconium Imides Prepared by Reductive C−N Bond Cleavage

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Received August 26, 2004

Toluene reflux of $ZrCl_4$ with Li(Nacnac) (Nacnac$^-$ = [Ar]NC(tBu)CHC(tBu)N[Ar], Ar = 2,6-$[CH(CH_3)_2]_2C_6H_3$) provides the complex (Nacnac)$ZrCl_3$ in 75% yield. Cl^- substitution for OTf^- is readily achieved with 3 equiv of AgOTf to yield 77% of the complex (Nacnac)Zr(OTf)$_2$(η^2-OTf). The coordination mode of the three triflato groups was determined by a combination of single-crystal X-ray analysis and ^{19}F COSY experiments. Addition of 2 equiv of $LiCH_2XMe_3$ (X = C, Si) to (Nacnac)$ZrCl_4$ in Et_2O affords the bis(alkyl) systems (Nacnac)Zr$(CH_2XMe_3)_2$Cl in good yield (X = C, 86%; X = Si, 91%). In contrast, reaction of (Nacnac)Zr(OTf)$_2$(η^2-OTf) with 2 equiv of $LiCH_2CMe_3$ leads instead to formation of the terminal zirconium−imido complex [(Nac$t$Bu)Zr=NAr(μ_2-OTf)]$_2$ (Nac$t$Bu$^-$ = [2,6-$(CHMe_2)_2C_6H_3$]NC(tBu)CHC(tBu)). Likewise, reduction of (Nacnac)$ZrCl_3$ with 2 equiv of KC_8 in THF also affords a terminal zirconium−imido species, (Nac$t$Bu)Zr=NAr(Cl)(THF). The zirconium−imido compounds described herein result from reductive cleavage of the C−N bond of the imine functionality contained in the Nacnac$^-$ ligand. The complexes (Nacnac)$ZrCl_3$, (Nacnac)Zr(OTf)$_2$(η^2-OTf), (Nacnac)Zr$(CH_2XMe_3)_2$Cl, [(Nac$t$Bu)Zr=NAr(μ_2-OTf)]$_2$, and (Nac$t$Bu)Zr=NAr(Cl)(THF) have been fully characterized, and a single-crystal X-ray diffraction analysis is reported for each.

Introduction

β-Diketiminates (referred to as Nacnac$^-$) exhibit versatile properties and have received considerable attention as ancillary ligands for main-group-, transition-, lanthanide-, and actinide-metal complexes. Although this important class of ligand was prepared over 30 years ago,[1] the coordination chemistry of the β-diketiminate is just beginning to undergo a dramatic rebirth.[2,3]

Perhaps the most important feature associated with the Nacnac$^-$ ligand is the ability to support reactive (electron-deficient or -rich) metal fragments.[3] Previous studies by Lappert,[3] Theopold,[4] Piers,[5] Budzelaar,[6] and Smith,[7] among others, have established that β-diketiminates are compatible ligands with group 3−6 metal systems. In fact, the robust nature of Nacnac$^-$ with early-transition metal systems has prompted their use in olefin polymerization reactions.[3−8]

Even though the Nacnac$^-$ ligand has been considered robust, it can occasionally be transformed, depending on the metal system involved. Some of these transformations include C−H abstraction in the aryl groups attached to the α-nitrogens leading to metalation or metal−hydride formation.[3,5,7,8] Other transformations

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[1] (a) McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903−1912. (b) Dorman, L. C. *Tetrahedron Lett.* **1966**, *4*, 459−464. (c) Barry, W. J.; Finar, I. L.; Mooney, E. F. *Spectrochim. Acta* **1965**, *21*, 1095−1099. (d) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408−1416. (e) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241−401.

[2] Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*, 131−155.

[3] Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066.

[4] (a) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570−2577. (b) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543. (c) MacAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952−960. (d) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, 15−24. (e) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2003**, 1164−1165. (f) Theopold, K. H.; MacAdams, L. A.; Puttnual, C.; Buffone, G. P.; Rheingold, A. L. *Polym. Mater. Sci. Eng.* **2002**, *86*, 310.

[5] (a) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499−5509 and references therein. (b) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533−2544. (c) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622−5623.

[6] Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485−1494.

[7] (a) Kakaliou, L.; Scanlon, W. J., IV; Qian, B.; Baek, S. W.; Smith, M. R., III; Motry, D. H. *Inorg. Chem.* **1999**, *38*, 5964−5977. (b) Qian, B.; Scanlon, W. J.; Smith, M. R., III; Motry, D. H. *Organometallics* **1999**, *18*, 1693−1698. For other examples of zirconium β-diketiminate complexes: (c) Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315−1323. (d) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161−2169. (e) Cortright, S. B.; Johnston, J. N. *Angew. Chem., Int. Ed.* **2002**, *41*, 345−348.

[8] For some other examples of group 4−6 β-diketiminate complexes and catalytic reaction reactions thereof see: (a) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G.; White, A. J. P.; Williams, D. J.; Maddox, P. J. *Chem. Commun.* **1998**, 1651−1652. (b) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895−1903. (c) Doherty, J. C.; Ballem, K. H. D.; Patrick, B. O.; Smith, K. M. *Organometallics* **2004**, *23*, 1487−1489. (d) Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315−1323. (e) Deelman, B.-J.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Lee, H.-K.; Mak, T. C. W. *Organometallics* **1999**, *18*, 1444−1452. (f) Giannini, L.; Solari, E.; Angelis, S. D.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801−5811. (g) Martin, A.; Uhrhammer, R.; Gardener, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382−397.

10.1021/om049332t CCC: $27.50

include electrophilic attack of the γ-carbon[3,9−14] and deprotonation of the methyl group attached to the β-carbon in the NCCCN ring.[3,14a,15] On the other hand, N−C bond cleavage of the imine functionality of Nacnac$^-$-based systems have been reported scarcely, and the fate of the organic byproduct generated by N−C bond rupture remains uncertain.[14b,16]

Recently, our group has discovered that the imine functionality of the Nacnac$^-$-based systems can become readily transformed via a cross-metathesis reaction between terminal neopentylidene,[14b,17] phosphinidene,[18] and alkylidyne[19] ligands. Our recent success in kinetically stabilizing four-coordinate and terminal alkylidene[14b,17] and alkylidyne[19] functionalities within (Nacnac)Ti and (Nacnac)V templates, respectively, inspired the pursuit of Zr alkylidene analogues. Of the vast majority of alkylidene species known, only a handful of group 4 complexes having a terminal alkylidene have been isolated,[14b,17,20−24] and from this limited group the majority appear to be titanium-based.[14b,17,20−22,24] In the context of zirconium alkylidenes, Fryzuk's complexes $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2P\textit{i}Pr_2)_2]Zr{=}CHR(Cl)$ (R = Ph, $SiMe_3$) stand as the only structurally characterized complexes containing a terminal zirconium benzylidene or (trimethylsilyl)methylidene ligand.[23a,23b]

Herein, we report that preliminary attempts to incorporate the alkylidene functionality on the (Nacnac)-Zr template have resulted instead in unprecedented formation of terminal zirconium imides, vis-à-vis reductive cleavage of the imine C−N functionality in the Nacnac$^-$ ligand (Nacnac$^-$ = [Ar]NC(*t*Bu)CHC(*t*Bu)N-[Ar], Ar = 2,6-$[CH(CH_3)_2]_2C_6H_3$). C−N rupture appears to occur via a putative low-valent zirconium species, which is generated by reduction of the precursors (Nacnac)$ZrCl_3$ and (Nacnac)$Zr(OTf)_2(\eta^2\text{-}OTf)$, respectively.

Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques under an argon atmosphere.[25] Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in Sure-Seal reservoirs (18 L) and dried by passage through one column of activated alumina and one of Q-5.[26] Diethyl ether and CH_2Cl_2 were dried by passage through two columns of activated alumina.[26] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratory (CIL), degassed, and dried over 4 Å molecular sieves and CaH_2, respectively. CD_2Cl_2 was vacuum-transferred from the CaF_2 mixture and stored in a reaction vessel under N_2. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Li(Nacnac)[6] (Nacnac$^-$ = [Ar]NC(*t*Bu)CHC(*t*Bu)N[Ar], Ar = 2,6-$(CHMe_2)_2C_6H_3$), $LiCH_2\textit{t}Bu$,[27] and KC_8[28] were prepared according to the literature. $LiCH_2SiMe_3$ was recrystallized from pentane at −35 °C. TBAH (tetrabutylammonium hexafluorophosphate) was recrystallized from THF and dried under vacuum at 60 °C for 24 h. CHN analysis was performed by Desert Analytics, Tucson, AZ. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian 400 or 300 MHz NMR spectrometers. ^1H and ^{13}C NMR are reported with reference to solvent resonances (residual C_6D_5H in C_6D_6, 7.16 and 128.0 ppm; residual $CHDCl_2$ in CD_2Cl_2, 5.32 and 53.8 ppm). ^{19}F NMR chemical shifts are reported with respect to external $HOCOCF_3$ (−78.5 ppm). Cyclic voltammetry was collected with the assistance of an E2 Epsilon potentiostat/galvanostat with a PC unit controlled by Bioanalytical Systems (BAS) software. X-ray diffraction data were collected on a SMART6000 (Bruker) system under a stream of N_2(g) at low temperatures.

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[9] Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307−6321 and references therein.

[10] Yokota, S.; Tachi, Y.; Nishiwaki, N.; Ariga, M.; Itoh, S. *Inorg. Chem.* **2001**, *40*, 5316−5317.

[11] Davies, I. W.; Marcoux, J.-F.; Wu, J.; Palucki, M.; Corley, E. G.; Robbins, M. A.; Tsou, N.; Ball, R. G.; Dormer, P.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **2000**, *65*, 4571−4574.

[12] Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384−9385.

[13] Electrophilic substitution with Ph_2P^+ or $PhClP^+$ at the γ-carbon of the Nacnac$^-$ backbone has been recently reported: (a) Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E. *Chem. Commun.* **2003**, 1142−1143. (b) Ragogna, P. J.; Burford, N.; D'eon, M.; McDonald, R. *Chem. Commun.* **2003**, 1052−1053 and references therein. In addition, α-alkoxylithium-β-diimine ligands have been prepared from the reaction of the lithium−Nacnac salt and the corresponding ketone: (c) Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafé, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton* **2003**, 1083−1093.

[14] (a) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2003**, *42*, 8003−8010. (b) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. Submitted for publication. (c) Brown, E. C.; Aboelella, N. W.; Reynolds, A. M.; Aullón, G.; Santaigo, A.; Tolman, W. B. *Inorg. Chem.* **2004**, *43*, 3335−3337.

[15] Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806−4811.

[16] Nikiforov, G. B.; Roesky, H. W.; Magull, J.; Labahn, T.; Vidovic, D.; Noltemeyer, M.; Schmidt, H.-G.; Hosmane, N. S. *Polyhedron* **2003**, *22*, 2669−2681.

[17] Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052−6053.

[18] Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170−10171.

[19] Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.*, in press.

[20] Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145−179.

[21] Beckhaus, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 687−713.

[22] Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822−7836.

[23] (a) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336−5337. (b) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 2478−2487. (c) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608−1613. (d) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178−5186. (e) Cheon, J.; Rogers, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1997**, *119*, 6804−6813. (f) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604−606. (g) Rice, G. W.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1983**, *2*, 154−157. (h) van der Heijden, H.; Hessen, B. *Chem. Commun.* **1995**, 145−146. (i) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583−589. (j) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721−724. (k) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640−641. (l) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organomeatllics* **2004**, *23*, 4700−4705. Attempts to prepare group 4 alkylidene species have been reported: (m) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319−327.

[24] (a) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1995**, *14*, 1278−1283. (b) Kahlert, S.; Gorls, H.; Scholz, J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1857−1861. (c) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271−4277. (d) Sinnema, P.-J.; van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245−4247.

[25] For a general description of the equipment and techniques used in carrying out this chemistry see: Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society; Washington DC, 1987; pp 79−98.

[26] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

[27] Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359−3370.

[28] Schwindt, M.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814−2819.

Synthesis of (Nacnac)ZrCl$_3$ (1). In a reaction vessel equipped with a stir bar was placed ZrCl$_4$ (3.67 g, 0.016 mol) in toluene (~200 mL), and the suspension was cooled to −35 °C. To the cold solution was slowly added solid Li(Nacnac) (8.00 g, 0.016 mol) in portions. After it was warmed to room temperature, the reaction mixture was heated at 80 °C for 3 days. The dark solution was then filtered to remove a dark solid, and the filtrate was dried under reduced pressure. The solid was dissolved in dichloromethane, filtered, and this solution was then layered with pentane and stored at −35 °C for 24 h to afford large yellow blocks of (Nacnac)ZrCl$_3$ (**1**; 8.40 g, 0.012 mol, 75% yield, two crops).

Data for **1** are as follows. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.07 (d, $\mathrm{C_6}\mathit{H}_3$, 2H), 6.96 (t, $\mathrm{C_6}\mathit{H}_3$, 2H), 6.88 (d, $\mathrm{C_6}\mathit{H}_3$, 2H), 6.52 (s, C(*t*Bu)C*H*C(*t*Bu), 1H), 3.87 (septet, C*H*(Me)$_2$, 2H), 2.56 (septet, C*H*(Me)$_2$, 2H), 1.56 (d, CH*Me$_2$*, 6H), 1.36 (d, CH*Me$_2$*, 6H), 1.16 (s, C(*tBu*)CHC(*tBu*), 18H), 0.99 (d, CH*Me$_2$*, 6H), 0.76 (d, CH*Me$_2$*, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 167.3 (*C*(*t*Bu)CH*C*(*t*Bu)), 144.3 (*C*$_6$H$_3$), 141.8 (*C*$_6$H$_3$), 137.8 (*C*$_6$H$_3$), 126.5 (*C*$_6$H$_3$), 125.9 (*C*$_6$H$_3$), 124.7 (*C*$_3$H$_3$), 104.1 (C(*t*Bu)-*C*HC(*t*Bu), J_{C-H} = 158 Hz), 43.17 (C(*C*Me$_3$)CHC(*C*Me$_3$)), 32.32 (C(C*Me$_3$*)CHC(C*Me$_3$*)), 29.69 (*C*HMe$_2$), 27.52 (*C*HMe$_2$), 26.37 (*C*H$_3$), 26.25 (*C*H$_3$), 25.69 (*C*H$_3$), 25.57 (*C*H$_3$). Anal. Calcd for $C_{35}H_{53}N_2Cl_3Zr$: C, 60.10; H, 7.64; N, 4.00. Found: C, 60.09; H, 7.60; N, 3.92.

Synthesis of (Nacnac)Zr(OTf)$_2$(η^2-OTf) (2). In a reaction vessel equipped with a stir bar was dissolved (Nacnac)ZrCl$_3$ (**1**; 800 mg, 1.14 mmol) in THF (20 mL), and the solution was cooled to −35 °C. To the cold solution was added a cold THF solution (10 mL) containing AgOTf (940 mg, 3.66 mmol). After the mixture was stirred for 20 min, the solution was filtered to remove AgCl, and the filtrate was evaporated under reduced pressure. The yellow solid was dissolved in dichloromethane, this solution was filtered, and the filtrate was layered with pentane. The layered solution was stored at −35 °C for 24 h to afford yellow crystals of (Nacnac)Zr(OTf)$_2$(η^2-OTf) (**2**; 920 mg, 0.88 mol, 77% yield, three crops).

Data for **2** are as follows. ^{1}H NMR (23 °C, 399.8 MHz, CD_2Cl_2): δ (m, $\mathrm{C_6}\mathit{H}_3$ and C(*t*Bu)C*H*C(*t*Bu), 7H), 2.97 (septet, C*H*(Me)$_2$, 2H), 2.07 (septet, C*H*(Me)$_2$, 2H), 1.28 (s, C(*tBu*)CHC(*tBu*), 18H), 1.19 (d, CH*Me$_2$*, 6H), 1.13 (d, CH*Me$_2$*, 6H), 1.07 (d, CH*Me$_2$*, 6H), 0.81 (d, CH*Me$_2$*, 6H). ^{13}C NMR (25 °C, 100.6 MHz, CD_2Cl_2): δ 171.8 (*C*(*t*Bu)CH*C*(*t*Bu)), 142.8 (*C*$_6$H$_3$), 141.6 (*C*$_6$H$_3$), 140.0 (*C*$_6$H$_3$), 128.6 (*C*$_6$H$_3$), 126.6 (*C*$_6$H$_3$), 125.9 (*C*$_6$H$_3$), 120.8−116.8 (overlapping m, O$_3$S*C*F$_3$), 98.65 (C(*t*Bu)*C*HC(*t*Bu), J_{C-H} = 162 Hz), 44.91 (C(*C*Me$_3$)CHC(*C*Me$_3$)), 30.35 (C(C*Me$_3$*)-CHC(C*Me$_3$*)), 29.26 (*C*HMe$_2$), 28.70 (*C*HMe$_2$), 26.99 (*C*H$_3$), 26.18 (*C*H$_3$), 25.65 (*C*H$_3$), 24.45 (*C*H$_3$). ^{19}F NMR (23 °C, 399.8 MHz, CD_2Cl_2): δ −73.8 (q, O$_3$SC*F$_3$*, J_{F-F} = 5 Hz), −74.8 (m, O$_3$SC*F$_3$*, J_{F-F} = 5 Hz), −75.7 (q, O$_3$SC*F$_3$*, J_{F-F} = 6 Hz). Anal. Calcd for $C_{38}H_{53}N_2O_9S_3F_9Zr\cdot CH_2Cl_2$: C, 41.63; H, 4.92; N, 2.48. Found: C, 41.17; H, 5.50; N, 2.43.

Synthesis of (Nacnac)Zr(CH$_2$*t*Bu)$_2$Cl (3). In a vial containing 20 mL of Et$_2$O was suspended **1** (300 mg, 0.43 mmol), and the suspension was cooled to −35 °C. To the cold suspension was added a cold Et$_2$O solution (~10 mL) containing LiCH$_2$CMe$_3$ (67 mg, 0.86 mmol). Upon warming the mixture was stirred for 30 min, the solution was filtered, and the filtrate was concentrated and stored at −35 °C for 24 h to afford yellow crystals of (Nacnac)Zr(CH$_2$*t*Bu)$_2$Cl (**3**; 286 mg, 0.37 mmol, 86% yield, two crops).

Data for **3** are as follows. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.30−7.10 (m, $\mathrm{C_6}\mathit{H}_3$, 6H), 6.26 (s, (*t*Bu)C*H*C(*t*Bu), 1H), 3.66 (br, C*H*(Me)$_2$, 2H), 2.40 (br, C*H*(Me)$_2$, 2H), 1.55 (d, CH*Me$_2$*, 6H), 1.33 (overlap of s and d, ZrCH$_2$C*Me$_3$* and CH*Me$_2$*, 15H), 1.25−1.16 (br, ZrCH$_2$C*Me$_3$*, C(*tBu*)CHC(*tBu*) and ZrC*H$_2$*CMe$_3$, 31H), 1.01 (br, CH*Me$_2$*, 6H), 0.81 (br, CH*Me$_2$*, 6H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 176.3 (br, C(*t*Bu)CH*C*(*t*Bu)), 159.6 (br, *C*(*t*Bu)CHC(*t*Bu)), 145.9 (br, *C*$_6$H$_3$), 142.1 (br, *C*$_6$H$_3$), 138.7 (*C*$_6$H$_3$), 125.4 (*C*$_6$H$_3$), 125.1 (*C*$_6$H$_3$), 95.14 (Zr*C*H$_2$CMe$_3$, J_{C-H} = 104 Hz), 94.43 (C(*t*Bu)*C*HC(*t*Bu), J_{C-H} = 157 Hz), 90.90 (Zr*C*H$_2$CMe$_3$, J_{C-H} = 107 Hz), 43.40 (br, C(*C*Me$_3$)CHC(*C*Me$_3$)), 37.34 (ZrCH$_2$C*Me$_3$*), 36.22 (ZrCH$_2$C*Me$_3$*), 34.87 (C(CMe$_3$)CHC-(C*Me$_3$*)), 34.67 (C(C*Me$_3$*)CHC(CMe$_3$)), 34.46 (*C*HMe$_2$), 30.44 (*C*HMe$_2$), 27.05 (*C*H$_3$), 26.64 (*C*H$_3$). Anal. Calcd for $C_{45}H_{75}N_2ClZr$: C, 70.12; H, 9.80; N, 3.36. Found: C, 69.86; H, 9.48; N, 3.71.

Synthesis of (Nacnac)Zr(CH$_2$SiMe$_3$)$_2$Cl (4). In a vial was suspended (Nacnac)ZrCl$_3$ (**1**; 300.3 mg, 0.43 mmol) in 20 mL of Et$_2$O, and the solution was cooled to −35 °C. To the cold suspension was added dropwise a cold Et$_2$O solution (~10 mL) containing LiCH$_2$SiMe$_3$ (84.7 mg, 0.90 mmol). After it was warmed to room temperature, the mixture was stirred for 30 min. The solution was then filtered, and the filtrate was concentrated and stored at −35 °C for 24 h to afford yellow crystals of (Nacnac)Zr(CH$_2$SiMe$_3$)$_2$Cl (**4**; 315.2 mg, 0.39 mmol, 91% yield, two crops).

Data for **4** are as follows. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.08−6.94 (m, $\mathrm{C_6}\mathit{H}_3$, 6H), 6.52 (s, C(*t*Bu)C*H*C(*t*Bu), 1H), 3.87 (br, C*H*(Me)$_2$, 2H), 2.46 (br, C*H*(Me)$_2$, 2H), 1.53 (d, CH*Me$_2$*, 6H), 1.37 (br, CH*Me$_2$*, 6H), 1.46−1.07 (overlapping peaks, C(*tBu*)CHC(*tBu*) and CH*Me$_2$*, 30H), 0.71 (s, ZrC*H$_2$*SiMe$_3$, 2H), 0.43 (s, ZrCH$_2$Si*Me$_3$*, 9H), 0.40 (s, ZrCH$_2$Si*Me$_3$*, 9H); the additional ZrC*H$_2$*SiMe$_3$ resonance could not be located. ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 138.4 (br), 125.0 (br), 96.04 (C(*t*Bu)*C*HC(*t*Bu)), 63.85 (Zr*C*H$_2$SiMe$_3$), 63.53 (Zr*C*H$_2$-SiMe$_3$), 43.05 (br, C(*C*Me$_3$)CHC(*C*Me$_3$)), 30.34 (C(C*Me$_3$*)CHC-(C*Me$_3$*)), 27.17 (br), 27.34 (br), 26.12 (br), 3.36 (ZrCH$_2$Si*Me$_3$*). ^{1}H NMR (−40 °C, 399.8 MHz, $C_6D_5CD_3$): δ 7.12−6.72 (m, $\mathrm{C_6}\mathit{H}_3$, 6H), 6.30 (s, C(*t*Bu)C*H*C(*t*Bu), 1H), 3.87 (br, C*H*(Me)$_2$, 1H), 3.35 (br, C*H*(Me)$_2$, 2H), 2.10 (br, C*H*(Me)$_2$, 1H), 1.53 (br, CH*Me$_2$*, 6H), 1.33−0.92 (m, C(*tBu*)CHC(*tBu*) and CH*Me$_2$*, 30H), 0.78 (s, ZrC*H$_2$*SiMe$_3$, 2H), 0.49 (s, ZrC*H$_2$*SiMe$_3$, 2H), 0.47 (s, ZrCH$_2$Si*Me$_3$*, 9H), 0.42 (s, ZrCH$_2$Si*Me$_3$*, 9H), 0.38 (d, CH*Me$_2$*, 6H). ^{13}C NMR (−40 °C, 100.6 MHz, $C_6D_5CD_3$): δ 175.9 (C(*t*Bu)-CH*C*(*t*Bu)), 157.2 (*C*(*t*Bu)CHC(*t*Bu)), 148.6 (*C*$_6$H$_3$), 146.3 (*C*$_6$H$_3$), 143.8 (*C*$_6$H$_3$), 141.1 (*C*$_6$H$_3$), 138.7 (*C*$_6$H$_3$), 137.2 (*C*$_6$H$_3$), 126.6 (*C*$_6$H$_3$), 126.0 (*C*$_6$H$_3$), 125.7 (*C*$_3$H$_3$), 124.6 (*C*$_6$H$_3$), 123.7 (*C*$_6$H$_3$), 95.51 (C(*t*Bu)*C*HC(*t*Bu), J_{C-H} = 155 Hz), 63.43 (Zr*C*H$_2$SiMe$_3$, J_{C-H} = 103 Hz), 61.58 (Zr*C*H$_2$SiMe$_3$, J_{C-H} = 111 Hz), 44.06 (C(CMe$_3$)CHC(*C*Me$_3$)), 42.48 (C(*C*Me$_3$)CHC(CMe$_3$)), 30.84, (C(CMe$_3$)CHC(C*Me$_3$*)), 30.84, (C(C*Me$_3$*)CHC(CMe$_3$)), 28.92 (*C*HMe$_2$), 28.59 (*C*HMe$_2$), 27.69 (*C*HMe$_2$), 27.21 (*C*HMe$_2$), 26.74 (*C*H$_3$), 26.44 (*C*H$_3$), 25.41 (*C*H$_3$), 24.82 (*C*H$_3$), 24.59 (*C*H$_3$), 24.36 (*C*H$_3$), 3.52 (ZrCH$_2$Si*Me$_3$*). Anal. Calcd for $C_{43}H_{75}N_2Si_2ClZr$: C, 64.32; H, 9.41; N, 3.49. Found: C, 63.97; H, 9.03; N, 3.76.

Synthesis of [(Nac*t*Bu)Zr=NAr(μ_2-OTf)]$_2$ (5). In a reaction vessel was dissolved **2** (300 mg, 0.29 mmol) in 50 mL of toluene, and the solution was cooled to −35 °C. To the cold solution was slowly added a cold toluene solution (~15 mL) containing LiCH$_2$CMe$_3$ (45 mg, 0.58 mmol). After it was warmed to room temperature, the reaction mixture was stirred for 1 h. The solution was filtered, and the filtrate was evaporated under reduced pressure and washed with pentane. The solid was then dissolved in Et$_2$O, this solution was filtered, and the filtrate was concentrated and stored at −35 °C for 48 h to afford dark red crystals of [(Nac*t*Bu)Zr=NAr(μ^2-OTf)]$_2$ (**5**; 156 mg, 0.11 mmol, 76% yield, two crops).

Data for **5** are as follows. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.12−6.80 (m, $\mathrm{C_6}\mathit{H}_3$ and C(*t*Bu)C*H*C(*t*Bu)Zr, 7H), 4.35 (septet, C*H*(Me)$_2$, 1H), 4.13 (septet, C*H*(Me)$_2$, 1H), 3.56 (septet, C*H*(Me)$_2$, 1H), 2.70 (septet, C*H*(Me)$_2$, 1H), 1.42 (d, CH*Me$_2$*, 6H), 1.33 (overlap of two d, CH*Me$_2$*, 6H), 1.28 (C(*t*Bu)CHC(*tBu*)-Zr), 9H), 1.12 (d, CH*Me$_2$*, 3H), 1.03 (overlap of two d, CH*Me$_2$*, 6H), 0.94 (CH*Me$_2$*, 3H), 0.91 (C(*tBu*)CHC(*t*Bu)Zr), 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 248.6 (C(*t*Bu)CH*C*(*t*Bu)Zr), 192.1 (*C*(*t*Bu)CHC(*t*Bu)Zr), 145.0 (*C*$_6$H$_3$), 141.7 (*C*$_6$H$_3$), 141.3 (*C*$_6$H$_3$), 141.0 (*C*$_6$H$_3$), 138.3 (*C*$_6$H$_3$), 128.5 (*C*$_3$H$_3$), 127.9 (*C*$_3$H$_3$), 127.5 (*C*$_3$H$_3$), 125.5 (*C*$_3$H$_3$), 124.0 (*C*$_3$H$_3$), 122.9 (*C*$_3$H$_3$), 122.3 (*C*$_3$H$_3$), 120.9 (C(*t*Bu)*C*HC(*t*Bu)Zr), 120.2 (OSO$_2$*C*F$_3$), 43.5 (C(CMe$_3$)CHC(*C*Me$_3$)Zr), 42.11 (C(*C*Me$_3$)CHC(CMe$_3$)Zr), 30.30 (C(CMe$_3$)CHC(C*Me$_3$*)Zr), 30.11 (*C*HMe$_2$), 29.91 (C(C*Me$_3$*)CHC-

(CMe_3)Zr), 28.66 (*C*HMe$_2$), 28.26 (*C*HMe$_2$), 27.25 (*C*HMe$_2$), 25.64 (*C*H$_3$), 25.38 (*C*H$_3$), 24.86 (*C*H$_3$), 24.40 (*C*H$_3$), 22.11 (*C*H$_3$). Anal. Calcd for $C_{72}H_{106}N_4O_6S_2F_6Zr_2 \cdot C_5H_{12}$: C, 59.42; H, 7.38; N, 3.60. Found: C, 60.69; H, 7.42; N, 3.88.

Synthesis of (Nac*t*Bu)Zr=NAr(Cl)(THF) (6). In a reaction vessel equipped with a stir bar was dissolved (Nacnac)-$ZrCl_3$ (**1**; 208.3 mg, 0.30 mmol) in toluene (30 mL), and the solution was cooled to −35 °C. To the cold solution was added a cold THF suspension (~15 mL) containing KC_8 (84.6 mg, 0.62 mmol). After it was warmed to room temperature, the mixture was stirred for 2 h. The solution was then filtered, and the filtrate was evaporated under reduced pressure. The solid was dissolved in Et_2O, this solution was filtered, and the filtrate was concentrated and stored at −35 °C for 48 h to afford dark red crystals of (Nac*t*Bu)Zr=NAr(Cl)(THF) (**6;** 156 mg, 0.11 mmol, 76% yield, three crops).

Data for **6** are as follows. ^{1}H NMR (23 °C, 399.8 MHz, C_6D_6): δ 7.16−6.78 (m, C_6H_3, and C(*t*Bu)C*H*C(*t*Bu)Zr, 7H), 4.93 (br, C*H*(Me)$_2$, 1H), 4.31 (br, C*H*(Me)$_2$, 1H), 3.67 (br, THF, 2H), 3.51 (septet, C*H*(Me)$_2$, 1H), 3.13 (br, THF, 2H), 2.88 (septet, C*H*(Me)$_2$, 1H), 1.58 (br, THF, 2H), 1.49 (s, C(*t*Bu)CHC(*tBu*)Zr and THF, 11H), 1.41 (d, CH*Me*$_2$, 9H), 1.26 (d, CH*Me*$_2$, 3H), 1.21 (d, CH*Me*$_2$, 3H), 1.13 (d, CH*Me*$_2$, 3H), 1.10 (CH*Me*$_2$, 3H), 1.07 (CH*Me*$_2$, 3H), 1.03 (C(*tBu*)CHC(*t*Bu)Zr), 9H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 255.40 (C(*t*Bu)CH*C*(*t*Bu)Zr), 194.0 (*C*(*t*Bu)CHC(*t*Bu)Zr), 153.7 (*C*$_6$H$_3$), 143.3 (*C*$_6$H$_3$), 142.0 (*C*$_6$H$_3$), 140.4 (*C*$_6$H$_3$), 126.5 (*C*$_6$H$_3$), 124.8 (*C*$_3$H$_3$), 123.6 (*C*$_3$H$_3$), 119.8 (C(*t*Bu)*C*HC(*t*Bu)Zr, J_{C-H} = 156 Hz), 73.94 (THF), 43.69 (C(CMe$_3$)CHC(*C*Me$_3$)Zr), 42.35 (C(*C*Me$_3$)CHC(CMe$_3$)Zr), 30.80 (C(CMe$_3$)CHC(C*Me$_3$*)Zr), 30.08 (C(C*Me$_3$*)CHC(CMe$_3$)Zr), 28.78 (*C*HMe$_2$), 28.20 (*C*HMe$_2$), 27.68 (THF), 26.02 (*C*H$_3$), 24.73 (*C*H$_3$), 24.61 (*C*H$_3$), 24.48 (*C*H$_3$), 22.34 (*C*H$_3$). Multiple attempts to obtain a satisfactory elemental analysis were unsuccessful.

X-ray Crystallography. Inert-atmosphere techniques were used to place the crystal onto the tip of a glass capillary (0.04−0.10 mm diameter), which was then mounted on a SMART6000 diffractometer (Bruker) at approximately 120 K. A preliminary set of cell constants was calculated from reflections obtained from three nearly orthogonal sets of 20−30 frames. The data collection was carried out using graphite-monochromated Mo Kα radiation with a frame time of 2−15 s with a detector distance of 5.0 cm (except for crystals of compounds **3** and **5**). A randomly oriented region of a sphere in reciprocal space was surveyed. Three sections of 606 frames were collected with 0.30° steps in ω at different ϕ settings, with the detector set at −43° in 2θ. Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT).[29] The structure was solved using SHELXS-97 and refined with SHELXL-97.[30]A direct-methods solution was calculated, which provided most non-hydrogen atoms from the *E* map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were refined with isotropic displacement parameters (unless otherwise specified).

For $\mathbf{1} \cdot CH_2Cl_2$, single crystals were grown at −35 °C from a saturated CH_2Cl_2/pentane solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. One CH_2Cl_2 molecule was confined in the asymmetric unit. The remaining electron density is located in bonds.

For **2**, single crystals were grown at −35 °C from a saturated CH_2Cl_2/pentane solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The remaining electron density is located in bonds.

For $\mathbf{3} \cdot {}^1\!/_2 Et_2O$, single crystals were grown at −35 °C from a saturated Et_2O solution layered with pentane. A preliminary examination of reflections obtained from three nearly orthogonal sets of 30 frames failed to yield a suitable cell. It appeared that there was one long axis and that some splitting might be present. Examination of the data using RLATT yielded a unique set of reflections that could be indexed as *C*-centered monoclinic. Intensity statistics and systematic absences suggested the centrosymmetric space group $C2/c$. All non-hydrogen atoms were refined with anisotropic displacement parameters, with the exception of carbon atoms in a disordered diethyl ether. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. There were several large peaks in the vicinity of the Zr and Cl atoms, suggesting that the integration did not properly handle the splitting. It was obvious that significant overlap occurred in some regions of reciprocal space. The structure was found to consist of two independent molecules and one Et_2O per asymmetric unit.

For $\mathbf{4} \cdot Et_2O$, crystals were grown at −35 °C from a saturated Et_2O solution. The crystals occur as transparent yellow rectangular prisms that tend to grow in clumps. Intensity statistics and systematic absences suggested the centrosymmetric space group $P2_1/n$, and subsequent solution and refinement confirmed this choice. All hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. The remaining electron density is located in bonds. One Et_2O molecule was confined in the asymmetric unit.

For **5**, single crystals were grown at −35 °C from a saturated Et_2O solution. The crystals occur as orange plates of various morphologies. Initial attempts to determine the crystallographic parameters failed because of twinning. The Bruker-AXS program CELL-NOW was used to determine the twinning and to create an HKL5 file for solution and refinement. Final cell constants were calculated from the *xyz* centroids of 1000 strong reflections from the actual data collection after integration (SAINT). Intensity statistics and systematic absences suggested the centrosymmetric space group $P\bar{1}$, and subsequent solution and refinement confirmed this choice. Two independent dimeric molecules are present in the cell. All non-hydrogen atoms were refined with anisotropic displacement parameters, with the exception of the atoms C53, C144, N95, and N156, which were assigned isotropic parameters due to a convergence to an NPD anisotropic parameter. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. It should be noted that the structure is not of high quality; thus, values for bond lengths and angles are not completely reliable.

For **6**, single crystals were grown at −35 °C from a saturated diethylether solution. Intensity statistics and systematic absences suggested the centrosymmetric space group $P\bar{1}$, and subsequent solution and refinement confirmed this choice. A disorder was observed in the THF ligand but was easily modeled. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms, with the exception of those on the THF, were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement. Hydrogen atoms for the THF were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Results and Discussion

Transmetalation of equimolar amounts of Li(Nacnac) (Nacnac$^-$ = [Ar]NC(*t*Bu)CHC(*t*Bu)N[Ar], Ar = 2,6-[CH-

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[29] SAINT 6.1; Bruker Analytical X-ray Systems, Madison, WI.

[30] SHELXTL-Plus V5.10; Bruker Analytical X-ray Systems, Madison, WI.

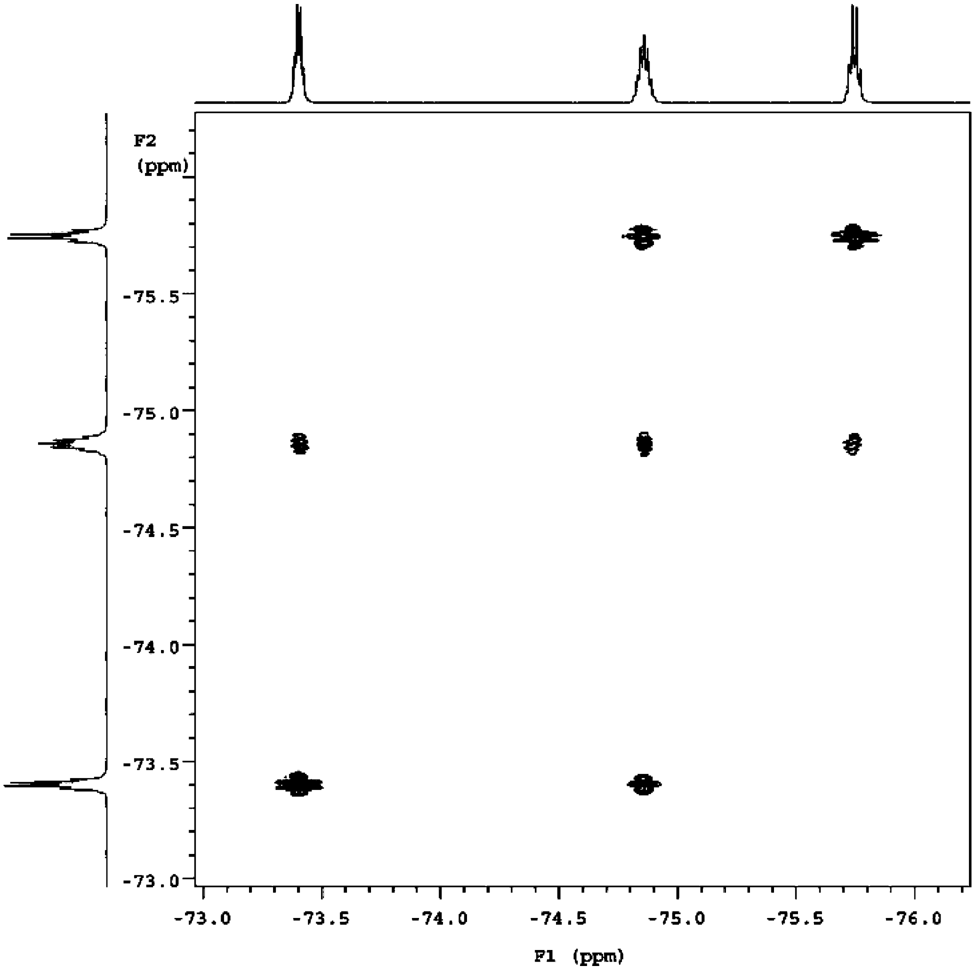
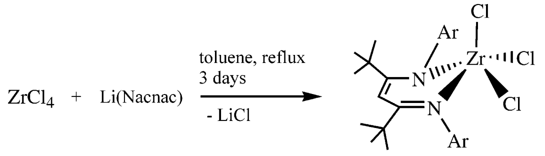


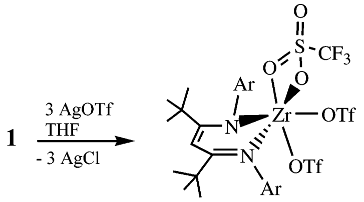
Figure 1. ^{19}F COSY spectrum of complex **2** displaying $J_{\mathrm{F-F}}$ coupling between three distinct OTf$^-$ groups.

Scheme 1. Synthetic Route to the Zirconium Trichloride Complex (Nacnac)ZrCl$_3$ (1)



1

Scheme 2. Synthetic Routes to (Nacnac)Zr(OTf)$_2$(η^2-OTf) (2) from the Addition of 3 Equiv of AgOTf to (Nacnac)ZrCl$_3$ (1)



2

(CH$_3$)$_2$]$_2$C$_6$H$_3$) and ZrCl$_4$ in refluxing toluene for 3 days affords in 75% yield bright yellow blocks of the trichloro precursor (Nacnac)ZrCl$_3$ (**1**), after recrystallization from CH$_2$Cl$_2$/pentane solution at −35 °C (Scheme 1). ^{1}H and ^{13}C NMR spectra are consistent with a fluxional ZrCl$_3$ unit, which is manifested by the presence of only four diastereotopic isopropyl methyls. The presence of two methine environments suggests that the Zr metal is not along the NCCCN mean plane. Similar systems studied by Smith and co-workers have established that the MCl$_3$ unit (M = Ti, Zr) deviates significantly from the NCCCN plane of the ligands [ArNC(CH$_3$)CHC(CH$_3$)NAr]$^-$ (Ar = Ph, 2,6-[CH(CH$_3$)$_2$]$_2$C$_6$H$_3$).[7] Perhaps the most salient feature for **1** was the ^{13}C NMR resonance for the β-**C***t*Bu resonance, which was centered at 167 ppm. This value compares well with those for trichloro Ti(IV) and Zr(IV) systems possessing less hindered β-diketiminate ligands (170−160 ppm).[7]

Addition of 3 equiv of AgOTf to **1** in THF forms cleanly the tris(triflato) complex (Nacnac)Zr(OTf)$_2$(η^2-OTf) (**2**) in 77% yield, after recrystallization from a CH$_2$Cl$_2$/pentane layered solution at −35 °C (Scheme 2). The reaction is clean, which is reflected partially by the precipitation of ~3 equiv of AgCl (>95% yield based on Zr). A notable spectroscopic feature for **2** is the ^{19}F NMR, which displays three OTf$^-$ resonances in a 1:1:1 ratio. This feature suggests that the OTf$^-$ groups are not all monodentate (X-ray crystallographic analysis confirms this hypothesis; vide infra) and are nonfluxional on the NMR time scale. The three ^{19}F NMR resonances appear as multiplets due to long-range coupling constants between the OTf$^-$ groups. Long-range ^{19}F−^{19}F spin−spin couplings are explained by a Fermi contact mechanism, which will be a sum of through-bond and through-space effects, and are also greatly dependent on molecular geometry.[31] In complex **2**, the ^{19}F COSY reveals that the quartet multiplicity of two resonances originates from coupling of η^1-OTf$^-$ with η^2-OTf$^-$, while

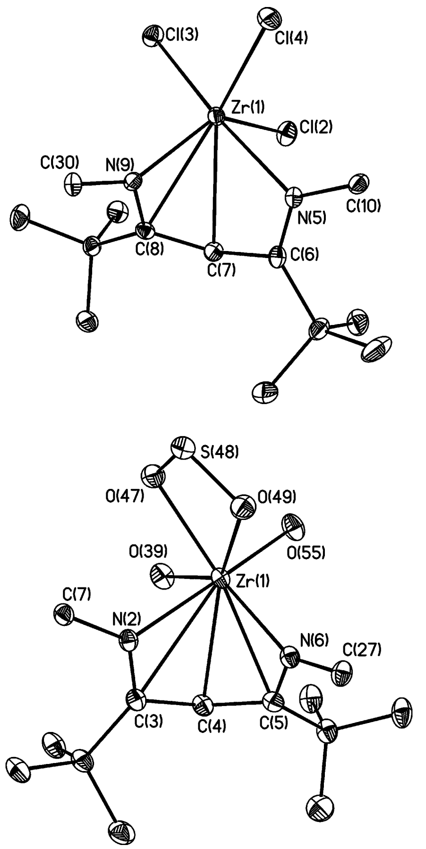
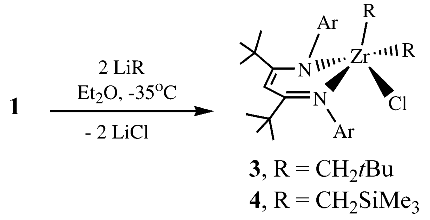


Figure 2. Molecular structures of complexes **1** (top) and **2** (bottom) showing atom-labeling schemes with thermal ellipsoids at the 50% probability level. H atoms and aryl groups on the nitrogens, with the exception of the ipso carbon, have been omitted for clarity. The O_2SCF_3 groups on O39 and O55 and O and CF_3 groups on S48 have also been excluded (structure of complex **2**).

the third resonance, a septet, results from coupling of η^2-OTf$^-$ with two adjacent η^1-OTf$^-$ groups (Figure 1).[31] As observed with complex **1**, the ^{13}C NMR spectrum of **2** displays a significantly downfield β-**C***t*Bu resonance at 172 ppm.

Single crystals of compounds **1** and **2** were grown from a CH_2Cl_2/pentane layered solution at −35 °C. The molecular representation for each complex is depicted in Figure 2. Crystallographic data are displayed in Table 1, and selected metrical parameters are shown in Table 2. Upon inspection, the structure of complex **1** displays a five-coordinate zirconium center having a highly distorted trigonal bipyramidal geometry with variable Zr−Cl distances (2.38−2.45 Å). The Zr atom sits ~1.65 Å out of the mean plane defined by the NCCCN atoms of the Nacnac$^-$ ligand, which compensates for the acuteness of the N−Ti−N angle (82.72(4)°). This value compares well with those for similar Zr(IV) systems studied by Smith and co-workers.[7,32] Examination of the molecular structure of **1** also reveals close interactions of the metal center with the β- (2.540(3) Å) and γ-carbons (2.601(4) Å) of the NCCCN ring. The NCCCN ring is not planar, and the γ-C and Zr atom are staggered to give the six-membered ring a "boatlike" conformation. This feature suggests that the Nacnac$^-$ ligand is not acting as a chelate but rather is more sandwich-like. The sterically encumbering *t*Bu group on the β-carbon positions provoke acute Zr−N−C$_{ipso}$ angles (129.34(8) and 141.83(9)°), consequently pushing the metal center out of the NCCCN mean plane.

Scheme 3. Synthetic Route to the Zirconium Bis(alkyl) Complexes (Nacnac)Zr(CH$_2$*t*Bu)$_2$Cl (3) and (Nacnac)Zr(CH$_2$SiMe$_3$)$_2$Cl (4) from Alkylation of Precursor 1



3, R = CH$_2$*t*Bu
4, R = CH$_2$SiMe$_3$

Complex **2** crystallizes in the space group $P2_1/n$, and the structure displays a Zr center in a saturated coordination environment. Two of the OTf$^-$ groups are monodentate, while the third triflate ligand is bidentate, which is consistent with the ^{19}F COSY spectrum (vide supra). The replacement of chlorides for more labile groups such as OTf$^-$ consequently causes the electron-deficient metal center to interact with two β- (2.538(7) and 2.770(6) Å) and γ-carbons (2.508(7) Å) of the NCCCN ring. This feature is not only manifested by interactions with all three carbons but also by the significant deviation of the Zr atom from the NCCCN plane (~1.63 Å). As observed with complex **1**, the NCCCNZr ring in **2** is staggered to give a "boatlike" conformation (Figure 2).

When an ethereal solution of **1** is treated with 2 equiv of LiCH$_2$XMe$_3$, the *bis*(alkyl) complexes (Nacnac)Zr(CH$_2$XMe$_3$)$_2$Cl (X = C (**3**), 86%; X = Si (**4**), 91%) are formed in good yield (Scheme 3). Complexes **3** and **4** display broader than usual ^{1}H and ^{13}C NMR spectra, which can likely be attributed to a fluxional process occurring in solution. Two inequivalent SiMe$_3$ groups are clearly evident at room temperature. When the temperature is lowered for a solution containing **4**, the isopropyl methine and Zr−*CH*$_2$SiMe$_3$ groups sharpen to inequivalent resonances in the ^{1}H NMR spectra (see the Experimental Section). Attempts to incorporate the third alkyl group led to a mixture of bis- and tris(alkyl) species as well as decomposition products. Interestingly, no α-hydrogen abstraction is observed in either complex **3** or **4**, suggesting that both the alkyls and chloride do not appear to provide sufficient steric crowding.[20,33] Single-crystal X-ray diffraction analysis confirmed the proposed connectivity of **3** and **4**, and the molecular representation of each complex is depicted in Figure 3. Crystallographic data are displayed in Table 1, and selected

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[31] Eight-bond long-range and through-space J_{F-F} values have been reported in the literature: (a) Gakh, J. G.; Gakh, A. A.; Gronenborn, M. G. *Magn. Reson. Chem.* **2000**, *38*, 551−558. (b) Peralta, J. E.; Contreras, R. H.; Snyder, J. P. *Chem. Commun.* **2000**, 2025−2026.

[32] Neutral and saltlike β-diketiminate complexes of zirconium halides have been prepared: Hitchcock, P. B.; Lappert, M. F.; Layh, M. *Dalton* **2001**, 2409−2416.

[33] (a) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249−262. (b) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359−3370. (c) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389−2399. (d) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236−6244. (e) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774−6776. (f) Fellmann, J. D.; Ruprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964−5966. (g) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 687−713.

Table 1. Crystallographic Data for Complexes 1−6

	1·CH_2Cl_2	**2**	**3**·$^1/_2Et_2O$	**4**·Et_2O	**5**	**6**
empirical formula	$C_{36}H_{55}Cl_5N_2Zr$	$C_{38}H_{53}F_9N_2$-O_9S_3Zr	$C_{47}H_{80}ClN_2$-$O_{0.50}Zr$	$C_{47}H_{85}ClN_2$-OSi_2Zr	$C_{72}H_{106}F_6N_4$-$O_6S_2Zr_2$	$C_{39}H_{61}ClN_2$-OZr
fw	784.29	1040.22	807.80	877.02	1484.17	700.57
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	10.162(1)	12.0380(9)	78.47(6)	1.316(4)	17.709(5)	11.127(2)
b (Å)	19.683(2)	17.948(3)	11.430(3)	17.769(6)	20.592(6)	17.397(4)
c (Å)	19.555(9)	20.903(5)	21.035(4)	18.582(7)	22.911(6)	19.846(4)
α (deg)					90.375(9)	
β (deg)	102.310(3)	98.421(2)	102.159(7)	91.059(2)	107.78(1)	97.755(5)
γ (deg)					105.27(1)	
V (Å^3)	3821.5(7)	4467.5(6)	18444(7)	5056.1(8)	7641(4)	3807(4)
Z	4	4	16	4	4	4
D_{calcd} (g cm^{-3})	1.363	1.547	1.164	1.152	1.290	1.222
cryst size (mm)	0.30 × 0.30 × 0.25	0.28 × 0.25 × 0.25	0.15 × 0.15 × 0.10	0.30 × 0.30 × 0.30	0.30 × 0.20 × 0.05	0.30 × 0.30 × 0.30
solvent, color	pentane/CH_2Cl_2, yellow	pentane/CH_2Cl_2, yellow	Et_2O, yellow	Et_2O, yellow	X, orange	Et_2O, orange
indes ranges (h, k, l)	$-14 \le h \le 14$, $-27 \le k \le 27$, $-27 \le l \le 27$	$-16 \le h \le 16$, $-25 \le k \le 25$, $-29 \le l \le 29$	$-101 \le h \le 68$, $-14 \le k \le 14$, $-25 \le l \le 27$	$-14 \le h \le 14$, $-27 \le k \le 27$, $-27 \le l \le 27$	$-22 \le h \le 22$, $-26 \le k \le 26$, $-29 \le l \le 29$	$-14 \le h \le 14$, $-22 \le k \le 22$, $-25 \le l \le 25$
F(000)	1640	2144	6992	2024	3120	1496
θ range	2.07−30.05	1.97−30.02	1.80−27.42	1.99−27.52	1.88−27.47	2.07−27.59
linear abs coeff (mm^{-1})	0.664	0.477	0.329	0.351	0.392	0.389
total no. of rflns collected	51 480	121 475	95 439	75 328	141 982	34 986
no. of unique rflns, $F > 4\sigma(F)$	11 156	13 044	20 906	14 767	141 982	8798
no. of obsd rflns	8896	9361	10 202	10 211	49 048	4285
R_{int}	0.0762	0.0750	0.1634	0.0854	0.0000	0.1306
no. of data/params	11 156/617	13 044/771	20 906/961	14 767/827	141 982/1694	8798/655
R1, wR2 (for $I > 2\sigma(I)$)	0.0280, 0.0620	0.0344, 0.0807	0.0943, 0.2053	0.0346, 0.0681	0.0926, 0.1917	0.0459, 0.0755
GOF	0.991	0.959	0.979	0.906	0.852	0.763
peak, hole (e/Å^{-3})	0.620, −0.469	0.533, −0.374	2.559, −1.098	0.644, −0.693	2.472, −1.785	1.311, −0.773

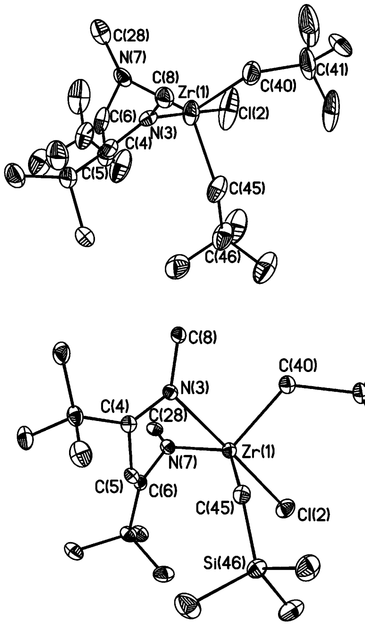

Figure 3. Molecular structures of complexes **3** (top) and **4** (bottom) showing atom-labeling schemes with thermal ellipsoids at the 50% probability level. H atoms and the aryl groups on the nitrogen atoms, with the exception of the ipso carbons, have been omitted for clarity. Disordered solvent molecules in the structure of **3** and **4** have been also omitted. Zr−C interactions with the β-C and γ-C atoms in **3** and **4** have been also omitted for the purpose of clarity.

metrical parameters are shown in Table 2. The gross structural features of complexes **3** and **4** are similar with Zr−C_{alkyl} (~2.23−2.28 Å range) and Zr−Cl (~2.42 Å) bond distances in the typical range. As observed with precursor **2**, there are close Zr−C interactions with the two β- (**3**, 2.612(7) Å; **4**, 2.582(5) Å) and γ-carbons (**3**, 2.634(7) Å; **4**, 2.626(6) Å) of the NCCCN ring. In both structures the Zr dips significantly out of the NCCCN mean plane (**3**, 1.79 Å; **4**, 1.75 Å).

Realizing that OTf^- groups are more sterically crowding and electron-withdrawing than chloride ligands, we reasoned that alkylation of complex **2** could provide the putative (Nacnac)Zr(CH_2R)$_2$(OTf), which could then undergo α-hydrogen abstraction to form the alkylidene (Nacnac)Zr=CHR(OTf). Precedent in the literature suggests tantalizingly that sterically demanding β-diketiminates can stabilize terminal and reactive functionalities such as alkylidenes,[17] alkylidynes,[19] imides,[16,34,35] and phosphinidenes.[18] In fact, previous work by Smith and co-workers on β-diketiminate zirconium systems proposed an alkylidene as a viable intermediate along a CH activation reaction of the aryl ring attached to the α-nitrogen (ortho metalation),[7b] but isotopic labeling kinetic studies supported direct CH activation through a four-centered transition state, thus ruling out the former pathway.[7b] In our system, ortho metalation is prohibited, since sterically demanding isopropyl groups occupy this vulnerable position.

Accordingly, treatment of **2** with 2 equiv of $LiCH_2CMe_3$ affords cleanly the unprecedented complex [(Nac*t*Bu)Zr=NAr(μ_2-OTf)]$_2$ (**5**; Nac*t*Bu$^-$ = [2,6-(CHMe$_2$)$_2$C$_6$H$_3$]NC(*t*Bu)CHC(*t*Bu)) in 76% yield instead of the anticipated (Nacnac)Zr(CH_2CMe_3)$_2$(OTf) product (Scheme 4). Formation of **5** is supported by a combination of ^1H, ^{13}C, and ^{19}F NMR spectra in addition to

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(34) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2003**, 1554−1555.

(35) (a) Dai, X.; Kapoor, P.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 4798−4799. (b) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085−10094.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Complexes 1−6

Compound **1**·CH$_2$Cl$_2$							
Zr1−N5	2.302(2)	Zr11−N9	2.100(1)	Zr1−Cl2	2.4285(4)	Zr1−Cl3	2.4530(4)
Zr1−Cl4	2.3814(4)	Zr1−C7	2.601(4)	Zr1−C8	2.540(3)	N5−C6	1.298(7)
N5−C10	1.458(7)	N9−C8	1.387(7)	N9−C30	1.445(7)	C6−C7	1.481(9)
C7−C8	1.381(9)						
Cl2−Zr1−N5	87.44(3)	Zr1−N5−C6	101.90(9)	Zr1−N9−C8	91.17(8)	Cl2−Zr1−Cl3	86.08(4)
Zr1−N5−C10	129.34(8)	Cl2−Zr1−N9	132.04(3)	Cl2−Zr1−Cl4	109.98(4)	Zr1−N9−C30	141.83(9)
N5−Zr1−N9	82.72(4)	N5−Zr1−Cl3	173.07(3)	N5−Zr1−Cl4	85.85(3)	N9−Zr1−Cl3	103.48(3)
C7−C8−N9	117.1(2)	N9−Zr1−Cl4	115.90(3)	N5−C6−C7	115.6(2)	C6−C7−C8	128.8(2)
Compound **2**							
Zr1−N2	2.231(4)	Zr1−N6	2.116(4)	Zr1−C3	2.770(6)	Zr1−C4	2.508(7)
Zr1−C5	2.538(7)	Zr1−O39	2.103(2)	Zr1−O47	2.270(2)	Zr1−O49	2.228(2)
Zr1−O55	2.108(2)	N2−C3	1.306(2)	C3−C4	1.486(2)	C4−C5	1.396(2)
C5−N6	1.376(2)	N2−C7	1.465(2)	N6−C27	1.455(2)		
Zr1−N6−C5	90.7(1)	Zr1−N2−C7	129.4(1)	Zr1−N6−C27	142.4(1)	Zr1−N2−C3	129.7(4)
N6−Zr1−O39	135.15(5)	N6−Zr1−O47	144.99(5)	N6−Zr1−O49	84.50(5)	N6−Zr1−N2	84.52(5)
N2−Zr1−O39	87.96(5)	N2−Zr1−O47	87.08(5)	N2−Zr1−O49	92.57(5)	N6−Zr1−O55	99.72(5)
O39−Zr1−O47	78.21(5)	O39−Zr1−O49	140.07(5)	O39−Zr1−O55	84.17(5)	N2−Zr1−O55	171.90(5)
O47−Zr1−O55	93.18(5)	O49−Zr−O55	94.71(5)	O47−S48−O49	102.70(7)	O47−Zr1−O49	61.97(4)
C3−C4−C5	128.4(5)	C4−C5−N6	116.0(5)			N2−C3−C4	115.7(4)
Compound **3**·$^1/_2$Et$_2$O							
Zr1−N3	2.386(5)	Zr1−N7	2.207(5)	Zr1−C40	2.282(7)	Zr1−C45	2.239(7)
Zr1−C5	2.634(7)	Zr1−C6	2.612(7)	Zr1−Cl2	2.423(2)	N7−C6	1.379(9)
C4−C5	1.471(9)	C5−C6	1.393(9)	N3−C4	1.312(8)	N3−C8	1.469(8)
C40−C41	1.57(1)	N7−C28	1.439(9)	C45−C46	1.54(1)		
Zr1−N3−C4	100.8(4)	Zr1−N7−C28	144.5(4)	Zr1−N3−C8	128.6(4)	Zr1−N7−C6	90.5(4)
N3−Zr1−N7	78.6(8)	N3−Zr1−Cl2	179.3(6)	N7−Zr1−Cl2	101.8(5)	C45−Zr1−Cl2	90.7(2)
C40−Zr1−Cl2	98.0(2)	N3−Zr1−C45	88.7(2)	N7−Zr1−C45	136.8(2)	N7−Zr1−C40	120.6(2)
Zr1−C40−C41	130.3(6)	Zr1−C45−C46	145.3(5)	C5−C6−N7	115.9(6)	C40−Zr1−C45	97.9(3)
						N3−C4−C5	116.0(6)
Compound **4**·Et$_2$O							
Zr1−N3	2.369(3)	Zr1−N7	2.184(3)	Zr1−C40	2.248(7)	Zr1−C45	2.241(7)
Zr1−C5	2.626(6)	Zr1−C6	2.582(5)	Zr1−Cl2	2.4282(5)	N7−C6	1.380(9)
C4−C5	1.476(2)	C5−C6	1.385(2)	N3−C4	1.298(9)	N3−C8	1.454(9)
C40−Si41	1.868(7)	N7−C28	1.439(9)	C45−Si46	1.861(7)		
Zr1−N3−C4	101.2(1)	Zr1−N7−C28	144.8(1)	Zr1−N3−C8	129.33(9)	Zr1−N7−C6	89.93(9)
N3−Zr1−N7	80.38(4)	N3−Zr1−Cl2	176.34(3)	N7−Zr1−Cl2	101.92(3)	C45−Zr1−Cl2	90.57(5)
C40−Zr1−Cl2	95.15(5)	N3−Zr1−C45	85.79(5)	N7−Zr1−C45	133.14(6)	N7−Zr1−C40	119.61(6)
Zr1−C40−Si41	124.20(9)	Zr1−C45−Si46	140.12(9)	C5−C6−N7	117.5(4)	C40−Zr1−C45	103.64(6)
C4−C5−C6	128.3(4)					N3−C4−C5	116.1(3)
Compound **5**							
Zr1−N51	1.834(4)	Zr2−N64	1.820(5)	Zr1−C6	2.315(6)	Zr2−C30	2.319(7)
Zr1−N3	2.271(5)	Zr2−N27	2.305(5)	Zr1−O77	2.224(4)	Zr1−O85	2.233(4)
Zr2−O79	2.283(4)	Zr2−O87	2.212(4)	O87−S86	1.480(4)	O79−S78	1.459(4)
S86−O85	1.480(4)	S78−O77	1.467(4)	C6−C5	1.349(8)	C5−C4	1.461(9)
C4−N3	1.295(7)	N27−C28	1.318(7)	C28−C29	1.481(9)	C29−C30	1.327(8)
Zr1−N51−C52	177.1(4)	Zr1−C6−C5	109.5(5)	Zr2−N64−C65	178.5(5)	Zr2−C30−C29	111.7(5)
Zr1−N3−C4	117.9(4)	Zr2−N27−C28	115.3(4)	N51−Zr1−O85	113.9(7)	N51−Zr1−O77	108.7(8)
N3−Zr1−C6	73.2(2)	N51−Zr1−C6	101.2(2)	N51−Zr1−N3	104.1(2)	O77−Zr1−O85	81.3(5)
O77−Zr1−C6	96.6(2)	O85−Zr1−N3	89.0(7)	O77−Zr1−N3	147.1(6)	O85−Zr1−C6	143.7(8)
N64−Zr2−O79	110.4(8)	N64−Zr2−O87	108.5(8)	N64−Zr2−N27	105.1(9)	N64−Zr2−C30	98.6(2)
C30−Zr2−O79	148.4(7)	C30−Zr2−O87	102.0(2)	N27−Zr2−O79	86.8(6)	N27−Zr2−O87	146.4(5)
C30−Zr2−N27	73.4(2)	O79−Zr2−O87	80.94(14)	C6−C5−C4	123.2(6)	C5−C4−N3	114.4(6)
N27−C28−C29	116.7(6)	C28−C29−C30	121.2(6)	O79−S78−O77	110.9(2)	O87−S86−O85	110.6(2)
Compound **6**							
Zr1−N26	1.831(3)	Zr1−O40	2.41(2)	Zr1−C5	2.318(3)	Zr1−N2	2.327(3)
Zr1−Cl39	2.452(1)	N2−C3	1.296(4)	C3−C4	1.462(4)	C4−C5	1.343(5)
C5−C6	1.527(4)	N2−C10	1.455(4)	N26−C27	1.397(4)		
Zr1−C5−C6	128.4(2)	Zr1−C5−C4	111.2(2)	C5−C4−C3	122.6(3)	Zr1−N26−C27	177.0(3)
Zr1−N2−C3	117.0(2)	Zr1−N2−C10	114.7(9)	N2−Zr1−N26	107.4(1)	C4−C3−N2	115.2(3)
N2−Zr1−C5	72.4(1)	N2−Zr1−O40	92.5(3)	C5−Zr1−O40	157.7(3)	N2−Zr1−Cl39	140.65(6)
C5−Zr1−Cl39	98.84(8)	Cl39−Zr1−O40	82.4(3)	Cl39−Zr1−N26	111.62(9)	C5−Zr1−N26	95.0(1)
						N26−Zr1−O40	105.3(3)

HMQC[36] and HMBC[37] NMR experiments. ^{1}H NMR spectra reveal the presence of 4 inequivalent methine and aryl groups, while ^{13}C NMR spectra displayed 31 distinct carbon environments (excluding the CF$_3$ group

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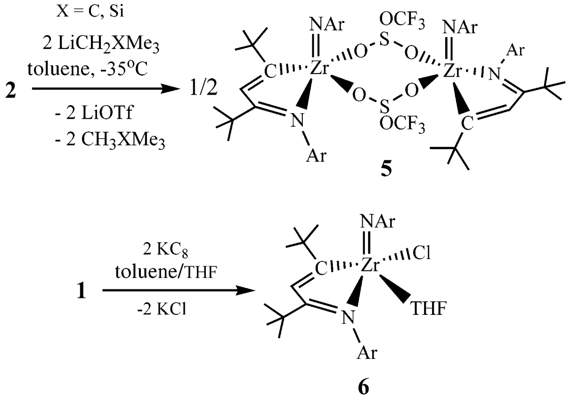
(36) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285−4294.

(37) Zhu, G.; Renwick, A.; Bax, A. *J. Magn. Reson.* **1994**, *110*, 257−261.

Scheme 4. Synthetic Routes to the Zirconium−Imido Dimer Complex [(Nac*t*Bu)Zr=NAr(μ_2-OTf)]$_2$ (5) (Top Reaction) and the Monomer (Nac*t*Bu)Zr=NAr(Cl)(THF) (6) (Bottom Reaction) via Two-Electron Reduction of 2 and 1, Respectively



of OTf$^-$). Interestingly, 1 of the 31 carbon environments resonates at an unusual chemical shift (249 ppm). Although the latter ^{13}C NMR resonance was not coupled to a proton, such a downfield-shifted resonance did couple, however, through two and three bonds, to one aromatic CH group and one *t*Bu group, respectively (via an HMBC experiment).[37] In addition, the low symmetry observed in the NMR spectra of complex **5** suggested significant alteration of the former Nacnac$^-$ ligand. One OTf$^-$ environment was evident from the ^{19}F NMR spectrum, suggesting at least one triflate group being present in a low-symmetry system.

Single crystals of **5** were grown slowly from Et$_2$O at −35 °C, and the molecular representation confirms the proposed connectivity as well as degree of aggregation. Figure 4 displays one of the two crystallographically independent molecules confined in the crystal structure of **5**. Crystallographic data are given in Table 1, and selected metrical parameters are shown in Table 2. Upon direct inspection, the structure of **5** reveals a dimer system possessing two terminal and thus short Zr=N bonds (Zr=N, 1.834(4) and 1.820(5) Å; Zr=N−C$_{\mathrm{ipso}}$, 177.1(4) and 178.5(5)°).[38] Dimer formation occurs via bridging of the OTf$^-$ groups, with both metals residing nearly in the plane defined by the NCCC ring (0.36 and 0.34 Å). Interestingly, the imido functionalities are oriented syn to each other, and cleavage of the N−C$_{\mathrm{imine}}$ bond leads consequently to formation of a monoanionic azabutadiene ligand (ArN=C(*t*Bu)CH=C-(*t*Bu)$^-$). Although the molecular structure of **5** is of low quality, it clearly depicts the correct connectivity, as suggested by multinuclear NMR data.

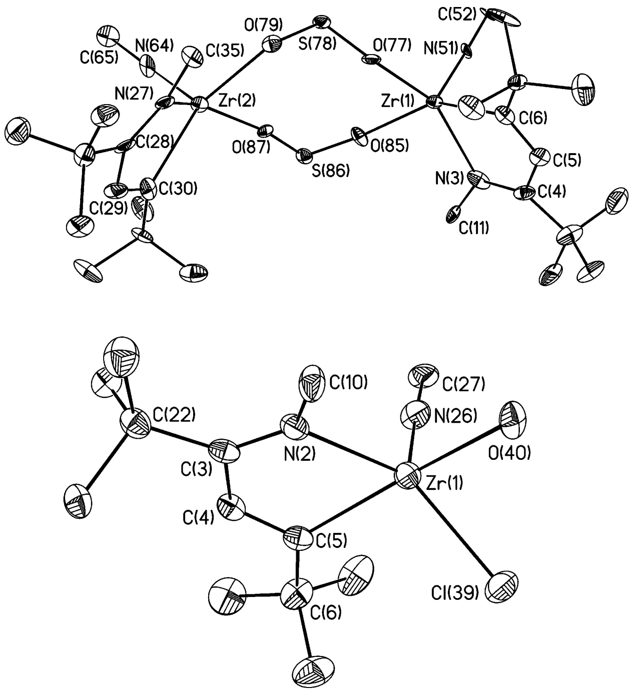


Figure 4. Molecular structures of complex **5** (top) and **6** (bottom) showing atom-labeling schemes with thermal ellipsoids at the 50% probability level. H atoms and the aryl groups on the nitrogen atoms, with the exception of the ipso carbons, have been omitted for clarity. The two OSCF$_3$ groups in **5** and the carbons of the THF ligand in **6** have been also excluded for clarity. There is considerable disorder in the bound THF ligand of complex **6**; hence, there is an alternative position for O40 (O105, not depicted).

Complex **5** results likely from reductive cleavage of the N−C$_{\mathrm{imine}}$ bond of the Nacnac$^-$ ligand. We propose that rupture of the N−C bond occurs via the putative Zr(II) species "(Nacnac)Zr(OTf)", which is generated from the two-electron reduction of **2** by the alkyl nucleophiles. The more electron withdrawing OTf$^-$ groups account for the Zr center being more readily reduced. In fact, a cyclic voltammogram of **1** and **2** (THF/TBAH) showed irreversible reduction waves at −2.21 and −1.95 V (vs FeCp$_2$/FeCp$_2^+$), respectively, thus suggesting that complex **2** is reduced more readily than **1** under the CV conditions utilized.[39] Stronger evidence for a Zr(II) species being involved in the N−C bond cleavage reaction is the two-electron reduction of **1** with KC$_8$, which provides the monomer and chloro analogue of **5**, namely (Nac*t*Bu)Zr=NAr(Cl)(THF) (**6**; Scheme 4, 76% yield). ^{1}H and ^{13}C NMR spectra are in accordance with the proposed connectivity. The most diagnostic chemical shift is the ^{13}C NMR vinylic carbon, which resonates at 255 ppm. The monomeric nature of **6** was confirmed by single-crystal X-ray diffraction studies

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(38) For some examples of structurally characterized zirconium complexes having a terminal imide ligand: (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729−8731. (b) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591−611. (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723. (d) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795−4809. (e) Blake, A. J.; Collier, P. E.; Gade, L. H.; Mountford, P.; Lloyd, J.; Pugh, S. M.; Schubart, M.; Skinner, M. E. G.; Trösch, D. J. M. *Inorg. Chem.* **2001**, *40*, 870−877. (f) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *Organometallics* **1998**, *17*, 846−853. (g) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1−3. (h) Thorman, J. L.; Guzei, I. A.; Young, V. C., Jr.; Woo, L. K. *Inorg. Chem.* **1999**, *38*, 3814−3824. (i) Profilet, R. D.; Zambrano, C. H.; Fanwick, P. E.; Nash, J. J.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 4362−4364. (j) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914−11921. (k) Arney, D. J.; Bruck, M. A.; Huber, S. R.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 3749−3755. (l) Bai, G.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Dalton* **2002**, 2437−2440. (m) Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689−708. (n) Blake, A. J.; Nikonov, G. I.; Mountford, P. *Acta Crystallogr.* **1997**, *C53*, 874−876. (o) Bai, Y.; Roesky, H. W.; Noltemeyer, M.; Witt, M. *Chem. Ber.* **1992**, *125*, 835−831.

(39) Although we were able to observe a second wave at −2.60 V for complex **1**, our attempts to clearly locate the second reduction wave for **2** were not successful, presumably due to decomposition of the compound under these conditions.

(Figure 4). The molecular structure of **6** displays a five-coordinate Zr system supported by a monoanionic azabutadiene, a terminal aryl−imido group (Zr═N, 1.831(3) Å), THF, and a chloride ligand. Interestingly, the Zr atom sits in the plane of the azabutadiene motif (0.32 Å), a feature which is also observed for the two metal atoms in complex **5**. Crystallographic data and selected metrical parameters are reported in Tables 1 and 2, respectively. Unlike **5**, formation of the dimer is probably not favored for kinetic reasons. Realizing that unsaturated group 4 imido complexes are exceedingly reactive,[38a−d,40] it is not surprising that complex **6** contains an additional THF ligand occupying the fifth coordination site. The α-C(*t*Bu)−Zr bond length (2.318(3) Å) is longer than typical $\text{Zr}-\text{C}_{\text{alky;l}}$ (vide supra) but similar to a few $\text{Zr}-\text{C}_{\text{vinyl-imine}}$ distances reported in the literature (2.43−2.30 Å).[41] The $\text{Zr}-\text{N}_{\text{imine}}$ distance (2.327(3) Å) is considerably longer than typical $\text{Zr}-\text{N}_{\text{anilide}}$ bond distances (2.00−2.06 Å).[38m] Hence, we best describe the ligand in complex **5** or **6** as a monoanionic η^2-vinyl−imine. Only a handful of zirconium η^2-vinyl−imine complexes have been reported in the literature.[41−42]

Conclusion

The sterically demanding β-diketiminate ligand Nacnac⁻ (Nacnac⁻ = [Ar]NC(*t*Bu)CHC(*t*Bu)N[Ar], Ar = 2,6-$[\text{CH}(\text{CH}_3)_2]_2\text{C}_6\text{H}_3$) can be incorporated readily on Zr(IV) species, and such systems have been shown to undergo smooth C−N bond rupture of the Nacnac⁻ imine functionality under reducing conditions. More specifically, the complexes (Nacnac)ZrCl_3 and (Nacnac)$\text{Zr(OTf)}_2(\eta^2\text{-OTf})$ can undergo two-electron-reduction reactions to form a putative "(Nacnac)Zr(X)" (X⁻ = OTf, Cl) species, which subsequently promotes reductive $\text{C}-\text{N}_{\text{imine}}$ bond cleavage to form the zirconium−imido complexes $[(\text{Nac}t\text{Bu})\text{Zr}{=}\text{NAr}(\mu_2\text{-OTf})]_2$ and (Nac*t*Bu)Zr═NAr(Cl)(THF). However, a stepwise reduction process not involving Zr(II) is also feasible, since one-electron reduction of (Nacnac)ZrCl_3 and (Nacnac)$\text{Zr(OTf)}_2(\eta^2\text{-OTf})$ can lead to C−N bond rupture via a Zr(IV) imine−vinyl radical intermediate, which can be further reduced by a second electron to furnish the final product. Such a stepwise two-electron process is not unreasonable, since green solutions are observed during the two-electron reduction of both (Nacnac)ZrCl_3 and (Nacnac)$\text{Zr(OTf)}_2(\eta^2\text{-OTf})$ and qualitatively suggest a transient Zr(III) species been formed in the course of the reaction. Unfortunately, attempts to isolate a Zr(III) species supported by the present Nacnac⁻ system have so far eluded us.

Part of the reason for C−N bond cleavage can be attributed to the π-type coordination mode of the Nacnac⁻ ligand, which invokes interaction of the Zr center not only with the α-nitrogens but also with the γ- and β-carbons in the NCCCN ring. Interestingly, complex (Nacnac)ZrCl_3 appears to be less susceptible to redox chemistry, unlike the triflate analogue (Nacnac)$\text{Zr(OTf)}_2(\eta^2\text{-OTf})$, which undergoes facile reduction in the presence alkyllithium reagents. CV studies also support this notion, since the reduction potential of (Nacnac)$\text{Zr(OTf)}_2(\eta^2\text{-OTf})$ is at least 0.26 V lower in energy than that of the trichloro analogue. Our inability to generate low-coordinate and terminal zirconium−alkylidene species is likely attributed to inherent reactivity of the Nacnac⁻ imine functionality. However, the possibility remains that under the right conditions a complex such as (Nacnac)$\text{Zr(CH}_2\text{XMe}_3)_2$(OTf) could be generated, which could ultimately lead to α-hydrogen abstraction concomitant with formation of a Zr═CHXMe_3 linkage (X = C, Si). We are currently pursuing other synthetic routes to incorporate a terminal alkylidene functionality on zirconium as well as attempting to stabilize monomeric Zr(II) and Zr(III) species.

Acknowledgment. For financial support of this research we thank Indiana University−Bloomington, the Camille and Henry Dreyfus Foundation, and the U.S. National Science Foundation (Grant CHE-0348941). U.J.K. was supported by NSF Grant CHE-0097388 under the auspices of the Research Experience for Undergraduates Program at Indiana University.

Supporting Information Available: Complete crystallographic data for compounds **1**−**6** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049332T

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(40) (a) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179−2180. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731−8733. (c) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719. (d) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216*−*217*, 65−97. (e) Mountford, P. *Perspectives in Organometallic Chemistry*; Royal Society of Chemistry: London, 2003; pp 28−46. (f) Blake, A. J.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Schubart, M.; Scowen, I. J. *Chem. Commun.* **1997**, 1555−1556. (g) Bashall A.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Pugh, S.; Radojevic, S.; Schubart, M.; Scowen, I. J.; Trösch, D. J. M. *Organometallics* **2000**, *19*, 4784−4794. (h) Blum, S. A.; Bergman, R. G. *Organometallics* **2004**, *23*, 4003−4005. (i) Krska, S. W.; Zuckerman, R. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11828−11829. (j) Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F.; Wilson, D. J.; Mountford, P. *Chem. Commun.* **1999**, 661−662.

(41) (a) Binger, P.; Sandmeyer, F.; Kruger, C. *Organometallics* **1995**, *14*, 2969−2976. (b) Arndt, P.; Lefeber, C.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1996**, 129, 207−211.

(42) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *488*, 241−248.