Zirconium Complexes of a Cross-Bridged Cyclam

Paul O'Connor,* David J. Berg,* and Brendan Twamley†

Department of Chemistry, University of Victoria, P.O. Box 3065,
Victoria, British Columbia, Canada V8W 3V6

Received July 14, 2004

The acid−base reaction of tetrabenzylzirconium with 1,4,8,11-tetraazabicyclo[6.6.2]-hexadecane (H_2(CBC), **1**) produces (CBC)Zr(CH_2Ph)$_2$, **2**. Similarly, reaction of **2** with phenols yields (CBC)Zr(CH_2Ph)(O-2,6-$C_6H_3Bu^t{}_2$), **3**, and (CBC)Zr(O-2,6-$C_6H_3Me_2$)$_2$, **5**. Prolonged heating of **3** leads to the metalated product (CBC)Zr[κ^2(C,O)-OC_6H_3(6-Bu^t)(2-CMe_2CH_2)], **4**. Reaction of $ZrCl_2[N(SiMe_3)_2]_2$ with H_2(CBC) leads to (CBC)$ZrCl_2$, **6**, which subsequently affords (CBC)Zr(X)(Y) by salt metathesis (**7**, X = Cl, Y = $N(SiMe_3)_2$; **8**, X = Y = CH_3; **9**, X = Y = $CH_2Si(CH_3)_3$). Compounds **3** and **7** show restricted rotation about the Zr−O and Zr−N bonds, respectively, on the NMR time scale. For **3**, the energy of activation for this process was determined to be 69 ± 1 kJ/mol. Neither **6** nor **8** shows ethylene polymerization activity when treated with 500 equiv of MAO. Reaction of **6** with 2 equiv of n-BuLi in the presence of excess diphenylacetylene leads to the zirconacyclopentadiene **10**, (CBC)Zr(C_4Ph_4). The structures of **5**, **9**, and **10** have been determined by X-ray crystallography, and all three display distorted octahedral geometry.

Introduction

Several diamido ligands bearing additional neutral donors have been explored as alternatives to cyclopentadienyl-based systems for group 4 organometallic chemistry.[1] These include macrocycles such as porphyrins,[2,3] tetraaza[14]annulenes,[4,5] tropocoronand,[6] and P_2N_2 [7−9] rings as well as tripodal[10,11] and linear systems.[12,13] These ligands have been exploited in such diverse areas as olefin polymerization catalysis,[11,14,15] unusual insertion chemistry,[4,6,16−18] imide reactions,[19] and dinitrogen activation.[9]

In previous work, we reported a number of zirconium dialkyls, $LZrR_2$, and their analogous cations, $LZrR^+$, supported by the macrocycle 4,13-diaza-18-crown-6 (Figure 1, DAC)[20] and the "half macrocycle" system [(C_6F_5)$NHCH_2CH_2OCH_2$]$_2$ (NOON).[21] The DAC cation took part in interesting catalytic reactions with alkynes, while the neutral NOON dibenzyl species underwent photolytic Zr−C bond cleavage and subsequent C−F bond activation.[22] Both supporting ligands displayed fluxional behavior in solution; we believe that the high flexibility of these systems may be contributing to the decomposition of the alkyl complexes and limiting their reaction chemistry.

Accordingly, we have turned our attention to the organometallic chemistry of cross-bridged cyclam (H_2(CBC), 1,4,8,11-tetraazabicyclo[6.6.2]hexadecane).[23] This ligand is attractive for two reasons: the cross-bridge restricts the conformations of the ligand while it is coordinated to the metal, and the ligand is saturated, precluding the alkyl migrations to the ligand observed in Schiff base systems.[4,5,24,25]

The coordination chemistry of protio and N-alkylated cross-bridged cyclams has been reported with lithium,[27] copper,[23,28] manganese,[29] iron,[29,30] zinc,[31,28e] cadmium,[31b,c] mercury,[31c] nickel,[23,32] palladium,[33] gallium,[34] and in-

---

* To whom correspondence should be addressed. E-mail: djberg@uvic.ca.

† Present address: University Research Office, 109 Morrill Hall, University of Idaho, Moscow, ID 83844-3010.

(1) Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 468.

(2) Brand, H.; Arnold, J. *Coord. Chem. Rev.* **1995**, *140*, 137.

(3) Kim, H.; Jung, S.; Jeon, Y.; Whang, D.; Kim, K. *Chem. Commun.* **1997**, 2201.

(4) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801.

(5) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F. *Organometallics* **1998**, *17*, 382.

(6) Scott, M. J.; Lippard, S. J. *Organometallics* **1998**, *17*, 1769.

(7) Fryzuk, M. D.; Kozak, C. M.; Mehrkhodavandi, P.; Morello, L.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 516.

(8) Fryzuk, M. D.; Love, J.; Rettig, S. J. *Organometallics* **1998**, *17*, 846.

(9) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.

(10) Skinner, M. E. G.; Li, Y.; Mountford, P. *Inorg. Chem.* **2002**, *41*, 1110.

(11) Mehrkhodavandi, P.; Schrock, R. R.; Pryor, L. L. *Organometallics* **2003**, *22*, 4569.

(12) Schrodi, Y.; Schrock, R. R.; Bonitatebus, P. J., Jr. *Organometallics* **2001**, *20*, 3560.

(13) Li, Y.; Turnas, A.; Ciszewski, J. T.; Odom, A. L. *Inorg. Chem.* **2002**, *41*, 6298.

(14) Britovesek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

(15) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236.

(16) Scott, M. J.; Lippard, S. J. *Organometallics* **1997**, *16*, 5857.

(17) Scott, M. J.; Lippard, S. J. *Organometallics* **1998**, *17*, 466.

(18) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655.

(19) Mountford, P.; Gade, L. H. *Coord. Chem. Rev.* **2001**, *216*, 65.

(20) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1997**, *16*, 2556.

(21) O'Connor, P. E.; Morrison, D. J.; Steeves, S.; Burrage, K.; Berg, D. J. *Organometallics* **2001**, *20*, 1153.

(22) O'Connor, P. E.; Berg, D. J.; Barclay, T. *Organometallics* **2002**, *21*, 3947.

(23) Weisman, G. R.; Wong, E. H.; Hill, D. C.; Rogers, M. E.; Reed, D. P.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1996**, 947.

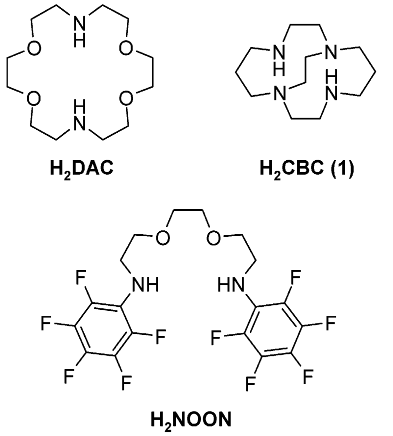
(24) Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539.

(25) Bonomo, L.; Toraman, G.; Solari, E.; Scopelliti, R.; Floriani, C. *Organometallics* **1999**, *18*, 5198.

(26) For an excellent review see: Springborg, J. *J Chem. Soc., Dalton Trans.* **2003**, 1653.

(27) Weisman, G. R.; Rogers, M. E.; Wong, E. H.; Jasinski, J. P.; Paight, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 8604.

10.1021/om049469j CCC: $30.25



H$_2$DAC **H$_2$CBC (1)** **H$_2$NOON**

Figure 1. Polydentate diamido ligands.

dium.[34] However, in this contribution we report the synthesis and structural studies of several coordination and organometallic zirconium complexes supported by the cross-bridged cyclam dianion (CBC^{2-}) as well as the thermal decomposition of one of these compounds. Additionally, since zirconacycles have a range of uses in organic chemistry,[35] materials chemistry,[36] macrocycle synthesis,[37] and metallacycle transfer reactions,[38] we report the synthesis and structure of a zirconcyclopentadiene supported by cross-bridged cyclam.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen or argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. Tetrabenzylzirconium[39] and Zr[N(SiMe$_3$)$_2$]$_2$Cl$_2$ [40] were prepared according to literature procedures. *N*-Butyllithium and MAO (methylaluminoxane) were obtained commercially (Aldrich) and were used as received.

NMR spectra were recorded using a Bruker AMX-360 MHz spectrometer: ^{1}H (360 MHz), ^{13}C (90.55 MHz), ^{29}Si (71.54 MHz), ^{11}B (115.54 MHz) unless otherwise specified. All deuterated solvents were dried over activated 4 Å molecular sieves except for tetrahydrofuran (THF), which was dried by distillation from sodium benzophenone ketyl under argon and stored over activated 4 Å molecular sieves. Spectra were recorded using 5 mm tubes fitted with a Teflon valve (Brunfeldt) at room temperature unless otherwise specified. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances. Melting points were recorded using a Büchi melting point apparatus in sealed capillary tubes and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, BC. Despite the use of co-oxidants such as V$_2$O$_5$ and PbO$_2$, the analytical data for most complexes were consistently 2−4% low in carbon, likely due to metal carbide formation. Despite repeated attempts, satisfactory analyses of **2**, **9**, and **10** were not obtained; this may be a result of decomposition of the compounds during shipping, storage, or handling of the samples, as they have been observed to slowly decompose in the solid state at room temperature even when stored in the glovebox. Mass spectra were recorded on a Kratos Concept H spectrometer using electron impact (70 eV) ionization.

H$_2$(CBC) (1). Cyclam was prepared via a nickel templated reaction, which does not require the use of perchlorate salts.[41] The free base was then obtained without isolating the nickel cyclam complex.[42] The synthesis of cross-bridged cyclam has been described previously;[28a] however, we found it necessary to sublime the oil obtained after benzene extraction from KOH and to store a toluene solution of the title compound over freshly activated molecular sieves for several days to thoroughly dry the product.

(CBC)Zr(CH$_2$Ph)$_2$ (2). H$_2$(CBC) (0.500 g, 2.21 mmol) was added to a solution of tetrabenzylzirconium (1.00 g, 2.19 mmol) in 20 mL of toluene. The solution was protected from light and stirred at room temperature overnight. Cooling to −30 °C afforded a yellow powder after decanting the mother liquor and drying under vacuum. Yield: 0.935 g, 85%. Mp: 171 °C (dec). NMR (d_6-benzene): ^{1}H δ 7.20 (m, 4H, *m*-aryl*H*), 7.14 (m, 4H, *o*-aryl*H*), 5.84 (tt, 2H, *p*-aryl*H*), 4.30 (m, 2H), 3.11 (dd, 2H), 2.90−2.84 (m, 4H), 2.78 (td, 2H), 2.56 (d, 2H, C*H*HPh, $^2J_{HH}$ = 10.2 Hz), 2.51 (td, 2H), 2.47 (d, 2H, C*H*HPh, $^2J_{HH}$ = 10.2 Hz), 2.41−2.36 (m, 2H), 1.80 (m, 2H), 1.64−1.54 (dd and m, 4H), 1.37 (m, 2H), 0.72 (m, 2H); ^{13}C{^{1}H} δ 151.9 (*quat*-aryl*C*), 128.7 (*m*-aryl*C*), 126.3 (*o*-aryl*C*), 120.3 (*p*-aryl*C*), 70.3 (*C*H$_2$Ph, t in the gated ^{13}C, $^1J_{CH}$ = 113 Hz), 60.4, 58.60, 54.2, 54.0, 50.8 (NCH$_2$), 22.2 (CH$_2$CH$_2$CH$_2$). Anal. Calcd for C$_{26}$H$_{38}$N$_4$Zr: C, 62.73; H, 7.69; N, 11.25. Found: C, 57.97; H, 7.19; N, 11.45.

(CBC)Zr(CH$_2$Ph)(O-2,6-C$_6$H$_3$Bu$^t_2$) (3). Toluene (5 mL) was added to an intimate mixture of (CBC)Zr(CH$_2$Ph)$_2$ (0.050 g, 0.10 mmol) and 2,6-di-*tert*-butylphenol (0.021 g, 0.10 mmol). The mixture was stirred at room temperature overnight and the solvent removed under reduced pressure. The powder was recrystallized by cooling a hot toluene solution to −30 °C to produce pale yellow microcrystals. Yield: 0.026 g, 43%. Mp: 220−224 °C. NMR (d_6-benzene): ^{1}H δ 7.50 (dd, 1H, *m*-phenoxide*H*), 7.42 (dd, 1H, *m*-phenoxide*H*), 7.12 (1H obscured by d_6-benzene, *p*-benzyl, or *p*-phenoxide) 6.97 (t, 1H, *p*-benzyl or

---

[28] (a) Wong, E. H.; Weisman, G. R.; Hill, D. C.; Reed, D. P.; Rogers, M. E.; Condon, J. S.; Fagan, M. A.; Calabrese, J. C.; Lam, K.-C.; Guzei, I. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 10561. (b) Hubin, T. J.; McCormick, J. M.; Alcock, N. W.; Clase, H. J.; Busch, D. H. *Inorg. Chem.* **1999**, *38*, 4435. (c) Hubin, T. J.; McCormick, J. M.; Collison, S. R.; Alcock, N. W.; Busch, D. H. *J. Chem. Soc., Chem. Commun.* **1998**, 1675. (d) Sun, X.; Wuest, M.; Weisman, G. R.; Wong, E. H.; Reed, D. P.; Boswell, C. A.; Motekaitis, R.; Martell, A. E.; Welch, M. J.; Andersen, C. J. *J. Med. Chem.* **2002**, *45*, 469. (e) Niu, W.; Wong, E. H.; Weisman, G. R.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L. *Polyhedron* **2004**, *23*, 1019. (f) Boswell, C. A.; Sun, X.; Niu, W.; Weisman, G. R.; Wong, E. H.; Rheingold, A. L.; Anderson, C. J. *J. Med. Chem.* **2004**, *47*, 1465. (g) Hubin, T. J.; Alcock, N. W.; Busch, D. H. *Acta Crystallogr., Sect. C* **2000**, *C56*, 37.

[29] Hubin, T. J.; McCormick, J. M.; Collinson, S. R.; Buchalova, M.; Perkins, C. M.; Alcock, N. W.; Kahol, P. W.; Raghunatan, A.; Busch, D. H. *J. Am. Chem. Soc.* **2000**, *122*, 2512.

[30] Hubin, T. J.; McCormick, J.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **2001**, *40*, 435.

[31] (a) Niu, W.; Wong, E. H.; Weisman, G. R.; Lam, K.-C.; Rheingold, A. L. *Inorg. Chem. Commun.* **1999**, *2*, 361. (b) Niu, W.; Wong, E. H.; Weisman, G. R.; Peng, Y.; Anderson, C. J.; Zakharova, L. N.; Golen, J. A.; Rheingold, A. L. *Eur, J. Inorg. Chem.* **2004**, 3310. (c) Niu, W.; Wong, E. H.; Weisman, G. R.; Zakharova, L. N.; Sommer, R. D.; Rheingold, A. L. *Abstracts of Papers*, 234th ACS National Meeting, Boston, MA, August 18−22, 2002. INOR-659.

[32] Hubin, T. J.; Alcock, N. W.; Clase, H. J.; Busch, D. H. *Supramol. Chem.* **2001**, *13*, 261.

[33] Hubin, T. J.; Alcock, N. W.; Busch, D. H. *Acta Crystallogr., Sect. C* **1999**, *C55*, 1404.

[34] Niu, W.; Wong, E. H.; Weisman, G. R.; Sommer, R. D.; Rheingold, A. L. *Inorg. Chem. Chem.* **2002**, *5*, 1.

[35] Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Japn.* **1998**, *71*, 755.

[36] Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulaszi, L.; Reau, R. *Chem. Eur. J.* **2001**, *7*, 4222.

[37] (a) Schafer, L. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 2683. (b) Nitschke, J. R.; Zurcher, S.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 10345.

[38] Fagan, M. A.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

[39] Zucchini, U.; Albizatti, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

[40] Andersen, R. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

[41] Berry, D. E.; Girard, S.; McAuley, A. *J. Chem. Educ.* **1996**, *73*, 551.

[42] BareField, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R.; Holt, S. *Inorg. Synth.* **1976**, *16*, 223.

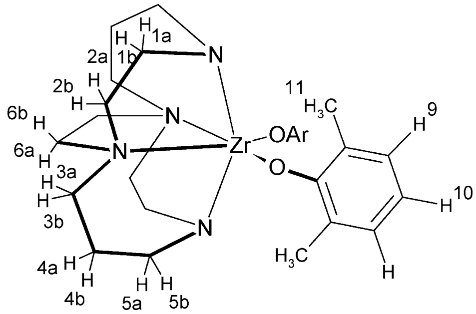


Figure 2. NMR numbering scheme for **5** (C_2 symmetry in solution). The coupling constants of H_a and H_b resonances are consistent with pseudoaxial and pseudoequatorial sites, respectively.

p-phenoxide*H*), 6.88−6.82 (m, 4H, *o*- and *m*-benzyl*H*), 4.64 (m, 1H), 4.03 (m, 1H), 3.13−2.96 (m, 10H), 2.79−2.71 (m, 2H), 2.61−2.54 (m, 3H), 2.54 (d, 1H, C*H*HPh, $^2J_{HH}$ = 10.7 Hz), 2.34 (d, 1H, C*H*HPh, $^2J_{HH}$ = 10.7 Hz), 2.00 (m, 2H), 1.88−1.67 (m, 1H), 1.85 (s, 9H, ^{t}Bu), 1.78 (s, 9H, ^{t}Bu), 1.38−1.22 (m, 2H), 0.88 (m, 2H); $^{13}C\{^1H\}$ δ 164.5 (O*C*), 153.0 (*quat*-benzyl*C*), 140.5 (*C*C(CH_3)$_3$), 139.4 (*C*C(CH_3)$_3$), 128.7 (*o*- or *m*-aryl obscured by d_6-benzene), 126.6 (*o*- or *m*-aryl*C*), 126.4 (*o*- or *m*-aryl*C*), 125.8 (*o*- or *m*-aryl*C*), 120.2 (*p*-aryl*C*), 118.9 (*p*-aryl*C*), 64.8 (*C*H_2Ph), 61.6, 60.7, 59.4, 58.1, 55.2, 54.7, 54.6, 52.5, 51.7, 49.7 (N*C*H_2), 36.7, 36.4 (*C*(CH_3)$_3$), 32.9, 32.1 (*C*H_3), 21.9, 21.5 (CH_2*C*H_2CH_2). Anal. Calcd for $C_{33}H_{52}N_4OZr$: C, 64.76; H, 8.56; N, 9.15. Found: C, 63.80; H, 8.25; N, 9.03.

(CBC)Zr[κ^2(C,O)-OC_6H_3(6-Bu^t)(2-CMe_2CH_2)] (4). A solution of (CBC)Zr(CH_2Ph)(O-2,6-C_6H_3Bu$^t_2$)] (0.140 g, 0.229 mmol) in 30 mL of toluene was sealed in a Kontes bomb and heated at 100 °C for 7 days. The solvent was removed and the product was recrystallized from a minimum volume of hot toluene. Cooling to −30 °C yielded the product as a pure colorless powder. Yield: 0.054 g, 39%. Mp: 224−229 °C (dec). NMR (d_6-benzene): ^{1}H δ 7.65 (dd, 1H, *m*-aryl*H*), 7.39 (dd, 1H, *m*-aryl*H*), 7.05 (t, 1H, *p*-aryl*H*), 4.25 (m 1H), 3.98 (m, 1H), 3.32 (m, 1H), 3.11−2.97 (m, 7H), 2.92−2.73 (m, 4H), 2.17 (m, 1H), 2.00−1.96 (m, 2H), 1.93 (m, 1H), 1.90−1.68 (m, 2H), 1.88 (s, 3H, C*H*$_3$), 1.81 (s, 3H, C*H*$_3$), 1.73 (s, 9H, C(C*H*$_3$)$_3$), 1.40 (dd, 1H), 1.29 (dd, 1H), 1.16 (d, 1H, ZrC*H*H, $^2J_{HH}$ = 13.3 Hz), 0.87 (d, 1H, ZrC*H*H, $^2J_{HH}$ = 13.3 Hz), 0.85 (m, 1H), 0.70 (m, 1H); $^{13}C\{^1H\}$ and DEPT δ 162.1 (O*C*), 143.7 (*o*-aryl*C*), 136.4 (*o*-aryl*C*), 125.8 (*m*-aryl*C*), 124.5 (*m*-aryl*C*), 118.8 (*p*-aryl*C*), 75.4 (Zr*C*H_2) 62.3, 62.0, 58.8, 58.3, 54.4, 53.2, 53.0, 51.4, 51.2, 51.2 (N*C*H_2), 42.9 (*quat-C*), 39.8 (*quat-C*), 35.8 (*C*H_3), 33.4 (*C*H_3), 31.3 (C(*C*H_3)$_3$), 22.0 (overlapping CH_2*C*H_2CH_2). Anal. Calcd for $C_{26}H_{44}N_4OZr$: C, 64.76; H, 8.56; N, 9.15. Found: C, 63.80; H, 8.25; N, 9.03.

(CBC)Zr(O-2,6-$C_6H_3Me_2$)$_2$ (5). (CBC)Zr(CH_2Ph)$_2$ (0.930 g, 1.87 mmol) was dissolved in 50 mL of warm toluene, and 2,6-dimethylphenol (0.456 g, 3.73 mmol) was added. The solution was stirred at room temperature for 2 h and then stored at −30 °C, resulting in clear colorless crystals of **5** (two crops). Yield: 0.89 g, 85%. Mp: 270 °C (dec). NMR (d_6-benzene): ^{1}H δ 7.04 (d, 4H, H_9), 6.77 (t, 2H, H_{10}), 4.01 (m, 2H, H_{5a}), 3.65 (m, 2H, H_{2a}), 3.15 (m, 2H, H_{1b}), 3.10−3.02 (m, 4H, H_{1a}, and H_{3a}), 2.99 (m, 2H, H_{6b}), 2.93(m, 2H, H_{5b}), 2.50 (s, 12H, H_{11}), 2.06 (m, 2H, H_{3b}), 1.98 (m, 2H, H_{2b}), 1.79 (m, 2H, H_{4a}), 1.38 (m, 2H, H_{6a}), 0.62 (m, 2H, H_{4b}); $^{13}C\{^1H\}$ δ 161.0 (C_7), 129.2 (C_9), 127.3 (C_8), 119.3 (C_{10}), 62.7 (C_2), 59.7 (C_3), 53.3 (C_1), 52.9 (C_5), 52.3 (C_6), 21.7 (C_4), 18.6 (C_{11}). Assignments given in Figure 2 are based on ^{1}H−^{1}H and ^{1}H−^{13}C COSY. Anal. Calcd for $C_{28}H_{42}N_4O_2Zr$: C, 60.28; H, 7.59; N, 10.04. Found: C, 60.24; H, 7.45; N, 10.05. MS (EI): M$^+$ 556.

(CBC)ZrCl_2 (6). H_2(CBC) (1.50 g, 6.63 mmol) and ZrCl_2[N(Si(CH_3)$_3$)$_2$]$_2$ (3.30 g, 6.62 mmol) were sealed in a Kontes bomb with 20 mL of toluene and heated at 100 °C for 2 days. The product precipitated from solution as a yellow powder and was washed twice with 5 mL of hexanes and dried at reduced pressure. Yield: 2.64 g, 90%. Mp: 271−5 °C (dec). NMR (d_6-benzene): ^{1}H δ 4.73 (m, 2H), 3.30 (m, 4H), 2.95 (m, 2H), 2.87 (m, 2H), 2.76 (dd 2H), 2.64 (m 2H), 1.91 (dd 2H), 1.71 (dd 2H), 1.56 (m 2H), 1.34 (m, 2H), 0.80 (m, 2H); $^{13}C\{^1H\}$ δ 61.8, 60.3, 54.0, 53.3, 52.8, 30.6 (*C*H_2N), 21.7 (CH_2*C*H_2CH_2). Anal. Calcd for $C_{12}H_{24}N_4Cl_2Zr$: C, 37.29; H, 6.26; N, 14.50. Found: C, 37.33; H, 6.54; N, 13.78.

(CBC)Zr(Cl)[N(Si(CH_3)$_3$)$_2$] (7). Method A: Complex **7** was isolated as a byproduct in the synthesis of (CBC)ZrCl_2 from ZrCl_2[N(Si(CH_3)$_3$)$_2$]$_2$, possibly due to the presence of ZrCl[N(Si(CH_3)$_3$)$_2$]$_3$ as a contaminant in the bis(trimethylsilylamide) complex. Method B: THF (15 mL) was added to a mixture of (CBC)ZrCl_2 (0.200 g, 0.518 mmol) and NaN(Si(CH_3)$_3$)$_2$ (0.095 g, 0.518 mmol), and the resulting solution was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the solid residue was extracted with toluene (15 mL), then filtered through Celite to afford a clear solution. The product was isolated as clear colorless crystals by layering a saturated toluene solution with hexamethyldisiloxane and storing at −30 °C. The crystals become opaque when removed from the solvent. Yield: 0.037 g, 14%. Mp: 173−176 °C (dec). NMR (d_6-benzene): ^{1}H δ 4.89 (m, 1H), 4.09 (m, 1H), 3.75 (m, 1H), 3.50 (m, 1H), 3.25−2.70 (m, 10H), 1.98 (m, 1H), 1.88 (m, 1H), 1.80−1.55 (m, 4H), 1.30 (m, 1H), 1.16 (m, 1H), 0.99 (m, 1H), 0.88 (m, 1H), 0.79 (s, 9H, C*H*$_3$), 0.54 (s, 9H, C*H*$_3$); $^{13}C\{^1H\}$ δ 61.9, 61.0, 60.0, 58.5, 54.8, 54.6, 54.5, 53.3, 53.0, 52.7 (*C*H_2N), 22.3 (CH_2*C*H_2CH_2), 21.5 (CH_2*C*H_2CH_2), 7.4 (*C*H_3), 7.2 (*C*H_3). Anal. Calcd for $C_{18}H_{42}N_5ClSi_2Zr$: C, 42.27; H, 8.28; N, 13.69. Found: C, 41.88; H, 7.87; N, 13.69.

(CBC)Zr(CH_3)$_2$ (8). MeLi (1.4 M, 1.85 mL, 2.6 mmol) was added to a suspension of (CBC)ZrCl_2 (0.500 g, 1.29 mmol) in 20 mL of THF and stirred at room temperature overnight. The solvent was removed under reduced pressure, and the solids were extracted twice with 50 mL of toluene. The extract was filtered (Celite), and the solvent removed under reduced pressure. The product was repeatedly recrystallized from warm toluene to yield colorless or pale yellow microcrystals. Yield: 0.107 g, 24%. Mp: 175 °C (dec). NMR (d_6-benzene): ^{1}H δ 4.50 (m, 2H), 3.25 (dd, 2H), 3.13−2.96 (m, 6H), 2.80 (m, 2H), 2.47 (m, 2H), 1.99 (m, 2H) 1.83 (dd, 2H), 1.81 (m, 2H), 1.75 (m, 2H), 0.80 (m 2H), 0.60 (s, 6H); $^{13}C\{^1H\}$ and DEPT δ 60.9, 59.8, 53.9, 53.8, 51.6 (*C*H_2N), 39.3 (*C*H_3, t in the gated ^{13}C, $^1J_{CH}$ = 109 Hz), 22.1 (CH_2*C*H_2CH_2). Anal. Calcd for $C_{14}H_{30}N_4Zr$: C, 48.65; H, 8.75; N, 16.21. Found: C, 48.38; H, 8.54; N, 16.13.

(CBC)Zr[CH_2Si(CH_3)$_3$]$_2$ (9). (CBC)ZrCl_2 (0.500 g, 1.29 mmol) was suspended in 50 mL of toluene, and LiCH_2Si(CH_3)$_3$ (0.244 g, 2.59 mmol) was added; the mixture was stirred at room temperature overnight. Filtration (Celite) of the reaction mixture and removal of the solvent at reduced pressure afforded a white powder. The product was dissolved in 14 mL of 5:2 toluene/hexanes and cooled to −30 °C to yield clear, colorless, rod-shaped crystals. Yield: 0.399 g, 63%. Mp: 127−128 °C. NMR (d_6-benzene): ^{1}H δ 4.30 (m, 2H), 3.22 (m, 2H), 3.02 (m, 4H), 2.95 (m, 2H), 2.75 (m, 2H), 2.50 (m, 2H) 1.97 (m, 2H), 1.81 (m, 2H), 1.78−1.67 (m, 2H), 1.51 (m, 2H), 0.76 (m, 2H) 0.47 (s, 18H, Si(C*H*$_3$)$_3$), 0.42 (d, 2H, ZrC*H*H, $^2J_{HH}$ = 12.1 Hz), 0.033 (d, 2H, ZrC*H*H, $^2J_{HH}$ = 12.1 Hz); $^{13}C\{^1H\}$ δ 60.7, 60.2, 54.0, 54.0 (*C*H_2N), 53.1 (*C*H_2Si, t in the gated ^{13}C, $^1J_{CH}$ = 102 Hz), 51.4 (*C*H_2N), 22.1 (CH_2*C*H_2CH_2), 4.3 (Si(*C*H_3)$_3$). Anal. Calcd for $C_{20}H_{46}N_4Si_2Zr$: C, 49.02; H, 9.46; N, 11.43. Found: C, 48.08; H, 8.75; N, 11.67.

(CBC)Zr(C_4Ph_4) (10). Diphenylacetylene (0.507 g, 2.84 mmol), (CBC)ZrCl_2 (0.500 g, 1.29 mmol), and 50 mL of THF were cooled in a dry ice−acetone (−78 °C) bath prior to the addition of n-BuLi (1.6 M, 1.62 mL, 2.6 mmol). The mixture was stirred at low temperature for 20 min and then transferred to an ice bath for 2 h. The solvent was removed under reduced pressure to yield a brown oil. Toluene (40 mL) was added, and

Table 1. Summary of Crystallographic Data[a]

	5	**9**	**10**
formula	$C_{28}H_{42}N_4O_2Zr$	$C_{20}H_{46}N_4Si_2Zr$	$C_{47}H_{52}N_4Zr$
fw	557.88	490.01	764.15
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pcc*2	*C*2/*c*	*C*2/*c*
a (Å)	11.9203(10)	14.891(3)	16.770(3)
b (Å)	11.9130(10)	18.461(4)	12.417(3)
c (Å)	19.4240(16)	9.4278(19)	18.247(4)
β (deg)	90	101.26(3)	91.34(3)
V (Å^3)	2758.3(4)	2541.8(9)	3798.6(14)
Z	4	4	4
density(cald) (Mg/m^3)	1.343	1.280	1.336
abs coeff (mm^{-1})	0.429	0.539	0.329
F(000)	1176	1048	1608
θ range for data collection (deg)	1.05 to 28.33	1.78 to 27.49	2.04 to 27.50
no. of obsd reflns	32 772	31 721	26 431
no. of unique reflns	6859 [*R*(int) = 0.0424]	2916 [*R*(int) = 0.0628]	4368 [*R*(int) = 0.0477]
completeness to θ	28.33°, 99.7%	27.49°, 99.5%	27.5°, 99.8%
no. of data/restraints/params	6859/1/321	2916/0/126	4368/0/268
goodness of fit on F^2	1.036	1.175	1.056
final *R* indices [$I > \sigma(I)$]	R1 = 0.0329, wR2 = 0.0720	R1 = 0.0386, wR2 = 0.0773	R1 = 0.0395, wR2 = 0.0884
R indices (all data)	R1 = 0.0402, wR2 = 0.0757	R1 = 0.0431, wR2 = 0.0785	R1 = 0.0534, wR2 = 0.0949

[a] All data were collected at 83(2) K using Mo Kα radiation λ = 0.71073 Å. Refinement method was full-matrix least-squares on F^2 for all compounds.

the suspension was filtered through Celite. The volume of the filtrate was reduced to 10 mL and the solution cooled to −30 °C. The resulting yellow powder was washed twice with 4 mL of hexanes and dried under reduced pressure. Yield: 0.307 g, 33%. Mp: turns red 135−140 °C, melts 169−173 °C (dec). NMR (d_6-benzene): ^{1}H δ 7.22 (d, 4H, *o*-aryl*H*, $^3J_{HH}$ = 6.9 Hz), 7.15 (8H, aryl, obscured by solvent), 6.83 (m, 6H, *o*- and/or *m*-aryl*H*), 6.62 (t, 2H, *p*-aryl*H*, $^3J_{HH}$ = 7.4 Hz), 4.94 (m, 2H), 3.23−3.09 (m, 8H), 2.73 (m, 2H), 2.23 (m, 2H), 1.76−1.62 (m, 6H), 1.11 (m, 2H), 0.7 (m, 2H); ^{13}C{^{1}H} δ 203.1 (Zr*C*), 151.2 (*quat-C*), 150.0 (*quat-C*), 143.8 (*quat-C*), 128.4 (signals obscured by solvent), 127.1 (*o*- or *m*-aryl*C*), 126.7 (*o*- or *m*-aryl*C*), 124.9 (*p*-aryl*C*), 122.4 (*p*-aryl*C*), 61.3, 57.2, 53.9, 52.9, 50.3 (*C*H$_2$N), 21.8 (CH$_2$*C*H$_2$CH$_2$). NMR (d_8-THF): ^{1}H δ 6.96 (t, 4H, *o*- or *m*-aryl*H*, $^3J_{HH}$ = 7.7 Hz), 6.74 (m, 8H, *o*- and/or *m*-aryl*H*), 6.63 (m, 6H, *o*- and/or *m*-aryl*H* and *p*-aryl*H*), 6.53 (t, 2H, *p*-aryl*H*, $^3J_{HH}$ = 7.3 Hz), 4.80 (m, 2H), 3.62 (m, 2H) 3.52 (m, 2H), 3.24 (dd, 2H), 3.15 (m, 2H), 3.04 (m, 2H), 2.27−2.17 (m, 8H), 2.09 (m, 2H), 0.95 (m, 2H); ^{13}C{^{1}H} δ 203.5 (Zr*C*), 152.1 (*quat-C*), 149.5 (*quat-C*), 144.1 (*quat-C*), 131.0 (*o*- or *m*-aryl*C*), 128.0 (*o*- or *m*-aryl*C*), 126.8 (*o*- or *m*-aryl*C*), 126.7 (*o*- or *m*-aryl*C*), 124.4 (*p*-aryl*C*), 122.1 (*p*-aryl*C*), 61.9, 57.7, 54.3, 53.7, 50.6 (*C*H$_2$N), 22.4 (CH$_2$*C*H$_2$CH$_2$). Anal. Calcd for the toluene solvate $C_{47}H_{52}N_4Zr$: C, 73.87; H, 6.86; N, 7.33. Found: C, 71.09; H, 6.82; N, 7.33. The yield improves slightly if the reaction is carried out in toluene (41%).

Red Product (11) from the Thermal Decomposition of Metallacycle 10. (CBC)Zr(C$_4$Ph$_4$) (0.250 g, 0.372 mol) and 20 mL of toluene were sealed in a bomb. The solution was stirred at 50 °C for 7 days, and then the solvent was removed under reduced pressure to yield a brown oily material. Dissolution of this oil in 3 mL of toluene followed by layering with 1 mL of hexane and cooling at −30 °C afforded a deep red material after filtration to remove a small amount of an insoluble tan solid. Recrystallization of the red solid from 1:1 toluene/hexane produced a dark red solid that displayed a clean NMR spectrum. Yield: 0.102 g (41%). Mp: 224−229 °C (dec). NMR (d_6-benzene): ^{1}H δ 7.46 (br s, 1H, aryl*H*), 7.26 (br s, 5H, aryl*H*), 7.14 (br s, 2H, aryl*H*), 7.10−6.98 (m, 7H, aryl*H*), 6.78 (m, 3H, aryl*H*), 6.46 (br s, 1H, aryl*H*), 6.26 (t, 1H, *p*-aryl*H*, $^3J_{HH}$ = 7.2 Hz), 5.67 (s, 1H, C=C*H*Ph), 3.72 (dt, 1H), 3.46 (dd, 1H), 3.14 (td, 1H), 3.02−2.95 (m, 2H), 2.59 (td, 1H), 2.47 (td, 1H), 2.27 (td, 1H, NC*H*H), 2.23−2.09 (m, 7H, six NC*H*H and one CH$_2$C*H*HCH$_2$), 1.87 (dd, 1H, NC*H*H), 1.75 (m, 2H, NC*H*H), 1.65 (m, 1H, CH$_2$C*H*HCH$_2$), 1.3−1.4 (m, 4H, two CH$_2$C*H*HCH$_2$, NC*H*H, and ZrC*H*); ^{13}C{^{1}H} δ 155.2, 145.1, 144.5, 144.4, 142.1, 138.6 (*quat-C*), 130.7, 128.6, 128.4, 128.2, 127.7, 127.1, 126.4, 125.6, 124.5 (aryl*C*H), 115.4 (*p*-aryl*C*), 77.9 (Zr*C*H, correlates with a δ1.3−1.4 ppm ^{1}H resonance), 75.0 (*quat*-C), 69.4 (N*C*H$_2$), 67.7 (C=*C*HPh, correlates with δ5.67 ppm ^{1}H resonance), 60.7, 60.42, 60.37, 59.5, 55.8, 51.54, 51.36, 51.24 (N*C*H$_2$), 31.9 (CH$_2$*C*H$_2$CH$_2$), 30.7 (CH$_2$*C*H$_2$CH$_2$). Assignments are based on DEPT, ^{1}H−^{1}H, and ^{1}H−^{13}C COSY. Anal. Calcd for $C_{40}H_{44}N_4Zr$: C, 71.49; H, 6.60; N, 8.34. Found: C, 66.76; H, 6.65; N, 6.61. A small sample of **11** in d_6-benzene was hydrolyzed with D$_2$O, and the organic and aqueous phases were separated. The ^{1}H NMR of the aqueous phase showed pure CBC ligand, but the integration of one resonance due to the central CH$_2$ of the three-carbon bridge (δ0.80 ppm) was decreased substantially. The organic phase contained 1,2,3,4-tetraphenylbutadiene and 1,2,3,4-tetraphenylbutadiene-d_1 by mass spectroscopy (M$^+$ = 358 and 359 amu, respectively).

X-ray Crystallographic Studies. Crystallographic data for **5**, **9**, and **10** are given in Table 1. Crystals of **9** and **10** were grown from a saturated toluene solution at −30 °C; crystals of **5** were obtained by cooling a warm (60 °C) toluene solution to room temperature. The crystals were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in a low-temperature nitrogen stream.[43] Data for **5**, **9**, and **10** were collected at 83(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using omega scans of 0.3° per frame for 30 s, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.75 Å for **5** and 0.77 Å for **9** and **10**. The first 50 frames were re-collected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[44] software and refined using SAINTPlus[45] on all observed reflections. Data reduction and corrections for Lorentz polarization and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[46] The structures were solved by direct methods

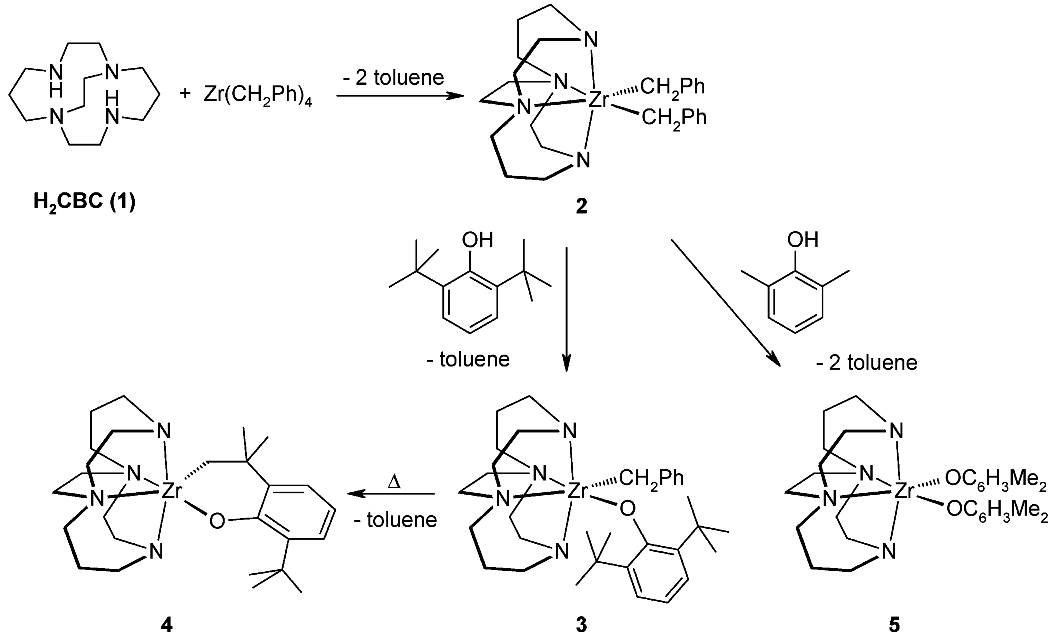
---

(43) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1.

(44) *SMART: v.5.626*, Bruker Molecular Analysis Research Tool; Bruker AXS: Madison, WI, 2002.

(45) *SAINTPlus: v. 6.22*, Data Reduction and Correction Program; Bruker AXS: Madison, WI, 2001.

Scheme 1



and refined by the least-squares method on F^2 using the SHELXTL program package.[47]

For compound **5**, the structure was solved in the space group *Pcc*2 (#116) by analysis of systematic absences. The compound was refined as a pseudo-merohedral twin using the twin law 0 1 0 1 0 0 0 0 −1. Although the absences suggest a higher symmetry, i.e., the tetragonal space group *P*-4*c*2, refinement using this solution clearly leads to a twinned structure with a higher *R* value. All atoms were refined anisotropically. For compound **9**, the structure was solved in the space group *C*2/*c* (#15) by analysis of systematic absences. All atoms were refined anisotropically. For compound **10**, the structure was solved in the space group *C*2/*c* (#15) by analysis of systematic absences. There is a half-occupied toluene molecule in the asymmetric unit that is disordered over the inversion center. All atoms were refined anisotropically. No decomposition was observed during data collection for any of these compounds. Structural plots were drawn with ORTEP3.[48] Further details are provided in the Supporting Information.

Results and Discussion

Synthesis and Reactivity. The reaction of cross-bridged cyclam (H_2(CBC): 1,4,8,11-tetraazabicyclo[6.6.2]-hexadecane) with tetrabenzylzirconium yields (CBC)-$Zr(CH_2Ph)_2$, **2**, efficiently, provided the amine has been suitably dried (Scheme 1). Compound **2** is a yellow powder that is soluble in aromatic solvents and sparingly soluble in aliphatic ones.

Compound **2** is thermally robust in solution: heating at 80 °C for 96 h causes 50% decomposition (compared to an internal standard by ^{1}H NMR); the process does not follow first-order kinetics and ultimately results in disappearance of ligand resonances into the baseline. The compound does degrade over the course of several weeks when stored at room temperature in a glovebox, as do all the bis(alkyls) described in this report. Given our previous observations of photolytic benzyl−Zr bond cleavage due to ambient light,[22] we were concerned that this might again be a possibility. Irradiation of (NOON)-$Zr(CH_2Ph)_2$ for 14 h at 435 nm led to complete transformation of the compound; in contrast, **2** showed minor degradation when irradiated at 375 nm for 24 h and bibenzyl was not produced. This suggests that **2** is not degraded by ambient light.

We initially encountered difficulties preparing (CBC)-$ZrCl_2$ (vide infra), so as an alternative, we explored protonolysis of **2** with phenols, since the resulting phenoxides can be used in metathesis reactions as an alternative to halides with group 3 metals.[49] Reaction of **2** with 2 equiv of 2,6-di-*tert*-butylphenol produces the monosubstituted product (CBC)Zr(CH_2Ph)(O-2,6-$C_6H_3Bu^t$), **3**, as a pale yellow powder. Presumably steric effects prevent the introduction of the second phenol at the metal center, since the less hindered 2,6-dimethylphenol reacts cleanly to give **5**. When the reaction of **2** with 2 equiv of 2,6-di-*tert*-butylphenol is followed by NMR, there is no evidence for either reaction of the benzyl group or the amido groups of the ligand with the second equivalent of phenol. Given the acidity of the phenol, it is surprising that the amido groups do not react, but this may be attributable to the strong chelate effect of the macrocycle and the steric congestion at the metal center.

Prolonged heating of **3** in aromatic solvents leads to the loss of toluene and the formation of a six-membered metallacycle (CBC)Zr[κ^2(C,O)-OC_6H_3(6-Bu^t)-(2-CMe_2CH_2)] (**4**, Scheme 1). This has been observed previously with a related aniline species.[50] Presumably the methyl group of the phenoxide can more readily adopt the correct orientation for the metalation to occur than any of the methylene groups of the cross-bridged cyclam ligand.

The reaction of (CBC)$Zr(CH_2Ph)_2$ with 2 equiv of 2,6-dimethylphenol yields the diphenoxide **5** in good yield.

---

(46) Sheldrick, G. M. *SADABS: v.2.01*, An Empirical Absorption Correction Program; Bruker AXS Inc.: Madison, WI, 2001.

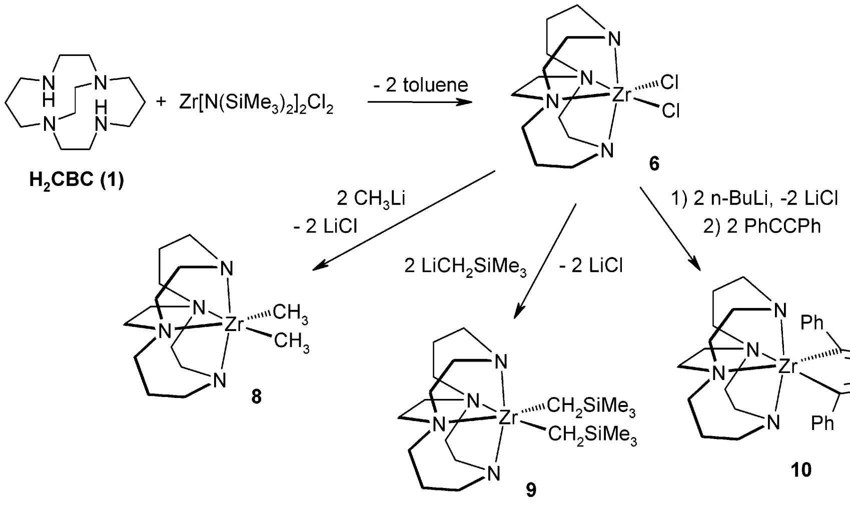
(47) Sheldrick, G. M. *SHELXTL: v. 6.10*, Structure Determination Software Suite; Bruker AXS Inc.: Madison, WI, 2001.

(48) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(49) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.

(50) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795.

Scheme 2



However, attempts to carry out metathesis reactions with MeLi or $LiCH_2SiMe_3$ and **5** were unsuccessful, and only the starting material was recovered. Consequently, we returned to $(CBC)ZrCl_2$, **6**, as a precursor to a range of organometallic compounds. Unfortunately, to date we have been unable to cleanly isolate the Li, Na, or K salts of cross-bridged cyclam for metathesis with zirconium tetrachloride. Likewise, we initially experienced low yields in the direct protonolysis of $ZrCl_2[N(SiMe_3)_2]_2$ with $H_2(CBC)$. Due to its extremely low solubility in toluene, **6** precipitates directly from the reaction mixture; investigation of the supernate led to the isolation of $(CBC)Zr(Cl)[N(Si(CH_3)_3)_2]$, **7**, as the other product. Its identity has been confirmed by the synthesis of **7** from **6** and $NaN(Si(CH_3)_3)_2$.

The initial batch of $ZrCl_2[N(Si(CH_3)_3)_2]_2$ had been prepared from zirconium tetrachloride and $NaN(Si(CH_3)_3)_2$. This likely resulted in the contamination of $ZrCl_2[N(Si(CH_3)_3)_2]_2$ with $ZrCl[N(Si(CH_3)_3)_2]_3$ and the subsequent low yield of **6**.[51] If $LiN(Si(CH_3)_3)_2$ is used in the preparation of $ZrCl_2[N(Si(CH_3)_3)_2]_2$, this problem does not occur and the subsequent yield of **6** is 90%.

$(CBC)ZrCl_2$ is only sparingly soluble in aromatic solvents and does not dissolve under our standard ethylene polymerization conditions[21] (50 °C toluene, 500 equiv of MAO). Accordingly, we wished to prepare the dimethyl analogue **8**. Metathesis reactions of $(CBC)ZrCl_2$ with methylating reagents have been investigated. The dimethyl species **8** can be produced in modest yield with the use of MeLi (Scheme 2), while use of MeMgBr results in even lower yields and contamination with the starting dichloride. Unlike the dichloride **6**, the dimethyl compound **8** does dissolve in toluene; however, when it was treated with 500 equiv of MAO, we found no evidence of polyethylene production.

The lack of ethylene polymerization activity shown by **8**, while disappointing, is not entirely surprising given previous reports. The octamethyldibenzotetraazaannulene zirconium cationic systems were found to have low ethylene polymerization activity. This was thought to be a result of the metal center being insufficiently electrophilic to coordinate alkenes, even pendant ones (Figure 3).[5] The octamethyldibenzotetraazaannulene is related to CBC in that it is an N_4 macrocycle of the same size, but in contrast, it has two delocalized anionic subunits rather than localized amido and amino donors.

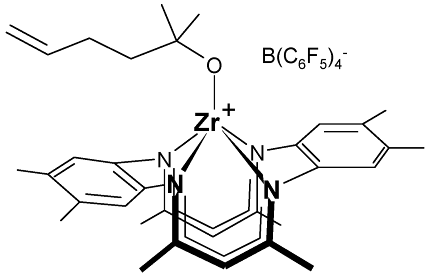


Figure 3. Dibenzotetraazaannulene zirconium cation with a noncoordinating pendant alkene.

Perhaps a better comparison is our previous zirconium diamido NOON^{2-} system, which showed low ethylene polymerization activity.[21] The difference in activity can be understood in the context of Schrock's work on $M(NON)R_2$ systems. The cationic $M(NON)R^+$ complexes were found to insert hexene or ethylene; however, addition of 1 equiv of diethyl ether inhibited insertion.[52] In our earlier work with NOON, the neutral donors were hemilabile, and this allowed for low polymerization activity. In the present work, it is unlikely that the amino donors are labile, thus precluding polymerization. Consequently, the CBC systems described here are better suited for other types of chemistry.

Zirconacycles are a class of compounds we are interested in. Since metalation of the *tert*-butyl moiety in **3** results in zirconacycle **4**, we wondered if hydrocarbon elimination might be a general route to zirconacycles in this system (Scheme 2). To test this, we prepared $(CBC)Zr[CH_2Si(CH_3)_3]_2$, **9**, via metathesis with **6** and $LiCH_2SiMe_3$. When a solution of **9** was heated, we did observe the production of tetramethylsilane; however, we have been unable to isolate any organometallic products from this reaction.

We investigated another route to prepare zirconacycles. By treating $(CBC)ZrCl_2$ with *n*-BuLi in the

---

(51) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928.

(52) Aizenberg, M.; Turculet, L.; Davis, W. M.; Schattenmann, F. J.; Schrock, R. R. *Organometallics* **2001**, *20*, 1153.

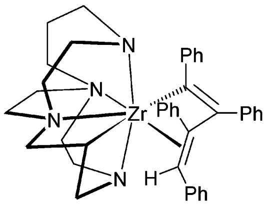


Figure 4. Possible structure of the thermal metalation product of **10**.

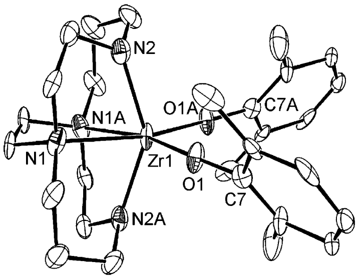


Figure 5. ORTEP3 drawing[48] (50% probability thermal ellipsoids) of complex **5**. Only one molecule of the asymmetric unit is shown, and hydrogen atoms have been removed for clarity.

presence of diphenylacetylene in a route analogous to that described by Negishi we obtained zirconcyclopentadiene **10** as a pale yellow powder with limited solubility in toluene.[53] Metallacycle **10** is stable in solution at room temperature in the absence of air, but heating it at 50 °C results in slow (days) conversion to a deep red product (**11**) that displays a ^{1}H NMR spectrum suggestive of a terminal butadienyl unit (C=CHPh resonance at δ 5.67 ppm). Hydrolysis of this red product with D_2O shows incorporation of D into the macrocycle at the central methylene carbon of one of the three carbon bridges and mass spectral evidence for the production of 1,2,3,4-tetraphenylbutadiene-d_1. Although we have been unable to establish the structure of **11** unequivocally, the results obtained so far seem to suggest that it is a CBC-metalated butadienyl of structure similar to that shown in Figure 4.

Attempts to isolate the tetramethyl analogue of **10** by reaction with 2-butyne have been unsuccessful thus far. Since the tetraphenyl zirconacyclopentadiene decomposes under relatively mild conditions, and it seems likely that both steric and electronic factors in the tetramethyl analogue would make it more prone to decomposition, it is unsurprising that this compound has not been isolated.

Solid State Structures. The solid state structure of the bis(phenoxide) (CBC)Zr(O-2,6-$C_6H_3Me_2$)$_2$, **5**, was determined by X-ray crystallography (Table 1). The structure is depicted in Figure 5, and important bond distances and angles are given in Table 2. The zirconium center is six-coordinate and best described as distorted octahedral. The ligand can be thought of as saddle shaped, with the amido nitrogens *trans* to one another and the amino nitrogens adopting a *cis* geometry, constrained by the cross-bridge to the points where the saddle is at its narrowest. The oxygen atoms are *trans* to the amino nitrogens and *cis* to one another. This is in contrast to the saddle shape of the tetraaza[14]annulenes, where the four nitrogens are equivalent and coplanar.

The largest distortion from octahedral is the average amide−Zr−amide angle of 145.2° (the asymmetric unit contains two half-molecules). The small amide−Zr−amide angle may be caused by the amido nitrogens trying to achieve the most planar geometry possible in order to maximize donation to zirconium. This would force the metal out of the cleft of the CBC ligand, thus narrowing the amide−Zr−amide angle.[54] Evidence for this proposal includes the observation that the amide−M−amide angle is much larger (160−170°) in six-coordinate complexes of Zn(II) even though this metal has an ionic radius very similar to Zr(IV).[31,54] The average amine−Zr−amine angle is constrained by the ethyl cross-bridge to 76.5°; accordingly, the O−Zr−O angle expands to an average 99.5°.

The amido−Zr bond lengths (2.094(4), 2.125(4) Å) in **5** are within the normal range (2.063−2.192 Å)[8,10,21,55] for polydentate ligands with amido donors, and the amino−Zr bonds (2.377(4), 2.394(4) Å) are short compared to the normal range (2.414−2.604 Å)[10,13,55c] for polydentate ligands with amino and amido donors in a six-coordinate environment. The oxygen bond lengths (1.997(3), 1.994(4) Å) and Zr−O−C angles (163.8(3)° and 164.2(3)°) are consistent with the range found for 2,6-dimethylphenoxide in other systems containing tris(pyrazolylborate), Cp, Cp*, and PNP supporting ligation (1.948−2.020 Å).[56] The Zr−O−C angles in these systems span a very large range (145.8−176.8°) that has been attributed to steric factors, meaning this angle is not a good indication of the extent of M−O π interactions.[56c]

Compound **9** has been characterized by X-ray crystallography (Table 1), and the structure is depicted in Figure 6. The significant bond lengths and angles are given in Table 2. The gross features of the complex are comparable to **5**, with the exception that the Zr−amine distance in **9** (2.452(2) Å) is longer and more typical of the usual range. The Zr−C bond length and C−Zr−C angle are within the typical range.[57] The Zr−C bond length (2.290(2) Å) and Zr−C−Si bond angle (120.69(12)°) do not suggest that an agostic interaction is present.[57b]

Of the over 30 zirconacyclopentadiene structures in the Cambridge Crystallographic Database, all contain

---

(53) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(54) The authors are indebted to one reviewer for pointing out this explanation. (a) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(55) (a) Mehrkhodavandi, P.; Schrock, R. R.; Bonitatebus, P. J., Jr. *Organometallics* **2002**, *21*, 5785. (b) Rogers, A. J.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Corrado, R. *J. Chem. Soc., Dalton Trans.* **1997**, 2385. (c) Giesbrecht, G. R.; Shafir, A.; Arnold, J. *Chem. Commun.* **2000**, 2135.

(56) (a) Kresinski, R. A.; Isam, L.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1835. (b) Benetollo, F.; Cavinato, G.; Crosara, L.; Milani, F.; Rossetto, G.; Scelza, C.; Zanella, P. *J. Organomet. Chem.* **1998**, *555*, 177. (c) Antinolo, A.; Carrillo-Hermosilla, F.; Corrochano, A.; Fernandez-Baeza, J.; Lara-Sanchez, A.; Ribeiro, M. R.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A.; Portela, M. F.; Santos, J. V. *Organometallics* **2000**, *19*, 2837. (d) Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J. *Inorg. Chem.* **1998**, *37*, 112.

(57) (a) Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593. (b) Cayias, J. Z.; Babaian, E. A.; Hrncir, D. C.; Bott, S. G.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1986**, 2743. (c) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (d) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789. (e) Dias, H. V. R.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77. (f) Scott, M. J.; Lippard, S. J. *Inorg. Chim. Acta* **1997**, *263*, 287. (g) Gentil, S.; Pirio, N.; Meunier, P.; Gallucci, J. C.; Schloss, J. D.; Paquette, L. A. *Organometallics* **2000**, *19*, 4169.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 5, 9, and 10

	5[a]	**9**	**10**
	Bond Distances		
Zr−amide	2.125(4) (Zr1−N2) 2.094(4) (Zr2−N4)	2.103(2) (Zr1−N3)	2.0820(19) (Zr1−N3)
Zr−amine	2.377(4) (Zr1−N1) 2.394(4) (Zr2−N3)	2.452(2) (Zr1−N6)	2.4269(19) (Zr1−N6)
Zr−X	1.997(3) (Zr1−O1) 1.994(4) (Zr2−O2)	2.290(2) (Zr1−C9)	2.313(2) (Zr1−C9)
	Bond Angles		
amide−Zr−amide	145.1(3) (N2−Zr1−N2) 145.3(3) (N4−Zr2−N4)	142.3(11) (N3−Zr1−N3)	142.4(10) (N3−Zr1−N3)
amine−Zr−amine	76.6(2) (N1−Zr1−N1) 76.4(2) (N3−Zr2−N3)	74.78(10) (N6−Zr1−N6)	76.81(9) (N6−Zr1−N6)
X−Zr−X	98.4(2) (O1−Zr1−O1) 100.6(2) (O2−Zr2−O2)	99.61(12) (C9−Zr1−C9)	77.19(11) (C9−Zr1−C9)
sum of angles at amido N	352.8 (N2) 353.3 (N4)	353.8 (N3)	354.4 (N3)

[a] The asymmetric unit contains two half-molecules.

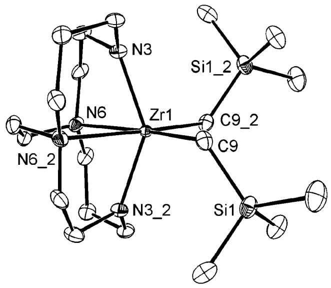


Figure 6. ORTEP3 drawing[48] (50% probability thermal ellipsoids) of complex **9**. The hydrogen atoms have been omitted for clarity.

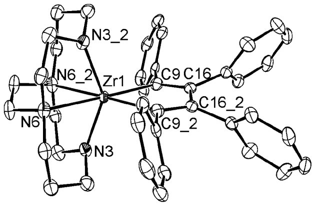


Figure 7. ORTEP3 drawing[48] (50% probability thermal ellipsoids) of complex **10**. The hydrogen atoms and toluene of solvation have been omitted for clarity.

at least one cyclopentadienyl ligand, albeit one is a phosphacyclopentadienyl ligand[58] (a metallacycle supported by benzamidinate ligands[59] has been reported, but its solid state structure has not been determined). To the best of our knowledge, compound **10** is the first zirconacyclopentadiene without a cyclopentadienyl ligand characterized by X-ray crystallography (Tables 1 and 2, Figure 7). The Zr−C bond lengths typically range from 2.172 to 2.324 Å for zirconacyclopentadienes; thus, at 2.313(2) Å, **10** falls at the long end of this range.[36,60] Accordingly, the C−Zr−C angle is reduced to 77.19(11)°, falling at the short end of the range 76.4−98.5°. The geometry of the cross-bridged cyclam moiety in **10** is remarkably similar to that of the bis(alkyl) **9**, especially given the large difference in the C−Zr−C angles (**9**, 99.61(12)°; **10**, 77.19(11)°). We take this to mean that the geometry of the ligand about the metal is constrained by the cross-bridge and largely invariant, regardless of the other substituents on the metal center.

Table 3. Structural Comparison of (CBC)ZrX$_2$ and Cp$_2$ZrX$_2$

X	CBC	Cp$_2$
2,6-C$_6$H$_3$Me$_2$O		
Zr−O (Å)	1.994(4) 1.997(3)	1.996(5)[56b] 1.997(5)
O−Zr−O (deg)	98.4(2) 100.6(2)	98.6(2)
Me$_3$SiCH$_2$		
Zr−C (Å)	2.290(2)	2.278(4)[57a] 2.281(4)
C−Zr−C (deg)	99.61(12)	97.8(1)
X$_2$ = C$_4$Ph$_4$		
Zr−C (Å)	2.313(2)	2.250(5)[60a] 2.265(6)
C−Zr−C (deg)	77.19(11)	77.5(2)

Overall, the similarities between the solid state structures of (CBC)ZrX$_2$ and Cp$_2$ZrX$_2$[56b,57a,60a] are striking, as illustrated in Table 3. The CBC system shows slightly longer bond lengths on average (0.02 Å). The average difference in bond angle between the substituents in the two systems is slightly more than 1°, remarkable given that, for example, the C−Zr−C angle for L$_2$Zr(CH$_2$Si(CH$_3$)$_3$)$_2$ systems ranges over 25°. This leads us to postulate that CBC and two Cp groups are sterically very similar.

Behavior in Solution. As might be expected, the ^{1}H and ^{13}C NMR of the cross-bridged cyclam moiety in compounds **2**, **5**, **6**, and **8**−**10** show effective C_2 symmetry in solution, with a complicated pattern of 12 resonances for six pairs of diasterotopic protons and six carbon resonances. In contrast, since compounds **3**, **4**, and **7** have two different groups in addition to the cross-bridged cyclam, the C_2 axis is lost, leading to 24 proton resonances and 12 carbon resonances.

Consistent with C_2 symmetry, the benzylic protons in **2** appear as AB doublets. Compound **2** does not display the features normally associated with η^2-benzyl coordination; namely, the *ortho* protons are downfield of 6.7 ppm (7.14 ppm) and the $^1J_{\mathrm{CH}}$ coupling constant for the CH_2Ph groups are less than 130 Hz (113 Hz).[61] Likewise, the geminal coupling constant of the CH_2SiMe$_3$ group in **9** (12 Hz) is slightly larger than in

---

(58) Buzin, F.; Nief, F.; Ricard, L.; Mathey, F. *Organometallics* **2002**, *21*, 259.

(59) Hagadorn, J. R.; Arnold, J. *Organometallics* **1994**, *13*, 4670.

(60) (a) Hunter, W. E.; Atwood, J. L. *J. Organomet. Chem.* **1981**, *204*, 67. (b) Metzler, N.; Noth, H.; Thomann, M. *Organometallics* **1993**, *12*, 2423. (c) Erker, G.; Zwettler, R.; Kruger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524. (d) Wieistra, Y.; Gambarotta, S.; Meetama, A.; de Boer, J. L. *Organometallics* **1989**, *8*, 2696.

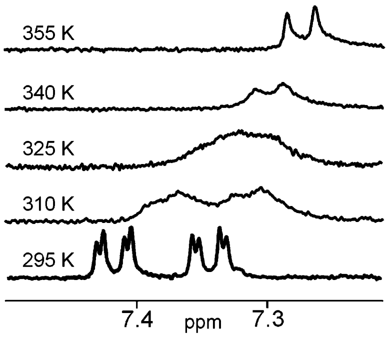


Figure 8. Variable-temperature ^{1}H NMR (d_8-toluene) spectrum of the *meta* proton region of **3**.

similar species[57d] and does not indicate any agostic interactions,[57e] consistent with the solid state structure.

The observation of two resonances each for the *ortho tert*-butyl groups and *meta* protons of the phenoxide in (CBC)Zr(CH_2Ph)(O-2,6-$C_6H_3Bu^t{}_2$) at room temperature suggests that the rotation about the O−C linkage is hindered. Increasing the temperature of **3** results in a coalescence of both the *tert*-butyl and *meta* protons (Figure 8) of the phenoxide. From the coalescence temperature for the two-site exchange of the t-Bu signals, the activation energy for this process is calculated to be 69 ± 1 kJ/mol at 325 K.[62,63] In contrast, (CBC)Zr(O-2,6-$C_6H_3Me_2$)$_2$ shows only one resonance for the methyl groups, suggesting that steric interactions hinder the rotation around the Zr−O bond in **3** because of the large steric size of the *tert*-butyl groups.

In **7**, the N(Si(CH_3)$_3$)$_2$ group shows two Si(CH_3)$_3$ resonances. Since the geometry of this group is usually trigonal planar,[50,64] this implies that the rotation about the Zr−N bond is hindered. Heating did result in broadening of the signals, but the coalescence temperature was greater than the boiling point of toluene.

Future Work. We look forward to studying the insertion and metallacycle transfer chemistry of these zirconium complexes to further compare and contrast their behavior with that of cyclopentadienyl and other tetraazamacrocycles. In addition, we are investigating the use of cross-bridged cyclam as a ligand for the group 3 metals and lanthanides.

Acknowledgment. D.J.B. (Discovery Grant) and P.O. (PGS Fellowship) gratefully acknowledge the support of the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **5**, **9**, and **10** and the ^{1}H NMR spectrum for **5** are available free of charge via the Internet at http://pubs.acs.org.

OM049469J

---

(61) (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (c) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235. (d) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echolls, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(62) (a) Bradley, D. C.; Chudzynska, H.; Backer-Dirks, J. D. J.; Hursthouse, M. B.; Ibrahim, A. A.; Motevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423. (b) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

(63) The free energy of activation was calculated from the coalescence temperature (T_c) using the equal population, two-site exchange equation: $G = (1.914 \times 10^{-2})T_c[9.972 + \log(T_c/v)]$ in kJ mol^{-1} where v is the separation of the resonances in Hz (25.2 Hz for the t-Bu resonances) and T_c is in K (325 K). The error in G was estimated to be 1 kJ mol^{-1} assuming an error of 3 K in T_c.

(64) Sandstrom, J. *Dynamic NMR Spectroscopy*; Pergamon: London, 1982.