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Cationic d^0 Metal Alkyls Incorporating Tetraaza-Macrocycle Ancillary Ligands. Synthesis and Reactivity of (Me$_8$taa)M(R)$^+$ and (Me$_4$taen)M(R)$^+$ (M = Zr, Hf) Complexes

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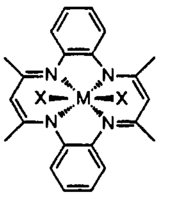
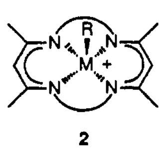
Electrophilic d^0 Cp$_2$M(R)$^+$ complexes have been exploited in stoichiometric and catalytic reactions, including olefin polymerizations.[1] A key feature of these compounds is the Cp$_2$M framework that (i) forces the vacant coordination sites to be cis to the reactive M–R bond, thus promoting insertion and σ-bond metathesis reactivity, and (ii) can be extensively modified, allowing tuning of steric, chirality, and electronic properties. A current challenge is to design new classes of cationic early metal alkyl complexes that incorporate these features but are based on ancillary ligands which are more easily modified than Cp ligands and which give rise to improved/complementary reactivity. Goedken and Floriani have prepared a series of *cis*-(Me$_4$taa)MX$_2$ complexes (**1**) (M = Ti, X = Cl; M = Zr, X = Cl, CH$_2$Ph),[2] and Arnold has pioneered the chemistry of related porphyrin complexes, including *cis*-(OEP)ZrR$_2$.[3] These authors have noted the analogy between Cp$_2$M and (N$_4$-macrocycle)M compounds. Here we describe the synthesis and chemistry of a series of reactive *cationic* d^0 (N$_4$-macrocycle)M(R)$^+$ complexes (**2**).



(Me$_4$taa)MX$_2$

1; X = Cl, CH$_2$Ph



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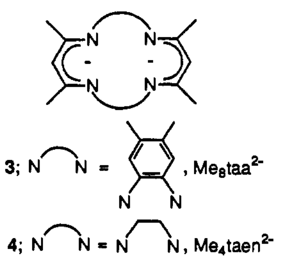
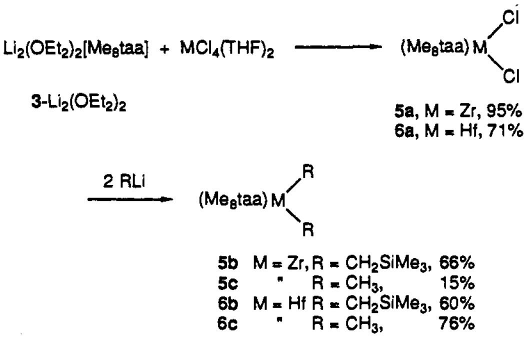
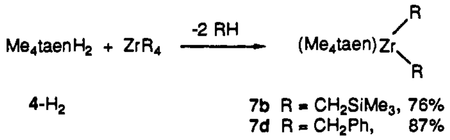


Our initial studies have focused on Me$_8$taa^{2-} (**3**)[4] and Me$_4$taen^{2-} (**4**)[5] as representative N$_4$-macrocycles. Neutral Zr and Hf (Me$_8$taa)M(R)$_2$ complexes (**5b,c**; **6b,c**) were prepared via anion metathesis (eq 1).[2,6] Analogous (Me$_4$taen)Zr(R)$_2$ complexes (**7b,d**) were prepared by direct alkane elimination (eq 2), (Me$_8$taa)Zr(CH$_2$Ph)$_2$ (**5d**, 87%) was prepared by a reaction analogous to eq 2. Cis orientations of the halide/alkyl ligands and "saddle" conformations of the Me$_8$taa^{2-} ligands are assumed for **5** and **6** on the basis of structural data for **1**.[2] For Me$_4$taen^{2-} complexes **7b,d**, distinct ^{1}H NMR resonances for the *endo*- and *exo*-Hs of the -CH$_2$CH$_2$- linkers indicate cis structures, which is confirmed by X-ray crystallography for **7d**.[7]

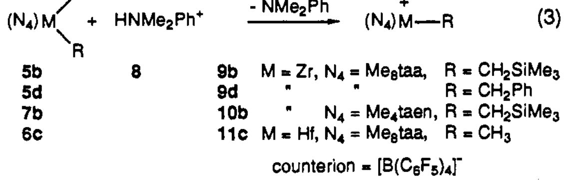


(1)



(2)

Protonolysis[8] of **5b** with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (**8**)[9] in C$_2$D$_2$Cl$_4$ yields 1 equiv of SiMe$_4$ and free NMe$_2$Ph, and [(Me$_8$taa)ZrCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] (**9b**, 80% NMR, eq 3) in situ. The ^{13}C NMR spectrum of **9b** contains a Zr*C*H$_2$ resonance at δ 53.0, which is downfield from the corresponding resonance of **5b** (δ 43.8). The cationic Hf methyl complex [(Me$_8$taa)HfCH$_3$][B(C$_6$F$_5$)$_4$] (**11c**) was generated in situ (87% NMR) in a similar manner from **6c** (δ Hf-*C*H$_3$ 46.6, vs 33.3 for **6c**). Reaction of **7b** with **8** in benzene yields a red oil which can be separated and vacuum dried, yielding [(Me$_4$taen)ZrCH$_2$SiMe$_3$][B(C$_6$F$_5$)$_4$] (**10b**) as a golden brown *solid* (56%, δ Zr*C*H$_2$ 64.1, vs 50.4 for **7b**). The extent of anion or solvent (CD$_2$Cl$_2$ or C$_2$D$_2$Cl$_4$) coordination to these base-free cations is unknown at present; however, such interactions must be weak as **9b**, **10b**, and **11c** all exhibit effective C_{2v} symmetry on the NMR time scale (23 °C).[10] Cationic benzyl complexes are generated in situ by analogous protonolysis reactions. Reaction of **5d** with **8** yields 1 equiv of toluene and free NMe$_2$Ph and [(Me$_8$taa)Zr(η^2-CH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**9d**, >80% NMR). A high-field ortho phenyl ^{1}H



(3)

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(1) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(2) (a) Yang, C. H.; Ladd, J. A.; Goedken, V. L. *J. Coord. Chem.* **1988**, *18*, 317. (b) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 70. (c) DeAngelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 2520. (d) Review; Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *21*, 2553.

(3) (a) Brand, H.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 2266. (b) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620. (c) Kim, H.-J.; Whang, D.; Kim, K.; Do, Y. *Inorg. Chem.* **1993**, *32*, 360. (d) Shibata, K.; Aida, T.; Inoue, S. *Chem. Lett.* **1992**, 1173. (e) Schavarien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.

(4) (a) Goedken, V. L.; Pluth, J. J.; Peng, S.-M.; Bursten, B. *J. Am. Chem. Soc.* **1976**, *98*, 8014. (b) Goedken, V. L.; Weiss, M. C. *Inorg. Synth.* **1980**, *20*, 115. (c) Cutler, A. R.; Alleyne, C. S.; Dolphin, D. *Inorg. Chem.* **1985**, *24*, 2276. (d) Place, D. A.; Ferrara, G. P.; Harland, J. J.; Dabrowiak, J. C. *Heterocycl. Chem.* **1980**, *17*, 439.

(5) (a) Truex, T. J.; Holm, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 4529. (b) Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1979**, *18*, 3145.

(6) Full experimental details and characterization data for **5**-**16** are given in the supplementary material. For **5c**, solid ether-free MeLi is required to avoid ligand-induced migration of a Zr-Me to an electrophilic imine carbon of the macrocycle (see ref 2b); this results in the low yield (15%).

(7) Details of the X-ray structural analyses of **7d** and **13** will be presented in a full report.

(8) (a) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (b) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413. (c) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (d) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (e) Lin, Z.; Le Marechal, J.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (f) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

(9) Turner, H. W.; Hlatky, G. G. *Eur. Pat. Appl.* 0 277 004, 1988.

(10) A *cis*-(N$_4$-macrocycle)M(X)(Y) complex has C_s symmetry (see **1**). Rapid site exchange of the X and Y ligands, e.g., by Y$^-$ dissociation to yield a configurationally labile (N$_4$-macrocycle)M(X)$^+$ species, results in effective C_{2v} symmetry. Rapid rotation of the macrocycle about Zr must also be considered, as (Me$_8$taa)Zr(CH$_2$SiMe$_3$)Cl exhibits effective C_{2v} symmetry (by NMR) in C$_2$D$_2$Cl$_4$ or C$_6$D$_6$ solution (23 °C). Low-temperature NMR studies are in progress.

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NMR resonance (δ 5.49), and a large $J_{CH}(CH_2)$ value (137 Hz) indicate that **9d** contains a distorted η^2-benzyl ligand.[11]

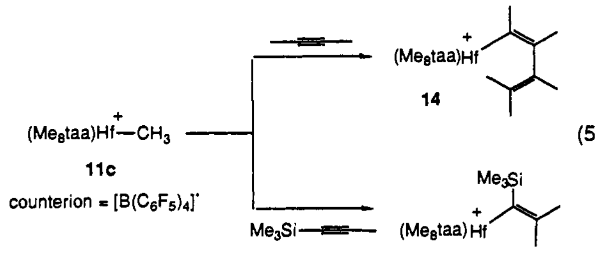
(4)

12a N_4 = Me_8taa, L = PMe_2Ph
12b " L = THF
12c " L = CH_3CN
13 N_4 = Me_4taen, L = THF
counterion = $[BPh_4]^-$

Base-free (N_4-macrocycle)M(R)$^+$ cations form isolable Lewis-base adducts (eq 4). The reaction of **5b** with $[HNBu_3][BPh_4]$ and 1 equiv of PMe_2Ph ($C_2H_4Cl_2$, 23 °C) yields $[(Me_8taa)Zr(CH_2SiMe_3)(PMe_2Ph)][BPh_4]$ (**12a**, 77% isolated). The lack of $J(^{31}P\text{-}CH_2Si)$ coupling in the ^1H and ^{13}C NMR spectra (CD_2Cl_2, 23 °C) of **12a** and the effective C_{2v} symmetry implied by these spectra indicate that PMe_2Ph exchange is rapid on the NMR time scale. Analogous labile THF and CH_3CN adducts **12b,c** were generated in clean NMR scale reactions. Similarly, the reaction of **7b** with $[HNBu_3][BPh_4]$ in the presence of THF yields the labile THF adduct $[(Me_4taen)Zr(CH_2SiMe_3)(THF)][BPh_4]$ (**13**, 60% isolated). The analogous $B(C_6F_5)_4^-$ salt is formed by addition of THF to preformed **10b**. Key NMR data for **13** include ^1H resonances for coordinated THF (δ 3.91, 1.99) and a low-field Zr-CH_2Si ^{13}C resonance (δ 56.2). The cis structure of **13** was confirmed by X-ray crystallography.[7]

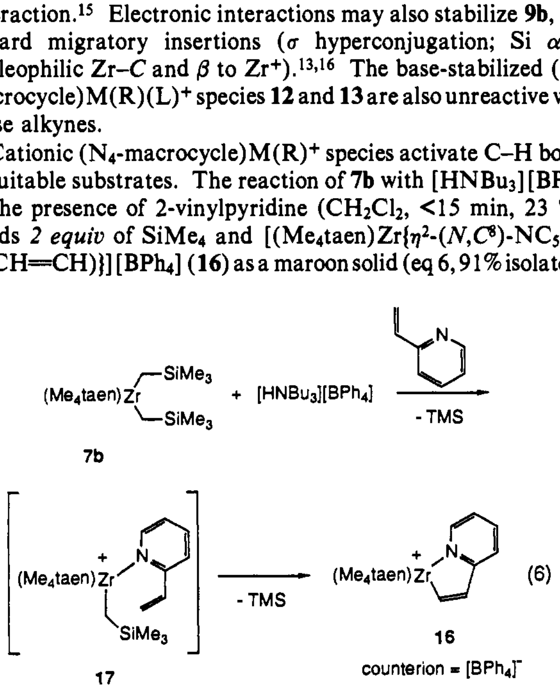
The reactions of representative (N_4-macrocycle)M(R)$^+$ species with unsaturated hydrocarbons have been explored for comparison to reactions of $Cp_2Zr(R)^+$ species. Cationic Hf methyl complex **11c** reacts with excess 2-butyne (CH_2Cl_2, 23 °C, 12 h) to yield the double insertion product $[(Me_8taa)HfCMe{=}CMeCMe{=}CMe_2][B(C_6F_5)_4]$ (**14**) as a golden brown solid (eq 5, 72% isolated). A similar reaction was reported for $Cp_2Zr(CH_3)^+$ species.[12] The ^1H NMR spectrum of **14** (CD_2Cl_2, 23 °C) includes five Me resonances and establishes that **14** has effective C_{2v} symmetry. The ^{13}C NMR spectrum contains four alkenyl carbon resonances (δ 214.0 (Hf-C), 147.1, 141.6, 139.1). There is no evidence for coordination of the pendant olefin to Hf or rearrangement of **14** to a pentadienyl species, as observed for analogous $Cp_2Zr(CMe{=}CMeCMe{=}CMe_2)^+$ species.[12]

Cation **11c** inserts 1-(Me_3Si)-1-propyne (<1 h, 23 °C) more rapidly to yield $[(Me_8taa)HfC(SiMe_3){=}CMe_2][B(C_6F_5)_4]$ (**15**), which is isolated (72%) as an orange solid (eq 5). The alkenyl regiochemistry is assigned on the basis of hydrolysis, which yields 2-methyl-1-(trimethylsilyl)propene. Similar 2,1 insertions of silylalkynes are observed for $Cp_2Zr(R)^+$ species.[13] At −20 °C, NMR data indicate a C_s structure for **15**, which suggests the presence of an agostic Hf-Me_3Si interaction, as is observed for $[Cp_2ZrCSiMe_3{=}CMe_2][B(C_6H_4F)_4]$.[13a]



In contrast, η^2-benzyl cation **9d**, and $ZrCH_2SiMe_3$ complexes **9b,10b** are unreactive with these alkynes under similar conditions.[14] The Zr–Ph interaction in **9d** may inhibit alkyne coordination as well as migratory insertion. The lower CH_3CN insertion reactivity of $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)^+$ vs $Cp_2Zr(CH_3)(CH_3CN)^+$ was ascribed to stabilization by the Zr–Ph interaction.[15] Electronic interactions may also stabilize **9b**, **10b** toward migratory insertions (σ hyperconjugation; Si α to nucleophilic Zr-C and β to Zr^+).[13,16] The base-stabilized (N_4-macrocycle)M(R)(L)$^+$ species **12** and **13** are also unreactive with these alkynes.

Cationic (N_4-macrocycle)M(R)$^+$ species activate C–H bonds of suitable substrates. The reaction of **7b** with $[HNBu_3][BPh_4]$ in the presence of 2-vinylpyridine (CH_2Cl_2, <15 min, 23 °C) yields *2 equiv* of $SiMe_4$ and $[(Me_4taen)Zr\{\eta^2\text{-}(N,C^{8})\text{-}NC_5H_3\text{-}(2\text{-}CH{=}CH)\}][BPh_4]$ (**16**) as a maroon solid (eq 6, 91% isolated).



The gated-{^1H} ^{13}C NMR spectrum of **16** contains six C–H doublets and one quaternary carbon resonance for the alkenylpyridine ligand; the absence of a $={CH_2}$ triplet rules out structures containing an intact $=CH_2$ group. Additionally, the largest J_{HH} value associated with the alkenylpyridine ^1H resonances is 6.4 Hz, confirming the absence of a pendant vinyl group.[17] The ^1H and ^{13}C NMR spectra indicate that **16** adopts a C_s structure, consistent with pyridine coordination. Complex **16** results from activation of a remote vinyl C–H bond in the presumed intermediate $(Me_4taen)Zr(CH_2SiMe_3)$(2-vinylpyridine)$^+$ (**17**). In contrast, $Cp_2Zr(R)(6\text{-}R'\text{-pyridine})^+$ species usually undergo metallation at the ortho pyridine H position.[18]

We have demonstrated here that d^0 (N_4-macrocycle)M(R)$^+$ complexes are accessible using routes developed for $Cp_2M(R)^+$ cations and, like the metallocene systems, undergo insertion and intramolecular C–H activation reactions. The possibilities for developing reactive early metal organometallics based on macrocycles as tunable ancillary ligands seem promising.

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Supplementary Material Available: Experimental details and full characterization data for **3-16** (16 pages). Ordering information is given on any current masthead page.

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[11] (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Scholz, J.; Schlegel, M.; Thiele, K. H. *Chem. Ber.* **1987**, *120*, 1369. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

[12] Horton, A. D.; Orpen, A. G. *Organometallics* **1992**, *11*, 8.

[13] (a) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. (b) Guram, A. S.; Jordan, R. F. *Organometallics* **1991**, *10*, 3470.

[14] However, these cations are low-activity ethene polymerization catalysts, with activities ca. 30 times less than that of $Cp_2Zr(R)^+$ species under identical conditions (23 °C, toluene, 1 atm).

[15] Wang, Y.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406.

[16] (a) Eisch, J. J.; Caldwell, K. R.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108. (c) Guram, A. S.; Jordan, R. F. *Organometallics* **1990**, *9*, 2190 and references therein.

[17] (a) A pendant vinyl would exhibit a large trans $^3J_{HH}$ value. (b) Hydrolysis of **16** with D_2O/NEt_3 yields 2-vinylpyridine-d_2 labeled only in the two β-vinyl positions and not in the pyridine ortho position. This results from Zr–C bond deuterolysis and secondary H/D exchange of the β-vinyl H/Ds with solvent.

[18] Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116.