Synthesis, X-ray Crystal Structure, and Reactivity of $Y(MAC)(CH_2SiMe_3)_2$ (MAC = Deprotonated aza-18-crown-6)

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*Summary: The yttrium dialkyl trans-Y(MAC)$(CH_2SiMe_3)_2$ (**1**; MAC = deprotonated aza-18-crown-6) has been isolated and characterized (NMR and X-ray). Complex **1** exhibits high stability toward ligand redistribution and metalation, reacts with CO to form a trans-bis(enolate) by silyl migration, and undergoes alkyl abstraction by $B(C_6F_5)_3$ to generate the highly unstable cation $[Y(MAC)(CH_2SiMe_3)]^+[B(C_6F_5)_3(CH_2SiMe_3)]^-$, in situ.*

The introduction of Cp^* (C_5Me_5) as an ancillary ligand almost two decades ago was a critical factor in the rapid development of organolanthanide chemistry.[1] More recently, macrocyclic nitrogen ligands such as porphyrins,[2] porphyrinogens,[3] and aza crown ethers[4] have seen increasing use as supporting ligation. Despite the wealth of chemistry developed for these systems, very few lanthanide dialkyls have been reported.[5−7] For the Cp^* system, this can be traced to the instability of most mono Cp^* derivatives with respect to facile ligand redistribution reactions. The tendency toward dialkyl redistribution can be minimized by using monoanionic ancillary ligands of very high steric bulk or multidentate coordination (or both). Our earlier success in preparing a stable yttrium alkyl using the dianionic deprotonated 4,13-diaza-18-crown-6 (DAC) ligand[4b] suggested that a monoanionic monoaza crown ether might provide similar access to lanthanide dialkyl complexes of high coordinative stability. In this contribution, we report the preparation of an yttrium dialkyl, *trans*-Y(MAC)$(CH_2SiMe_3)_2$ (**1**; MAC = deprotonated monoaza-18-crown-6), of surprising thermal stability. In addition, the reactivity of **1** with CO and the generation of an unstable yttrium alkyl cation are reported.

Complex **1** is isolated as colorless crystals in high yield by a protonation reaction (eq 1).[8] The observation

$$Y(CH_2SiMe_3)_3(THF)_2 + HMAC \rightarrow \underset{\mathbf{1}}{\textit{trans}\text{-}Y(MAC)(CH_2SiMe_3)_2} + SiMe_4 + 2THF \quad (1)$$

of only six multiplets in the MAC region (3−4.1 ppm) of the ^1H NMR spectrum of **1** clearly indicates a *trans*-

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(1) See for example: (a) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Marks, T. J., Ed.; Pergamon Press: New York, 1982; p 173. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (c) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (d) Evans, W. J. *Polyhedron* **1988**, *7*, 1693.

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(3) (a) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477. (b) Song, J.; Gambarotta, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2141.

(4) (a) Lee, L.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, *33*, 5302. (b) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 8. (c) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *15*, 5021.

(5) For examples of neutral yttrium or lanthanide dialkyls supported by Cp* ligation see: (a) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 962. (b) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637. (c) van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255. (d) Schaverien, C. J.; van der Heijden, H.; Orpen, A. G. *Polyhedron* **1989**, *8*, 1850. (e) van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J. *Organometallics* **1989**, *8*, 1459. (f) Schaverien, C. J. *Organometallics* **1992**, *11*, 3476. (g) Schaverien, C. J. *Organometallics* **1994**, *13*, 69.

(6) For some neutral lanthanide trialkyls see ref 2b above and the following: (a) Schumann, H.; Müller, J. *J. Organomet. Chem.* **1978**, *146*, C5. (b) Schumann, H.; Müller, J. *J. Organomet. Chem.* **1979**, *169*, C1. (c) Manzer, L. *J. Am. Chem. Soc.* **1978**, *100*, 8068. (d) Manzer, L. *J. Organomet. Chem.* **1977**, *135*, C6. (e) Wayda, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1984**, *3*, 939. (f) Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y. F.; Zakharov, L. N.; Struchkov, Y. T. *J. Organomet. Chem.* **1992**, *429*, 27. (g) Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45. (h) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1007. (i) Atwood, J. L.; Lappert, M. F.; Smith, R. G.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1308. (j) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126.

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(8) Synthesis of **1**: All operations were carried out in an argon-filled glovebox. A solution of HMAC[9] (0.27 g, 0.10 mmol) in 20 mL of toluene was added dropwise to a vigorously stirred solution of $Y(CH_2SiMe_3)_3(THF)_2$[6j] (0.50 g, 0.10 mmol) in 20 mL of toluene. The solution was stirred for 1 h, followed by removal of the solvent under reduced pressure. Recrystallization of the resulting white powder from a toluene-hexane mixture produced colorless crystals of **1** (0.40 g, 76%). Mp: 130 °C dec. ^1H NMR (360 MHz): δ 4.02, 3.88, 3.86, 3.79, 3.70, 3.19 (m, 4H each, MAC CH_2), −0.16 (s, 18H, $SiMe_3$), −1.59 (s, 4H, CH_2-Si, $^2J_{YH}$ = 2.5 Hz). ^{13}C NMR (90.55 MHz): δ 76.99, 72.01, 71.59, 70.44, 69.36, 56.76 (MAC *C*), 19.84 (CH_2Si, $^1J_{YC}$ = 32.4 Hz, $^1J_{CH}$ = 102.7 Hz), 5.13 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (49.69 MHz): δ −2.05 ppm. NMR spectra were recorded in d_8-THF (^1H and ^{13}C) and d_6-benzene (^{29}Si) at room temperature; all nuclei were referenced to external TMS. Anal. Calcd for $C_{20}H_{46}NO_5Si_2Y$: C, 45.70; H, 8.82; N, 2.66. Found: C, 45.57; H, 8.51; N, 2.98.

(9) The macrocycle was prepared by the procedure of: Maeda, H.; Furuyoshi, S.; Nakatsuji, Y.; Okahara, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 212. The product was purified by sublimation and dried over 4 Å sieves in toluene solution prior to use.

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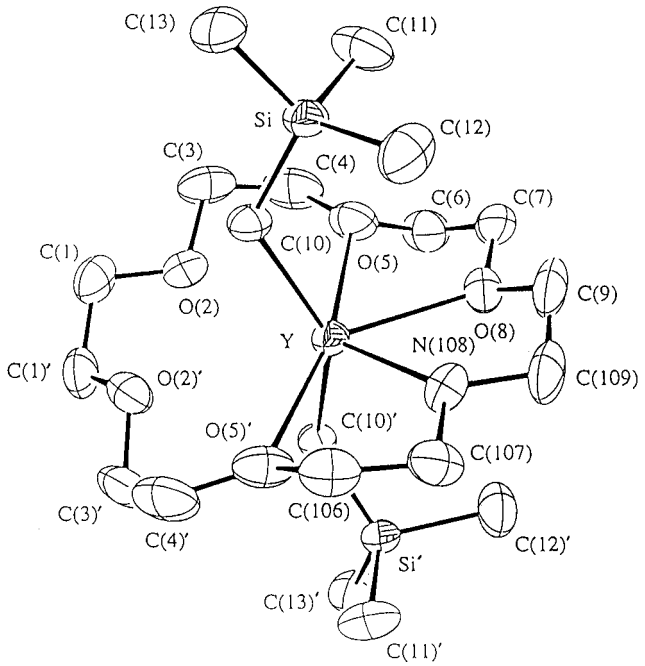


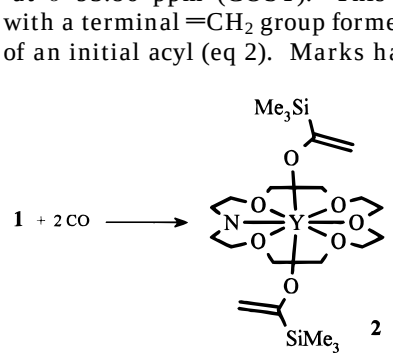
Figure 1. ORTEP[11] drawing of **1** at 213 K. The molecules were disordered about the crystallographic 2-fold axis, which passes through Y and the center of the C(1)−C(1)′ bond. For clarity only one of the two possible orientations of the molecule is shown in the diagram. Selected bond distances (Å) and angles (deg): Y−N(108) = 2.253(10), Y−O(2) = 3.033(3), Y−O(5) = 2.605(3), Y−O(8) = 2.482(8), Y−C(10) = 2.461(4); N(108)−Y−C(10) = 109.8(5), N(108)−Y−C(10)′ = 100.0(5), C(10)−Y−C(10)′ = 146.55(13), Y−C(10)−Si = 125.25(20).

dialkyl geometry. The *cis* isomer would possess C_s symmetry and must therefore display 12 proton resonances due to inequivalent exo and endo protons on each of the six unique MAC carbons. The presence of two equivalent dialkyls is confirmed by the observation of only one set of CH_2 and $SiMe_3$ resonances of appropriate intensity. Additionally, the $^1J_{YC}$ (32.4 Hz), $^2J_{YH}$ (2.5 Hz), and $^1J_{CH}$ (102.7 Hz) coupling constants associated with the CH_2 group directly bonded to yttrium are very similar to the coupling parameters found for the same group in Y(DAC)(CH_2SiMe_3) (39, 2.8, and 102 Hz, respectively).[4b]

The presence of *trans* alkyl groups was confirmed by X-ray crystallography (Figure 1).[10] The yttrium center in **1** lies on a crystallographic 2-fold axis which passes through the midpoint of the C(1)−C(1)′ and C(9)−C(109) bonds. The resulting disorder between N(108) and O(8) was successfully modeled, but the yttrium−donor distances associated with these atoms are necessarily unreliable. There are no intermolecular distances significantly less than the sums of the appropriate accepted van der Waals radii. The Y---O(2) distance (not depicted as a bond in Figure 1) must represent a relatively weak interaction, as it is ∼0.5 Å longer than the other Y−O bonds. Thus, the coordination number of Y might be described as either 6 or 8, depending upon whether these weak interactions are counted. The arrangement about Y may be described as distorted from hexagonal bipyramidal, by the displacement of O(2) and O(2)′ away from Y in the equatorial plane, accompanied by a complimentary tilting of the other vertices, especially the apical carbon atoms C(10) and C(10)′. Apart from the long Y−O(2) distances, the other bond distances to Y fall in the expected ranges.[4] The shortest bonds to Y, Y−N and Y−O(8), are anti with respect to the long Y−O(2) and Y−O(2)′ vectors. The Y−C distance (2.461(4) Å) and Y−C−Si angle (125.25(20)°) are very similar to those found in Y(DAC)(CH_2SiMe_3) (2.45(2) Å and 126.4(8)°).[4b] There is no evidence for agostic interactions between the alkyl α-CH_2 or $SiMe_3$ groups and the metal center.[12]

In contrast to Y(DAC)(CH_2SiMe_3), **1** is thermally stable for more than 1 week in d_6-benzene solution at room temperature. The major decomposition pathway for Y(DAC)(CH_2SiMe_3) was previously shown to involve metalation of the DAC backbone.[4b] Since the MAC ligand should be susceptible to similar attack, the much slower rate of decomposition may be attributable to greater ring strain in **1** than in the DAC complex. The notable distortion toward a six-coordinate geometry in the solid state (*vide supra*) illustrates that the macrocycle in **1** is unable to achieve a geometry which allows all five oxygens to coordinate. It therefore seems reasonable to assume that approach of the carbanionic α-carbon of the alkyl to a suitable CH_2 group of the MAC ligand will also be difficult in this macrocycle coordination geometry.

The reaction of **1** with CO proceeds smoothly to yield Y(MAC)(OC($SiMe_3$)=CH_2)$_2$ **2**.[13] The ^{1}H NMR spectrum of **2** shows two coupled doublets at δ 4.70 and 4.44 ppm ($^2J_{HH}$ = 2.2 Hz) which are also coupled to a ^{13}C resonance at δ 93.86 ppm (COSY). This pattern is consistent with a terminal =CH_2 group formed by $SiMe_3$ migration of an initial acyl (eq 2). Marks has reported



(2)

similar acyl to enolate rearrangements for ThCp*$_2$Cl(CH_2SiMe_3)[14a] and ThCp$_3$(CH_2SiMe_3).[14b] Surprisingly, in view of the ease of CO insertion, **1** was recovered unchanged after exposure to either ethylene or H_2 (2 atm, toluene, 1 week).[15] This striking difference in reactivity would appear to be electronic in origin since all of these substrates present similar steric demands.

Complex **1** appears to undergo alkyl abstraction with $B(C_6F_5)_3$ in d_8-THF to generate a colorless solution of the cationic species [Y(MAC)(CH_2SiMe_3)]$^+$[$B(C_6F_5)_3$(CH_2SiMe_3)]$^-$ (**3**).[16] The NMR spectra of **3**, generated

(10) Crystal data for **1**: $C_{20}H_{46}NO_5Si_2Y$, M_r = 525.68, monoclinic, space group *C2/c*, a = 18.487(3) Å, b = 11.030(2) Å, c = 13.908(3) Å, β = 101.50(2)°, V = 2779.1 Å^3, Z = 4, T = 213 K, μ(Mo Kα) = 22.0 cm^{-1}, λ = 0.709 32 C, F(000) = 1119.77, R_F = 0.039 for 1399 data ($I_o \geq 2.5\sigma(I_o)$) and 152 variables. The disorder of the structure was clearly evident and was modeled only for the MAC ligand atoms in the vicinity of O(8)/N(108), primarily because of the difference in the Y−O and Y−N bond lengths. Further details of the X-ray experimental procedure are provided in the Supporting Information.

(11) Johnson, C. K. ORTEPII; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(12) The absence of structural or spectroscopic evidence for agostic interactions in Y(DAC)(CH_2SiMe_3) was discussed in ref 4b. The structural and spectroscopic similarities between this complex and **1** argue strongly against agostic interactions in the present case.

in situ, indicate that alkyl transfer has taken place. Two ^{1}H signals due to the methylene group of the CH_2SiMe_3 ligand are distinguishable: one shows sharp coupling to ^{89}Y (δ −1.16, $^2J_{YH}$ = 3.2 Hz), while the second at δ 0.12 ppm shows broadening due to ^{11}B coupling. The ^{19}F NMR spectrum of **3** recorded in d_8-THF shows meta/para aryl F chemical shift differences consistent with noncoordinating anions.[17] Isolation of pure **3** was unsuccessful even in the presence of a Lewis base such as THF and PMe_3. Decomposition appears to occur over a period of a few minutes at room temperature in d_8-THF, as evidenced by the growth of resonances due to TMS. This contrasts with the high stability of the only other known lanthanide alkyl cation, [LaCp*{CH(SiMe$_3$)$_2$}]$^+$[BPh$_4$]$^-$.[5c] The latter features strong BPh_4^- coordination in the base-free form, but displacement of BPh_4^- by THF also produces a stable complex, [LaCp*{CH(SiMe$_3$)$_2$}(THF)$_3$]$^+$[BPh$_4$]$^-$. While it has previously been shown that fluorine substitution of phenyl groups in the tetraphenylborate anion destabilizes cationic alkyl complexes by decreasing the coordinating ability of the anion,[5c] it is not clear why a cation such as **3** should be so unstable in the presence of a good donor such as THF. It is possible that decomposition of **3** involves attack on THF, but we have not been able to confirm this due to the complexity of the product mixture obtained. Attempts to prepare **3** in CD_2Cl_2 resulted in rapid decomposition, presumably due to chloride abstraction from the solvent.[18,19]

The results presented here indicate the utility of a monoanionic macrocycle in stabilizing lanthanide dialkyls with respect to both metalation and ligand redistribution. General routes which avoid the limitations associated with direct protonolysis (eq 1) and provide access to the potentially more reactive *cis*-dialkyl isomers are clearly needed. Work is continuing to address these concerns and to further explore the reactivity of **1**.

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Supporting Information Available: Text listing X-ray experimental details and a discussion of the disorder model used and complete tables of fractional atomic coordinates, bond distances and angles, selected torsion angles, and anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

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(13) Synthesis of **2**: A solution of **1** (0.030 g, 0.057 mmol) in 0.75 mL of d_6-benzene was placed in an NMR tube fitted with a teflon valve (Brunfeldt). After it was cooled in liquid nitrogen, the sample was degassed and warmed to room temperature under an atmosphere of CO prior to sealing. The NMR spectra showed clean formation of **2**. Complex **2** was isolated as a greasy solid after washing with cold hexane. ^{1}H NMR (360 MHz): δ 4.70 (d, 2H, =CH_aH$_b$, $^2J_{HH}$ = 2.2 Hz), 4.44 (d, 2H, C=CH$_a$$H_b$, $^2J_{HH}$ = 2.2 Hz), 3.85 (m, 4H, MAC *H*), 3.44 (m, 4H, MAC *H*), 3.32 (m, 12H, overlapping MAC *H*), 3.19 (m, 4H, MAC *H*), 0.38 (s, 18H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (90.55 MHz): δ 176.63 (d, O*C*(SiMe$_3$)=, $^2J_{YC}$ = 4.5 Hz), 93.86 (C=*C*H$_2$), 75.71, 71.01, 69.85, 69.00, 68.33, 55.98 (MAC *C*), −1.38 (Si*Me*$_3$). Stereochemistry relative to the SiMe$_3$ group has not been assigned for H$_a$ and H$_b$. IR (Nujol, KBr): 1618, 1567 (w, ν(C=C)) cm^{-1}. Anal. Calcd for $C_{22}H_{46}NO_7Si_2Y$: C, 45.43; H, 7.97; N, 2.41. Found: C, 43.91; H, 7.48; N, 2.87. Despite repeated attempts, no better elemental analysis could be obtained.

(14) (a) ThCp*$_2$Cl(OC(SiMe$_3$)=CH$_2$) ^{1}H NMR: δ 4.88, 4.54 (=CH$_2$), 0.24 (SiMe$_3$). Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112. (b) ThCp$_3$(OC(SiMe$_3$)=CH$_2$) ^{1}H NMR: δ 4.87, 4.45 (=CH$_2$), 0.24 (SiMe$_3$). Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484.

(15) Complexes of the type (OEP)Ln(CH(SiMe$_3$)$_2$)$_2$ (OEP = octaethylporphyrin) have also been found to be inert toward hydrogenolysis.[2b]

(16) Synthesis of **3**: Complex **1** (0.030 g, 0.057 mmol) and B(C$_6$F$_5$)$_3$ (0.029 g, 0.057 mmol) were placed in an NMR tube under argon. Dry, degassed d_8-THF (0.50 mL) was added by syringe, and the sample was sealed. The sample was immediately examined by ^{1}H, ^{19}F, and ^{13}C{^{1}H} NMR spectroscopy at −10 °C. The reaction mixture contained resonances due to one major product, although minor resonances due to **1**, TMS, and other unidentified products were also present. ^{1}H NMR (360 MHz): δ 3.90−4.15 (16H, macrocycle), 3.45−3.65 (4H, macrocycle), 3.20 (4H, macrocycle), 0.12 (br s, BC*H*$_2$SiMe$_3$), −0.06, −0.11 (s, Si*Me*$_3$), −1.16 (d, YC*H*$_2$SiMe$_3$, $^2J_{YH}$ = 3.2 Hz). ^{19}F NMR (338.38 MHz): δ −132.4 (d, *o* aryl *F*, J_{FF} = 20 Hz), −165.2 (t, *p* aryl *F*, J_{FF} = 21 Hz), −167.7 (br t, *m* aryl *F*, J_{FF} = 18 Hz). ^{13}C{^{1}H} NMR (90.55 MHz): δ 74.4, 69.6, 69.0, 68.7, 68.5 (O*C*H$_2$, macrocycle), 54.1 (N*C*H$_2$, macrocycle), 32.4 (d, Y*C*H$_2$, $^1J_{YC}$ = 37 Hz), −1.9 (Si*Me*$_3$), −2.5 (Si*Me*$_3$). The ^{13}C resonance due to the CH$_2$ group bonded to boron was difficult to assign with confidence due to ^{11}B broadening. The TMS resonance slowly increased over time at the expense of the other SiMe$_3$ resonances, and the solution turned brown.

(17) It has been suggested that a chemical shift difference of less than 3 ppm between the meta and para ^{19}F resonances of the RB(C$_6$F$_5$)$_3^-$ (R = Me, CH$_2$Ph) anion is characteristic of a noncoordinating anion: Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(18) A small amount of TMS is also produced in this reaction.

(19) Alkyl abstraction using B(C$_6$F$_5$)$_3$ was also attempted in d_5-bromobenzene at the suggestion of one reviewer. A dark yellow, insoluble oil formed immediately upon mixing in this solvent. Removal of the solvent and dissolution in d_8-THF regenerated the spectrum reported in ref 16 above.