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Synthesis and Characterization of Yttrium Complexes Containing a Tridentate Linked Amido−Cyclopentadienyl Ligand

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Summary: The reaction of dilithium salts of the tridentate linked amido−cyclopentadienyl ligands $Li_2(C_5Me_4SiMe_2NCH_2CH_2X)$ (X = OMe, NMe_2, CH_2OMe) with $[Y(o\text{-}C_6H_4CH_2NMe_2)Cl_2(LiCl)(THF)_4]$ and $Y(\eta^5\text{-}C_5H_5)Cl_2(THF)_3$ give chloro-bridged ate complexes of the type $[Li(THF)][Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)(R)Cl]$, where R = $o\text{-}C_6H_4CH_2NMe_2$, $\eta^5\text{-}C_5H_5$.

Introduction

The efficient synthesis of rare earth half-sandwich complexes $(\eta^5\text{-}C_5R_5)LnX_2L_n$ remains a challenge in organolanthanide chemistry.[1] The problem of alkali metal salt incorporation during salt metathesis of rare earth halides[2] can be occasionally prevented by employing phenoxides,[3] triflates,[4] or acetylacetonates.[5] The use of chelating ligand systems based on functionalized cyclopentadienyl would solve yet another problem, viz., the facile intermolecular ligand exchange reactions. One bidentate amido−cyclopentadienyl ligand such as $C_5Me_4SiMe_2NCMe_3$, first introduced by Bercaw et al., has successfully been coordinated at scandium and yttrium centers by salt metathesis and by amine or alkane elimination reactions using appropriate amide and alkyl precursors.[6,7] However, irrespective of the molar ratios of the reactants, the reaction of yttrium trichloride with the lithium salts of a tridentate amido−cyclopentadienyl ligand $Li_2(C_5R_4SiMe_2NCH_2CH_2X)$ (C_5R_4 = C_5Me_4, 3-C_5H_3-*t*-Bu; X = OMe, NMe_2)[8] were shown to give exclusively the heterobimetallic yttrocene derivatives $Li[Y(\eta^5{:}\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$.[9] We report here that the yttrium mono(aryl) complex $[Y(o\text{-}C_6H_4CH_2NMe_2)Cl_2(LiCl)(THF)_4]$[10] and the yttrium mono(cyclopentadienyl) complex $Y(\eta^5\text{-}C_5H_5)Cl_2(THF)_3$[2b,i] allow the selective introduction of only one tridentate ligand system.

Results and Discussion

The mono(aryl) yttrium complex **1** can be prepared by reacting yttrium trichloride with 1 equiv of $Li(o\text{-}C_6H_4CH_2NMe_2)$ and isolated from concentrated THF solutions by adding pentane as colorless microcrystals in over 80% yield. It retains 1 equiv of LiCl and 4 equiv of THF, leading to the tentative assignment of the formula $[Y(o\text{-}C_6H_4CH_2NMe_2)Cl_2(LiCl)(THF)_4]$.[11] Subsequent reaction of **1** with $Li_2(C_5Me_4SiMe_2NCH_2CH_2X)$ (X = OMe (**a**), NMe_2 (**b**), CH_2OMe (**c**)) gives the half-sandwich complexes **2a**−**c**. In a convenient one-pot synthesis, sequential addition of $Li(o\text{-}C_6H_4CH_2NMe_2)$ and $Li_2(C_5Me_4SiMe_2NCH_2CH_2X)$ to yttrium trichloride results in the straightforward formation of crystalline **2a**−**c** in excellent yields (Scheme 1). All complexes have fully been characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses.

The ^1H NMR spectrum of **2a** shows four well-separated singlets for the ring methyl protons and two singlets for the methyl protons at the silicon atom, of which one is shifted downfield to 0.92 ppm, possibly due to the ring current of the aryl ligand. The observation of two singlets for the amine methyl protons and of a

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(1) (a) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (b) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 4, Chapter 2. (c) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (d) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74.

(2) (a) Manastyrskyj, S.; Maginn, R. E.; Dubeck, M. *Inorg. Chem.* **1963**, *2*, 904. (b) Jamerson, J. D.; Masino, A. P.; Takats, J. *J. Organomet. Chem.* **1974**, *65*, C33. (c) Schumann, H.; Albrecht, I.; Pickardt, J.; Hahn, E. *J. Organomet. Chem.* **1984**, *276*, C5. (d) Albrecht, I.; Hahn, E.; Pickardt, J.; Schumann, H. *Inorg. Chim. Acta* **1985**, *110*, 145. (e) Albrecht, I.; Schumann, H. *J. Organomet. Chem.* **1986**, *310*, C29. (f) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23. (g) Schumann, H.; Albrecht, I.; Gallagher, M.; Hahn, E.; Janiak, C.; Kolax, C.; Loebel, J.; Nickel, S.; Palamidis, E. *Polyhedron* **1988**, *7*, 2307. (h) van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 1459. (i) Zhou, X.; Wu, Z.; Ma, H.; Xu, Z.; You, X. *Polyhedron* **1994**, *13*, 375.

(3) (a) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637. (b) Schaverien, C. J.; Frijns, J. H. G.; Heeres, H. J.; van den Hende, J. R.; Teuben, J. H.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 642. (c) Schaverien, C. J. *Organometallics* **1994**, *13*, 69.

(4) Schumann, H.; Meese-Marktscheffel, J. A.; Dietrich, A. *J. Organomet. Chem.* **1989**, *377*, C5.

(5) Piers, W. E.; Bunel, E. E.; Bercaw, J. E. *J. Organomet. Chem.* **1991**, *407*, 51.

(6) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

(7) (a) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720.

(8) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129.

(9) (a) Hultzsch, K. C. Diploma Thesis, University of Mainz, Germany, 1996. (b) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4845. (c) Hultzsch, K. C.; Okuda, J. *Macromol. Rapid Commun.* **1997**, *18*, 809.

(10) van Koten et al. reported the synthesis of $[LnCl_2\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(\mu\text{-}Li(THF)_2)]_2$ (Ln = Y, Lu) with bridging lithium atoms, see: Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **1995**, *1*, 343.

(11) Implying a similar dimeric structure as found in $[LuCl_2\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(\mu\text{-}Li(THF)_2)]_2$ (see ref 10), one might expect to find three molecules of THF in **1**, one coordinated to yttrium and two to lithium.

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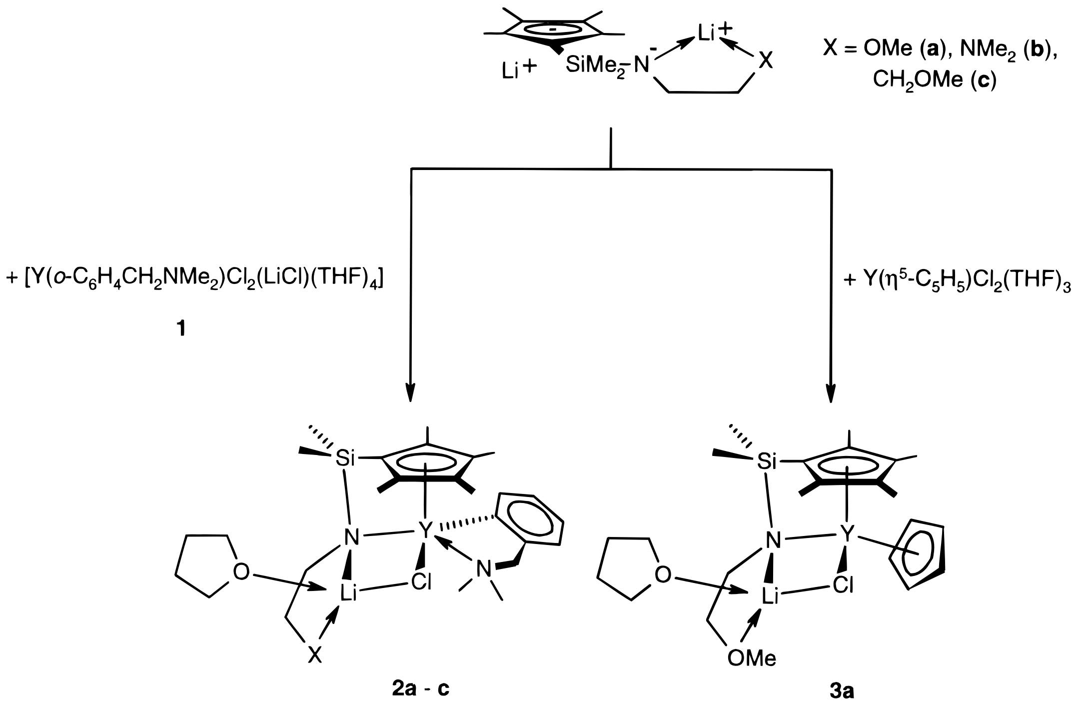
Scheme 1



pair of doublets for the benzylic protons at room temperature is consistent with an unsymmetrical coordination sphere around yttrium on the NMR time scale. The ^{13}C NMR spectrum is in agreement with this unsymmetrical structure. The Y−C(aryl) coupling constant $^{1}J_{Y-C}$ of 50.9 Hz is in the normal range for yttrium aryl complexes, e.g., $Y(o\text{-}C_6H_4CH_2NMe_2)_3$ ($^{1}J_{Y-C}$ = 43.3 Hz),[12a] $Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2$ ($^{1}J_{Y-C}$ = 43.4 Hz),[12a] $[YCl_2\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(\mu\text{-}Cl)(\mu\text{-}Li(THF)_2)]_2$ ($^{1}J_{Y-C}$ = 42.3 Hz),[10] $Cp^*{}_2Y(o\text{-}C_6H_4CH_2NMe_2)$ ($^{1}J_{Y-C}$ = 56.3 Hz),[13] and $Cp^*{}_2Y(o\text{-}C_6H_4OMe)$ ($^{1}J_{Y-C}$ = 51.6 Hz).[13] The elemental analyses for **2** suggest the presence of one THF molecule and 1 equiv of lithium chloride.

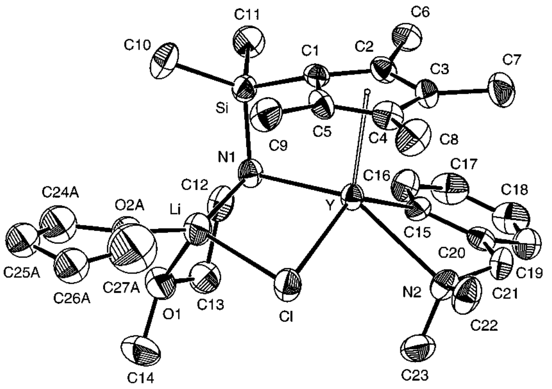


Figure 1. ORTEP diagram[14] of the molecular structure of **2a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and one position of the disordered THF molecule are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): $Cp_{Cent}-Y$ 2.351(7), Y−N1 2.315(5), Y−Cl 2.672(2), Y−C(15) 2.445(6), Y−N2 2.574(5), Y···Li 3.24(1), Li−O1 1.89(1), Li−O2A 1.87(2), Li−O2B 2.00(2), Li−N1 2.11(1), Li−Cl 2.38(1), $Cp_{Cent}-Y-C15$ 112.1(2), $Cp_{Cent}-Y-N1$ 96.1(2), $Cp_{Cent}-Y-N2$ 117.9(2), $Cp_{Cent}-Y-Cl$ 113.8(2), C15−Y−N2 68.6(2), N1−Y−Cl 86.0(1), Y−N1−Li 93.9(4), N1−Li−Cl 98.8(5), Y−Cl−Li 79.6(3).

The molecular structure of complex **2a** is confirmed by a single-crystal structure analysis. An ORTEP diagram of the structure of **2a** is shown in Figure 1. The 16-electron yttrium center is coordinated in a distorted square pyramidal fashion by one linked amido−cyclopentadienyl ligand, a chelating *o*-(*N*,*N*-dimethylamino)benzyl ligand, and a chlorine atom, with the cyclopentadienyl ligand occupying the apical position. The ether function of the side chain is coordinated to the lithium rather than to the yttrium atom. Numerous metallocene complexes with bridging monoanionic ligands of the general type $(\eta^5\text{-}C_5R_5)_2Ln(\mu\text{-}X)_2ML_2$ (R = H, Me; X = halide, amide, alkoxide; M = alkali metal, L = two-electron ligand) have been reported. However, **2a** appears to be the first complex with two different bridging ligands.[1c] The yttrium, lithium, chloro, and amido−nitrogen atoms form a slightly distorted four-centered ring with Li−N1−Y and Li−Cl−Y angles of 93.9(4)° and 79.6(3)°, respectively. The geometry of the amido−cyclopentadienyl ligand is very similar to that found in the bis(ligand)yttrium complex $Li[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]$.[9] However the Y−N−Li angle at the amido−nitrogen in **2a** is significantly larger than those found in the bis(ligand)yttrium complex (81.0(3)° and 81.2(3)°). The $Y-Cp_{Cent}$ distance (2.351(7) Å) is at the lower end of $Y-Cp_{Cent}$ distances found in other cyclopentadienyl yttrium complexes.[15] The Y−C(aryl) bond length of 2.445(6) Å is in the expected

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(12) (a) Booij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79. (b) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H. *Organometallics* **1989**, *8*, 2454.

(13) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.

(14) Zsolnai, L.; Pritzkow, H. *ZORTEP Ortep Program for PC*; Universität Heidelberg: Heidelberg, Germany, 1994.

(15) (a) $Cp^*Y(OAr)_2$ $Cp_{Cent}-Y$ = 2.363(3) Å, see ref 3b. (b) $Cp^*Y(o\text{-}C_6H_4CH_2NMe_2)_2$ $Cp_{Cent}-Y$ = 2.367(3) Å, see ref 12b. (c) $Cp^*[PhC(NSiMe_3)_2]Y(\mu\text{-}Me)_2Li(TMEDA)$ $Cp_{Cent}-Y$ = 2.392(3) Å, see Duchateau, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1996**, *15*, 1656. (d) $[Cp^*Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ $Cp_{Cent}-Y$ = 2.415 Å, see Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1993**, *12*, 3998.

range of Y−C bond lengths as found in $\mathrm{Cp^{*}Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)_2}$ (2.471(6) and 2.479(6) Å),[12b] $\mathrm{Cp_2Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)}$ (2.41(2) Å),[16] and $\mathrm{Cp^{*}_2YCH(SiMe_3)_2}$ (2.468(7) Å).[17] Within the five-membered metallacyclic ring, the three carbon atoms C15, C20, and C21 and the yttrium atom are coplanar (deviation within 0.017(5) Å), while the nitrogen atom N2 resides 0.72(1) Å out of the plane. The torsion angle that involves the nitrogen and three carbon atoms of the ring is 29.2(9)° and can be compared to 32.2° and −34.1° in $\mathrm{Cp_2Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)}$[16] for the two independent molecules and −45.6(7)° and 37(1)° in $\mathrm{Cp^{*}Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)_2}$.[12b] The yttrium amino−nitrogen bond length in **2a** of 2.574(5) Å is only slightly longer than those found in $\mathrm{Cp_2Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)}$ (2.43(2) and 2.54(2) Å for the two independent molecules)[16] and $\mathrm{Cp^{*}Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)_2}$ (2.568(5) and 2.506(6) Å).[12b]

In order to investigate the influence of the length of the amido side chain, an additional methylene carbon was introduced. On the basis of the NMR spectroscopic data and elemental analysis, complex **2c** retains one molecule of THF and lithium chloride again, suggesting a coordination of the ether function of the side chain at the lithium rather than at yttrium. Reaction of $\mathrm{Y(\eta^5\text{-}C_5H_5)Cl_2(THF)_3}$[2b,i] with 1 equiv of $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)}$ gives the mixed yttrocene complex **3a** as yellow crystals in good yields. NMR spectroscopic data clearly indicate the presence of both the Cp and the linked amido−cyclopentadienyl ligand as well as one molecule of THF.[18] The elemental analysis confirms that 1 equiv of LiCl is retained in **3a**, indicating the structure as depicted in Scheme 1.

Possibly due to the fast scrambling reaction between the yttrium trichloride and the various mixed alkyl species, sequential addition of 1 equiv of the lithium alkyl $\mathrm{LiCH_2SiMe_3}$ or $\mathrm{LiCH(SiMe_3)_2}$ and $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)}$ to $\mathrm{YCl_3(THF)_{3.5}}$ in THF resulted in the formation of the thermodynamically preferred bis(ligand) complex $\mathrm{Li[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]}$. We had hoped that under kinetic control half-sandwich complexes would have the chance to form.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous $\mathrm{YCl_3}$ (ALFA) was used as received. $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)}$ was prepared from $\mathrm{(C_5Me_4H)SiMe_2Cl}$ and $\mathrm{Li(NHCH_2CH_2CH_2OMe)}$ analogous to the synthesis of $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2NMe_2)}$ and $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)}$ as published previously.[8] All other chemicals were commercially available and used as received unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department.

$\mathrm{[Y(\mathit{o}\text{-}C_6H_4CH_2NMe_2)Cl_2(LiCl)(THF)_4]}$ (1). $\mathrm{YCl_3}$ (195 mg, 1.00 mmol) was slurried in THF (15 mL) and stirred at 50 °C for 30 min. The solution was cooled to room temperature, and solid $\mathrm{Li(\mathit{o}\text{-}C_6H_4CH_2NMe_2)}$ (148 mg, 1.05 mmol) was added slowly. After 3 h, the clear, colorless solution was concentrated to a volume of 2 mL in vacuo. The product was precipitated by addition of pentane (7 mL) followed by cooling to −78 °C. The mother liquor was decanted off, and the crystals were dried in vacuo to yield 515 mg (82 %) as colorless microcrystals: ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 1.35 (br s, 16 H, β-$\mathrm{CH_2}$), 2.63 (s, 6 H, $\mathrm{N(CH_3)_2}$), 3.75 (br s, 16 H, α-$\mathrm{CH_2}$), 3.88 (s, 2 H, $\mathrm{NC\mathit{H}_2C_6H_4}$), 7.06 (d, $^3J_{\mathrm{H-H}} = 7.0$ Hz, 1 H, 3-$\mathrm{C_6H_4}$), 7.24 (m, 2 H, 5-, 4-$\mathrm{C_6H_4}$), 8.13 (d, $^3J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, 6-$\mathrm{C_6H_4}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C) δ 25.4 (β-$\mathrm{CH_2}$), 46.4 ($\mathrm{NCH_3}$), 69.3 (α-$\mathrm{CH_2}$), 70.2 ($\mathrm{N\mathit{C}H_2C_6H_4}$), 124.0, 124.7, 125.8, 138.7 ($\mathrm{C_6H_4}$), 147.2 ($\mathrm{\mathit{C}CH_2}$), 185.4 (d, $^1J_{\mathrm{Y-C}} = 48.6$ Hz, *ipso*-C). Anal. Calcd for $\mathrm{C_{25}H_{44}Cl_3LiNO_4Y}$: C, 48.06; H, 7.10; N, 2.24. Found: C, 52.05; H, 6.39; N, 2.54. Several determinations were performed, but the results remained erratic probably due to facile loss of THF.[11]

$\mathrm{[Li(THF)][Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(\mathit{o}\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}Cl)]}$ (2a). $\mathrm{YCl_3}$ (391 mg, 2.00 mmol) was slurried in THF (30 mL) and stirred at 50 °C for 30 min. The solution was cooled again to room temperature, and solid $\mathrm{Li(\mathit{o}\text{-}C_6H_4CH_2NMe_2)}$ (296 mg, 2.10 mmol) was added slowly. After 3 h, $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)}$ (530 mg, 2.00 mmol) was added and the mixture was stirred for 15 h. The solvent was removed in vacuo, and the crude product was extracted with 3 × 20 mL of pentane. LiCl was filtered off, and the solution was concentrated to a volume of 10 mL. After crystallization at −78 °C for 24 h, the mother liquor was decanted off, and the crystals were dried in vacuo to yield 837 mg (71 %) of colorless microcrystals: ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 0.57, 0.92 (s, 3 H, $\mathrm{SiCH_3}$), 1.25 (m, 4 H, β-$\mathrm{CH_2}$), 1.95, 2.16 (s, 3 H, $\mathrm{C_5Me_4}$), 2.29 (s, 3 H, $\mathrm{N(CH_3)_2}$), 2.32 (s, 3 H, $\mathrm{C_5Me_4}$), 2.35 (s, 3 H, $\mathrm{N(CH_3)_2}$), 2.56 (s, 3 H, $\mathrm{C_5Me_4}$), 2.87 (s, 3 H, $\mathrm{OCH_3}$), 2.98 (d, $^2J_{\mathrm{H-H}} = 13.2$ Hz, 1 H, $\mathrm{NC\mathit{H}_2C_6H_4}$), 3.15 (m, 1 H, $\mathrm{NCH_2C\mathit{H}_2O}$), 3.22 (m, 1 H, $\mathrm{NC\mathit{H}_2CH_2O}$), 3.31 (m, 1 H, $\mathrm{NCH_2C\mathit{H}_2O}$), 3.48 (m, 4 H, α-$\mathrm{CH_2}$), 3.55 (d, $^2J_{\mathrm{H-H}} = 13.5$ Hz, 1 H, $\mathrm{NC\mathit{H}_2CH_2O}$), 4.07 (d, $^2J_{\mathrm{H-H}} = 13.2$ Hz, 1 H, $\mathrm{NC\mathit{H}_2C_6H_4}$), 7.03 (d, $^3J_{\mathrm{H-H}} = 7.3$ Hz, 1 H, 3-$\mathrm{C_6H_4}$), 7.22 (t, $^3J_{\mathrm{H-H}} = 7.3$ Hz, 1 H, 4-$\mathrm{C_6H_4}$), 7.33 ("t", 1 H, 5-$\mathrm{C_6H_4}$), 7.94 (d, $^3J_{\mathrm{H-H}} = 6.8$ Hz, 1 H, 6-$\mathrm{C_6H_4}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 25 °C) δ 2.3, 5.0 ($\mathrm{SiCH_3}$), 11.5, 11.8, 15.7, 15.8 ($\mathrm{C_5\mathit{Me}_4}$), 25.2 ($\beta$-$\mathrm{CH_2}$), 44.9, 46.8 ($\mathrm{NCH_3}$), 48.1 ($\mathrm{N\mathit{C}H_2CH_2O}$), 58.4 ($\mathrm{OCH_3}$), 68.5 (α-$\mathrm{CH_2}$), 69.8 ($\mathrm{N\mathit{C}H_2C_6H_4}$), 78.3 ($\mathrm{NCH_2\mathit{C}H_2O}$), 106.6 (ring C attached to $\mathrm{SiMe_2}$), 121.5, 122.6 ($\mathrm{\mathit{C}_5Me_4}$), 123.5 (3-$\mathrm{C_6H_4}$), 125.2 (4-, 5-$\mathrm{C_6H_4}$), 126.4, 126.7 ($\mathrm{\mathit{C}_5Me_4}$), 139.2 (6-$\mathrm{C_6H_4}$), 147.3 ($\mathrm{C_6H_4CH_2}$), 187.5 (d, $^1J_{\mathrm{Y-C}} = 50.9$ Hz, *ipso*-C); ^{29}Si NMR ($\mathrm{C_6D_6}$, 25 °C) δ −14.1 (d, $^2J_{\mathrm{Y-Si}} = 1.5$ Hz). Anal. Calcd for $\mathrm{C_{27}H_{45}ClLiN_2O_2SiY}$: C, 55.05; H, 7.70; N, 4.76. Found: C, 53.75; H, 7.61; N, 5.17.

$\mathrm{[Li(THF)][Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2NMe_2)(\mathit{o}\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}Cl)]}$ (2b). $\mathrm{YCl_3}$ (391 mg, 2.00 mmol) were slurried in THF (30 mL) and stirred at 50 °C for 30 min. The solution was cooled again to room temperature, and solid $\mathrm{Li(\mathit{o}\text{-}C_6H_4CH_2NMe_2)}$ (310 mg, 2.20 mmol) was added slowly. After 3 h, $\mathrm{Li_2(C_5Me_4SiMe_2NCH_2CH_2NMe_2)}$ (557 mg, 2.00 mmol) was added and the mixture was stirred for 17 h. The solvent was removed in vacuo, and the crude product was extracted with 2 × 20 mL of pentane. LiCl was filtered off, and the solution was concentrated to a volume of 10 mL. After crystallization at −78 °C for 24 h, the mother liquor was decanted off, and the crystals were dried in vacuo to yield 1.03 g (86 %) of pale yellow microcrystals: ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 0.56, 0.97 (s, 3 H, $\mathrm{SiCH_3}$), 1.25 (m, 4 H, β-$\mathrm{CH_2}$), 1.67, 1.94 (br m, 3 H, $\mathrm{NCH_2CH_2N(C\mathit{H}_3)_2}$), 1.96 (s, 3 H, $\mathrm{C_5Me_4}$), 2.00 (m, 1 H, $\mathrm{NCH_2C\mathit{H}_2NMe_2}$), 2.16 (s, 3 H, $\mathrm{C_5Me_4}$), 2.32, 2.33 (s, 3 H, $\mathrm{CH_2N(C\mathit{H}_3)_2}$), 2.35 (s, 3 H, $\mathrm{C_5Me_4}$), 2.39 (m, 1 H, $\mathrm{NCH_2C\mathit{H}_2NMe_2}$), 2.52 (s, 3 H, $\mathrm{C_5Me_4}$), 2.98 (d, $^2J_{\mathrm{H-H}} = 13.4$ Hz, 1 H, $\mathrm{NC\mathit{H}_2C_6H_4}$), 3.13 (m, 1 H, $\mathrm{NC\mathit{H}_2CH_2NMe_2}$), 3.49 (m, 4 H, α-$\mathrm{CH_2}$), 3.58 (m, 1 H, $\mathrm{NC\mathit{H}_2CH_2NMe_2}$), 4.06 (d, $^2J_{\mathrm{H-H}} = 13.4$ Hz, 1 H, $\mathrm{NC\mathit{H}_2C_6H_4}$), 7.04 (d, $^3J_{\mathrm{H-H}} = 7.3$ Hz, 1 H, 3−$\mathrm{C_6H_4}$), 7.24 (dt, $^4J_{\mathrm{H-H}} = 1.2$

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[16] Rausch, M. D.; Foust, D. F.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* **1984**, *265*, 241.

[17] den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.

[18] Upon prolonged evaporation in vacuo, **3a** loses THF partially. Attempts to remove the THF completely by heating in vacuo to 50 °C resulted in decomposition of the complex, obvious from the five signals observed for the cyclopentadienyl protons in the ^{1}H NMR spectrum.

Hz, $^3J_{H-H} = 7.3$ Hz, 1 H, 4-C_6H_4), 7.37 ("t", $^3J_{H-H} = 7.1$ Hz, 1 H, 5−C_6H_4), 8.06 (d, $^3J_{H-H} = 6.6$ Hz, 1 H, 6-C_6H_4); ^{13}C NMR (C_6D_6, 25 °C) δ 2.4, 6.3 ($SiCH_3$), 11.5, 11.9, 15.5, 15.8 (C_5Me_4), 25.1 (β-CH_2), 45.0 (CH_2NCH_3), 45.3 ($NCH_2CH_2NMe_2$), 46.8 (CH_2NCH_3), 66.1 (CH_2NMe_2), 68.8 (α-CH_2), 69.7 ($NCH_2C_6H_4$), 106.6 (ring C attached to $SiMe_2$), 121.4, 122.6 (C_5Me_4), 123.6 (3-C_6H_4), 125.2 (4-C_6H_4), 125.3 (5-C_6H_4), 126.2, 126.4 (C_5Me_4), 139.2 (6-C_6H_4), 147.4 ($C_6H_4CH_2$), 187.3 (d, $^1J_{Y-C} = 51.7$ Hz, *ipso*-C). Anal. Calcd for $C_{28}H_{48}ClLiN_3OSiY$: C, 55.86; H, 8.04; N, 6.98. Found: C, 55.53; H, 8.04; N, 7.07.

[Li(THF)][Y(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2CH_2OMe$)(*o*-$C_6H_4CH_2NMe_2$)($\mu$-Cl)] (2c). YCl_3 (195 mg, 1.00 mmol) was slurried in THF (15 mL) and stirred at 50 °C for 30 min. The solution was cooled again to room temperature, and solid Li(*o*-$C_6H_4CH_2NMe_2$) (148 mg, 1.05 mmol) was added slowly. After 3 h, $Li_2(C_5Me_4SiMe_2NCH_2CH_2CH_2OMe)$ (280 mg, 1.00 mmol) was added and the mixture was stirred for 15 h. The solvent was removed in vacuo, and the crude product was extracted with 3 × 20 mL of pentane. LiCl was filtered off, and the solution was concentrated to a volume of 10 mL. After crystallization at −78 °C for 24 h, the mother liquor was decanted off, and the crystals were dried in vacuo to yield 455 mg (75 %) of colorless microcrystals: ^{1}H NMR (C_6D_6, 25 °C) δ 0.57, 0.93 (s, 3 H, $SiCH_3$), 1.26 (m, 4 H, β-CH_2), 1.39, 1.71 (m, 1H, $NCH_2CH_2CH_2O$), 1.94, 2.15 (s, 3 H, C_5Me_4), 2.34 (s, 3 H, $N(CH_3)_2$), 2.36 (s, 6 H, $N(CH_3)_2$, C_5Me_4), 2.56 (s, 3 H, C_5Me_4), 2.81 (s, 3 H, OCH_3), 2.91 (m, 2 H, $NCH_2CH_2CH_2O$), 2.99 (d, $^2J_{H-H} = 13.3$ Hz, 1 H, $NCH_2C_6H_4$), 3.39 (m, 1 H, $NCH_2CH_2CH_2O$), 3.48 (m, 4 H, α-CH_2), 3.53 (m, 1 H, $NCH_2CH_2CH_2O$), 4.07 (d, $^2J_{H-H} = 13.3$ Hz, 1 H, $NCH_2C_6H_4$), 7.03 (d, $^3J_{H-H} = 7.4$ Hz, 1 H, 3-C_6H_4), 7.24 (dt, $^4J_{H-H} = 1.5$ Hz, $^3J_{H-H} = 7.4$ Hz, 1 H, 4-C_6H_4), 7.37 ("t", 1 H, 5-C_6H_4), 8.07 (d, $^3J_{H-H} = 6.7$ Hz, 1 H, 6-C_6H_4); ^{13}C NMR (C_6D_6, 25 °C) δ 2.0, 7.0 ($SiCH_3$), 11.6, 11.7, 15.8, 15.9 (C_5Me_4), 25.2 (β-CH_2), 35.9 ($NCH_2CH_2CH_2O$), 44.7 ($NCH_2CH_2CH_2O$), 46.9 (2 C, NCH_3), 58.7 (OCH_3), 68.4 (α-CH_2), 70.0 ($NCH_2C_6H_4$), 74.4 ($NCH_2CH_2CH_2O$), 106.4 (ring C attached to $SiMe_2$), 121.1, 123.2 (C_5Me_4), 123.5 (3-C_6H_4), 125.0 (4-C_6H_4), 125.1 (5-C_6H_4), 126.2, 126.6 (C_5Me_4), 139.9 (6−C_6H_4), 147.4 ($C_6H_4CH_2$), 187.5 (d, $^1J_{Y-C} = 52.0$ Hz, *ipso*-C); ^{29}Si NMR (C_6D_6, 25 °C) δ −13.2. Anal. Calcd for $C_{28}H_{47}ClLiN_2O_2SiY$: C, 55.77; H, 7.86; N, 4.65. Found: C, 54.45; H, 7.65; N, 4.88.

[Li(THF)][Y(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2OMe$)($\eta^5$-$C_5H_5$)($\mu$-Cl)] (3a). YCl_3 (391 mg, 2.00 mmol) was slurried in THF (10 mL) and stirred at 50 °C for 30 min. The solution was cooled again to room temperature, and a solution of NaCp (176 mg, 2.00 mmol) in THF (10 mL) was added dropwise. After 5 h, a solution of $Li_2(C_5Me_4SiMe_2NCH_2CH_2OMe)$ (530 mg, 2.00 mmol) in THF (15 mL) was added, and the mixture was stirred for 14 h. The solvent was removed in vacuo, and the crude product was extracted with 3 × 20 mL of toluene. LiCl was filtered off, and the solvent was removed in vacuo. The solid was washed with 20 mL of cold hexanes. The solid was redissolved in 3 mL of toluene and crystallized at −78 °C for 24 h. The mother liquor was decanted off, and the crystals were dried in vacuo to yield 910 mg (87 %) of slightly yellow microcrystals: ^{1}H NMR (C_6D_6, 25 °C) δ 0.46, 0.57 (s, 3 H, $SiCH_3$), 1.21 (m, 4 H, β-CH_2), 2.04, 2.21, 2.28, 2.36 (s, 3 H, C_5Me_4), 3.00 (s, 3 H, OCH_3), 3.08 (m, 3 H, NCH_2CH_2O), 3.42 (m, 4 H, α-CH_2), 3.52 (m, 1 H, NCH_2), 6.24 (s, 5 H, C_5H_5); ^{13}C NMR (C_6D_6, 25 °C) δ 2.3, 5.0 ($SiCH_3$), 10.9, 12.4, 14.8, 15.3 (C_5Me_4), 25.1 (β-CH_2), 49.4 (NCH_2), 58.4 (OCH_3), 68.5 (α-CH_2), 77.3 (CH_2O), 105.9 (ring C attached to $SiMe_2$), 110.7 (C_5Me_4), 111.4 (C_5H_5), 113.4, 122.6, 123.0 (C_5Me_4). Anal. Calcd for $C_{23}H_{38}ClLiNO_2SiY$: C, 53.13; H, 7.37; N, 2.69. Found: C, 51.69; H, 6.08; N, 2.80. More satisfactory elemental analysis could not be obtained supposedly due to partial loss of THF.[18]

X-ray Crystal Structure Analysis of 2a. The compound, $C_{27}H_{45}ClLiN_2O_2SiY$, $M_r = 589.04$, obtained as colorless crystals by slow cooling of a concentrated pentane solution to −30 °C, crystallizes in the monoclinic space group $C2/c$, crystal size 0.50 × 0.40 × 0.38 mm, $a = 17.174(5)$ Å, $b = 15.000(3)$ Å, $c = 24.571(8)$ Å, $\beta = 106.86(2)°$, $V = 6058(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.292$ g cm^{-3}, $F(000)$ 2480, $\mu = 2.078$ mm^{-1}. Data collection in the range $3° < \theta < 24°$ (index ranges $0 \leq h \leq 19$, $0 \leq k \leq 17$, $-28 \leq l \leq 26$) was performed using ω scans on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation at 193(2) K. Data correction for Lorentz polarization and absorption (empirically using ψ scans) was carried out using the program system MolEN.[19a] From 4891 measured reflections, all 4715 independent reflections were used and 423 parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-93).[19b] The structure was solved by patterson (SHELXS-86)[19c] and difference Fourier syntheses and refined with anisotropic thermal parameters for all non-hydrogen atoms except for the atoms of the disordered tetrahydrofuran ring (SHELXL-93). This fragment was refined with two independent orientations (each with a multiplicity of 0.5) and isotropic thermal parameters for the carbon and oxygen atoms. The hydrogen atoms were located in difference Fourier syntheses and refined in their positions (with fixed isotropic thermal parameters), except for those of the disordered fragment where the hydrogen atoms were included in idealized positions. The refinement converged with $R = 0.055$, wR2 = 0.091 for all 2903 observed F_o data ($I > 2\sigma(I)$); goodness of fit = 1.18.

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Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **2a** (9 pages). Ordering information is given on any current masthead page.

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[19] (a) Fair, C. K. *MolEN, An Interactive Structure Solution Procedure*: Enraf-Nonius, Delft: The Netherlands, 1990. (b) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993. (c) Sheldrick, G. M. *SHELXS-86, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.