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Facile Conversion of an Appended Silylamido to a Silyloxy Ligand via Isocyanate Elimination. Synthesis of $\{[(C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ via the Carboxylation of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$

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*Summary: The reaction of 2 equiv of CO_2 with $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$ proceeds with the formation of $\{[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ (**2**), which reacts with additional CO_2 to afford $\{[(C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ (**3**) with the concomitant elimination of OCN-t-Bu. The formation of OCN-t-Bu was confirmed by a combination of GC/MS and IR measurements; the molecular structures of **2** and **3** were determined by X-ray crystallography.*

Bifunctional monocyclopentadienyl ligands containing an appended π-donor ligand have attracted considerable interest due to their ability to modify the Lewis acidity and reduce the steric congestion at an electrophilic d^0 metal center. Bercaw and his co-workers[1] demonstrated several years ago that the dianionic *ansa*-monocyclopentadienyl amido ligand $[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]^{2-}$ provides a sterically less demanding alternative to a pair of linked or unlinked cyclopentadienyl rings. Researchers at Dow Chemical[2] and Exxon[3] have subsequently utilized this type of ligand system to develop a new generation of "constrained geometry"[4] Ziegler−Natta olefin polymerization catalysts that employ *ansa*-monocyclopentadienyl amido group 4 complexes, $[(\eta^5\text{-}C_5R_4)SiR'_2(NR'')]MCl_2$ (M = Ti, Zr, Hf; R = alkyl; R′, R″ = alkyl, aryl), in the presence of excess MAO to effect ethylene/1-alkene copolymerizations.

Several synthetic strategies have been used to prepare monocyclopentadienyl ligands with different molecular linkages to an anionic N or O functionality. Group 4 metal complexes containing a bifunctional cyclopentadienyl amido ligand are typically prepared by the metathesis[2,3,5] of the dilithio salt or Grignard reagent of $[(C_5R_4)L(NR'')]^{2-}$ (L = $SiMe_2$, Si_2Me_4, $(CH_2)_n$) with the appropriate metal halide or by the thermally induced amine elimination reaction[6] of $[(C_5R_4H)L(NHR'')]$ with $M(NMe_2)_4$ (M = Ti, Zr, Hf). Green and co-workers[7] have employed the desilylation of *N*,*N*-bis(trimethylsilyl)(3-(3-(trimethylsilyl)cyclopentadienyl)propyl)amine with $NbCl_5$ to prepare the Nb(V) imido complex $[(\eta^5\text{-}C_5H_4)CH_2CH_2CH_2N]NbCl_2$. Teuben and co-workers[8] have prepared complexes that contain a bifunctional cyclopentadienylalkoxide ligand, such as $[(\eta^5\text{-}C_5Me_4)CH_2CH_2CH_2O]TiCl_2$, by the elimination of $SiMe_3Cl$ from $[(\eta^5\text{-}C_5Me_4)CH_2CH_2CH_2OSiMe_3]TiCl_3$ or by the thermolysis of $[(\eta^5\text{-}C_5Me_4)CH_2CH_2CH_2OMe]TiCl_2(CHPPh_3)$. Metathesis routes[9] have also been reported for the preparation of *ansa*-monocyclopentadienylalkoxy bridged complexes. In all of these examples the O functionality is incorporated directly into the backbone of the cyclopentadienyl substituent prior to metal coordination. However, during our investigations of the carboxylation reaction of $[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$ (**1**), we observed the direct conversion of its coordinated silylamido group into the corresponding silyloxide. Preliminary details of this novel metal-mediated transformation are communicated herein.

The ambient addition of 2 equiv of CO_2 to **1** proceeds with insertion into the two Zr-C(Me) bonds to produce $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ (**2**).[10] The dinuclear structure of **2**[11] (Figure 1) contains a pair of chelating acetate ligands and a pair of bridging acetates which separate the two symmetry-related Zr centers by 5.375 Å. The pseudooctahedral geometry at each Zr is characterized by a Cp(c)−Zr−N angle of 99.6°. The formation of **2** leads to a notable elongation[12] of the Zr−N(amido) bond to 2.140(4) Å, thereby suggesting

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) (a) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (c) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(2) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Patent 416 815, 1990.

(3) (a) Canich, J. M. Eur. Patent 420 436, 1991. (b) Canich, J. M.; Hlatky, G. G.; Turner, H. W. U.S. Patent 542 236, 1990.

(4) The constrained geometry introduced by the short silyl bridge leads to a 25−35° reduction in the (ring centroid)−M−N angle relative to the typical (ring centroid)−M−(ring centroid) angle of 125−135° in conventional bent metallocenes. For the structures of the *ansa*-monocyclopentadienyl amido Ti and Zr complexes with a dimethylsilyl bridge reported by Stevens *et al.*,[2] the (ring centroid)−M−N bond angles range from 99.1° in $\{[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl(\mu\text{-}Cl)\}_2$ to 106.1° in $[(C_5Me_4)SiMe_2(NC_6H_5)]TiCl_2$.

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(7) Antonelli, D. M.; Green, M. L. H.; Mountford, P. *J. Organomet. Chem.* **1992**, *438*, C4.

(8) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59.

(9) (a) Reiger, B. *J. Organomet. Chem.* **1991**, *420*, C17. (b) Coolbaugh, T. S.; Santasiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 6310.

(10) ^{1}H NMR spectrum of **2** ($CDCl_3$, 270 MHz): δ 2.12, 1.85 (s, C_5Me_4), 2.05 (s, O_2CMe), 1.17 (s, $NCMe_3$), 0.57 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR data for **2** ($CDCl_3$, 67.8 MHz): 189.4 ($O_2\mathbf{C}Me$), 131.2, 129.7 (distal and proximal ring carbons of C_5Me_4), 104.7 (bridgehead C of C_5Me_4), 57.2 ($N\mathbf{C}Me_3$), 33.9 ($NC\mathbf{Me}_3$), 23.2 ($\eta^2\text{-}O_2C\mathbf{Me}$), 13.5, 10.4 ($C_5\mathbf{Me}_4$), 7.7 ($SiMe_2$). IR (Nujol, cm^{-1}): ν(OCO-bridging) 1603 (s), 1444 (m); ν(OCO-chelating) 1534 (m), 1466 (m). IR (toluene, cm^{-1}): ν(OCO-chelating) 1536 (s), 1474 (m). Anal. Calcd for $C_{19}H_{33}O_4NSiZr$ (empirical formula): C, 49.76; H, 7.25; N, 3.05. Found: C, 49.74; H, 7.32; N, 2.84.

(11) Crystallographic data for **2**: triclinic, space group $C2/c$, a = 30.170(5) Å, b = 9.157(2) Å, c = 20.498(2) Å, β = 129.61(1)°, V = 4441(2) Å^3, Z = 4 dimers per cell. Full-matrix refinement (based on F_o^2, SHELXL-93) of the positional and anisotropic thermal parameters for the 26 non-hydrogen atoms converged with R1 = 0.0395 and GOF = 1.013 for all 1964 data with $I \geq 2.0\sigma(I)$.

(12) The corresponding Zr−N(amido) bond distance in $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ is 2.052(2) Å.[13]

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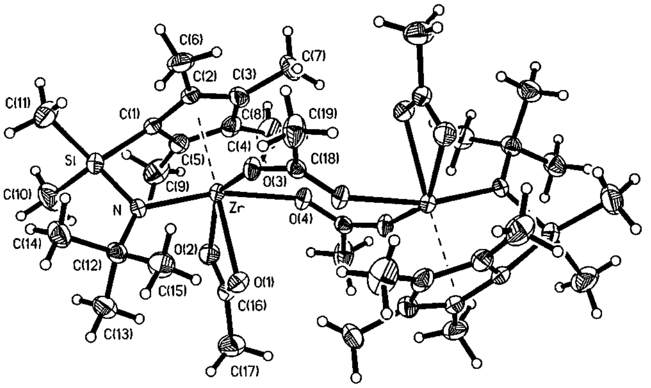


Figure 1. Molecular structure of **2** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. Important interatomic distances (Å) and bond angles (deg): Zr−O(1), 2.293(3); Zr−O(2), 2.224(3); Zr−O(3), 2.137(3); Zr−O(4), 2.211(3); Zr−N, 2.140(4); Zr···Zr′, 5.375; Cp(c)−Zr, 2.213; Cp(c)−Zr−N, 99.6; Cp(c)−Zr−O(1); 161.2; O(2)−Zr−O(3), 146.93(13); O(4)−Zr−N, 161.41(13).

that the amido group may also be susceptible to CO_2 insertion. An initial NMR-scale reaction of **1** with a 20-fold excess of CO_2 in benzene-d_6 led to the formation of a sparingly soluble product, **3**, which crystallized out of solution to leave one predominant proton NMR resonance at δ 0.92. The NMR spectrum of **3**[14] lacks an appropriate resonance for the *tert*-butyl substituent of a silylamido group; the upfield chemical shift of the singlet at δ 0.92 is identical with that observed for the *tert*-butyl group of OCN-*t*-Bu in benzene-d_6. GC/MS/IR analysis of the volatile products obtained from the reactions of **1** with excess CO_2 (60 psi) and $^{13}CO_2$ confirmed the formation of OCN-*t*-Bu (ν_{CO} 2262 cm^{-1}) and O^{13}CN-*t*-Bu ($\nu^{13}{}_{CO}$ 2202 cm^{-1}), respectively.

The identity of **3** as $\{[(\eta^5\text{-}C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ was verified by an X-ray crystallographic analysis.[15] Its molecular structure is also constrained by a crystallographic center of inversion located at the midpoint of the Zr···Zr line. The two Zr centers are linked by a pair of bridging acetate groups and the oxygen atom of the *ansa*-tetramethylcyclopentadienyl silyloxy ligand. The coordination sphere about each Zr center is completed with a single chelated acetate ligand and the appended tetramethylcyclopentadienyl ring. Of the six Zr-bound oxygen donor atoms, five are displayed in a nearly pentagonal arrangement with the sixth one, O(5)′, lying trans to the centroid of the tetramethylcyclopentadienyl ring.[16]

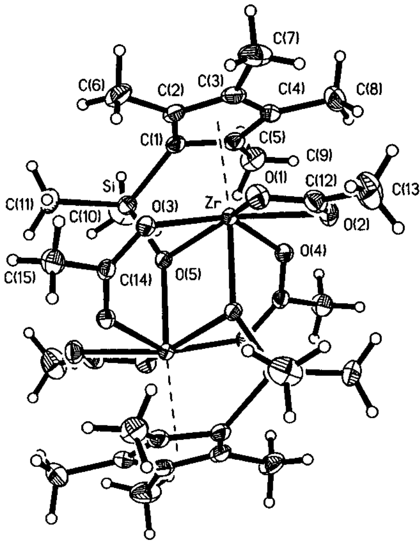
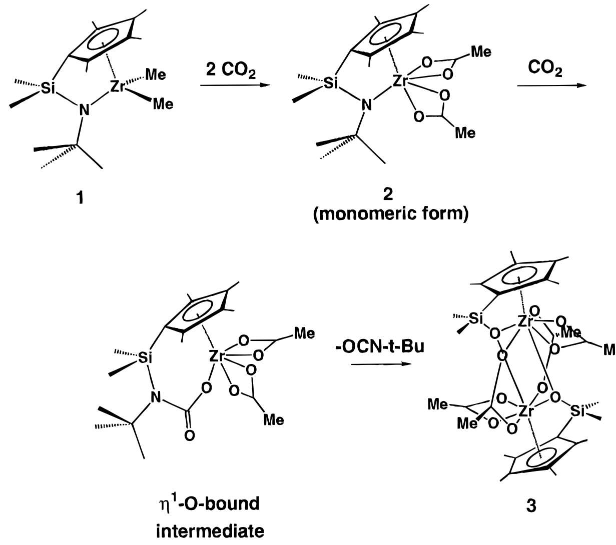


Figure 2. Molecular structure of **3** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. Important interatomic distances (Å) and bond angles (deg): Zr−O(1), 2.289(2); Zr−O(2), 2.268(2); Zr−O(3), 2.2042(14); Zr−O(4), 2.1929(14); Zr−O(5), 2.2570(13); Zr−O(5)′, 2.1260(13); Si−O(5), 1.6462(14); Zr···Zr′, 3.452; Cp(c)−Zr, 2.277; Cp(c)−Zr−O(5), 95.8; Cp(c)−Zr−O(5)′, 171.8.

Scheme 1



A reaction sequence for the formation of **2** and **3** during the carboxylation of **1** is proposed in Scheme 1. Although the crystallographic analysis for **2** confirms a dimeric structure in the solid state, the IR and NMR data for **2** indicate that a monomeric structure with only chelating acetates predominates in solution. Upon dissolution of **2** in toluene, the strong $\nu(OCO)_{asym}$ band for the bridging acetates at 1603 cm^{-1} in Nujol effectively disappears and the relative intensity for the $\nu(OCO)_{asym}$ stretch for the chelating acetates[18] at *ca.* 1535 cm^{-1} is significantly enhanced. The acetate groups

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(13) Kloppenburg, L.; Petersen, J. L., unpublished results.

(14) ^{1}H NMR spectrum of **3** ($CDCl_3$, 270 MHz): δ 2.18, 2.11 (s, O_2CMe), 2.01, 1.84 (s, C_5Me_4), 0.31 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR data for **3** ($CDCl_3$, 67.8 MHz): 187.5 (η^2-$O_2\mathbf{C}Me$), 177.4 (μ-$O_2\mathbf{C}Me$), 131.5, 128.0 (distal and proximal ring carbons of C_5Me_4), 105.5 (bridgehead C of C_5Me_4), 26.4 (μ-$O_2C\mathbf{Me}$), 23.2 (η^2-$O_2C\mathbf{Me}$), 14.7, 10.9 ($C_5\mathbf{Me}_4$), 3.9 ($SiMe_2$). IR (Nujol, cm^{-1}): ν(OCO-bridging) 1577 (s), 1449 (m); ν(OCO-chelating) 1535 (sh), 1476 (m). Anal. Calcd for $C_{15}H_{24}O_5SiZr$ (empirical form): C, 44.63; H, 5.99; N, 0.0. Found: C, 44.61; H, 6.09; N, 0.0.

(15) Crystallographic data for $\mathbf{3{\cdot}C_6D_6}$: triclinic, space group $P\bar{1}$, $a = 9.3277(4)$ Å, $b = 10.0887(5)$ Å, $c = 12.0840(5)$ Å, $\alpha = 73.545(3)°$, $\beta = 72.236(4)°$, $\gamma = 73.818(5)°$, $V = 1015.31(8)$ Å^3, $Z = 1$ (one dimer and one molecule of C_6D_6 per cell). Full-matrix refinement (based on F_o^2, SHELXL-93) of the positional and anisotropic thermal parameters for the 25 non-hydrogen atoms converged with $R1 = 0.0317$ and GOF = 1.054 for all 4436 data with $I \geq 0$. Crystallographic data for **3** (C_6D_6 free): triclinic, space group $P\bar{1}$, $a = 9.3845(5)$ Å, $b = 10.1418(7)$ Å, $c = 10.7199(5)$ Å, $\alpha = 63.580(6)°$, $\beta = 81.993(6)°$, $\gamma = 72.235(5)°$, $V = 870.1(1)$ Å^3, $Z = 1$ (one dimer per cell). Full-matrix refinement (based on F_o^2, SHELXL-93) of the positional and anisotropic thermal parameters for the 22 non-hydrogen atoms converged with $R1 = 0.0325$ and GOF = 1.057 for all 4711 data.

(16) The coordination geometry about each Zr atom in **3** is comparable to the pseudo-pentagonal-bipyramidal ligand arrangement reported by Royo and co-workers[17] for the Ti atom in $(C_5Me_5)Ti(O_2CC_6H_5)_3$.

(17) Gómez-Sal, M. P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147.

of **2** exhibit only one set of ^{1}H and ^{13}C NMR resonances. Subsequent carboxylation of the monomeric form of **2** presumably proceeds with the formation of an η^1-O-bound intermediate, from which OCN-*t*-Bu elimination is aided by formation of the Si−O bond.

Our results demonstrate that the carboxylation of the appended silylamido ligand of **2** provides a simple route for its conversion to the corresponding O functionality. Current efforts are being directed toward the preparation of other *ansa*-monocyclopentadienyl silyloxy group 4 complexes and the evaluation of their reactivity.

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Supporting Information Available: Text giving descriptions of syntheses and X-ray structural analyses of **2** and **3·C$_6$D$_6$** and tables of crystallographic data for **2** and **3·C$_6$D$_6$** (16 pages). Ordering information is given on any current masthead page.

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(18) The reported values[19] of ν(OCO)$_{asym}$ and ν(OCO)$_{sym}$ for the chelating acetate ligand in (C$_5$H$_5$)$_2$ZrCl(η^2-O$_2$CMe) are 1528 and 1477 cm^{-1}, respectively.

(19) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877.