Communications

Chemoselective "On-Site" Functionalization of Group 4 Metal Acetamidinates

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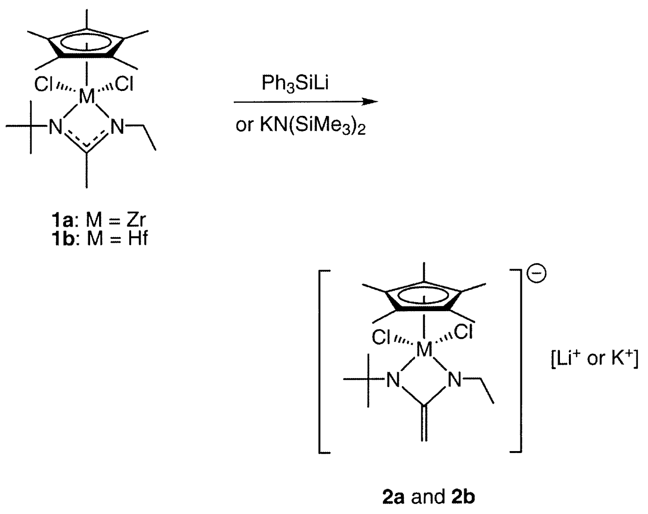
Summary: Deprotonation of group 4 monocyclopentadienyl metal acetamidinates can be achieved in high yield using sterically encumbered bases to provide enolate complexes that can subsequently be reacted with electrophiles to produce several new classes of metal amidinates that are not accessible by conventional routes.

The amidinate ligand fragment, $[N(R^1)C(R^2)N(R^3)]^-$, is a structural component found within a diverse range of mononuclear transition metal and main group metal complexes.[1] Synthetic methods available for the incorporation of this group into the coordination sphere of metals, however, still remain quite limited, and these include (1) classical salt elimination using metal halides and alkali metal amidinates, (2) condensation between metal halides and silyl substituted amidines, and (3) carbodiimide insertion into metal−carbon bonds.[1,2] Recently, we documented that d^0 group 4 monocyclopentadienyl metal amidinates of the general formula $(\eta^5\text{-}C_5R_5)MXY[N(R^1)C(R^2)N(R^3)]$ (**1**: M = Zr, R = H, Me, X = Y = Me, R^2 = Me) are highly active precatalysts for the stereoselective living polymerization of a wide variety of α-olefins and α,ω-nonconjugated dienes upon activation with a borate cocatalyst, such as $[Ph_3C][B(C_6F_5)_4]$.[3] In the pursuit of new derivatives of **1** that would permit the further development of structure/property relationships and that would allow for the heterogenization of this class of Ziegler−Natta precatalyst on solid supports,[4] we required amidinates that could not easily, or ever, be prepared through the conventional methods enumerated above. Herein, we now introduce a new synthetic procedure that circumvents this problem by providing rapid access to a number of new amidinate structural classes through the efficient deprotonation and chemoselective functionalization of an acetamidinate (R^2 = Me in **1**) fragment within a metal complex. Just as the direct deprotonation of η^5-cyclopentadienyl and η^6-arene metal complexes have provided new generations of these ligand types,[5] this new synthetic method may prove to be of general use for extending the scope of amidinate-based metal complexes.

Scheme 1



Ligands with enolizable protons can be functionalized prior to metal complexation through standard deprotonation with a strong base followed by reaction with an electrophile. On the other hand, to the best of our knowledge, no reports have appeared in which an attempt has been made to functionalize a metal-complexed ligand containing enolizable protons through the same process, and this includes metal complexes containing the ubiquitously occurring acetylacetonato (acac) ligand.[6] For the purposes of the present study, we selected complexes **1a** (M = Zr)[7] and **1b** (M = Hf)[8] as initial test subjects for deprotonation which we felt could be achieved using a sterically encumbered, non-nucleophilic base. As Scheme 1 reveals, this base proved to be lithium triphenylsilane, $LiSiPh_3$, which can easily be obtained in crystalline form as its tetrahydrofuran (THF) adduct.[9] More specifically, reaction of **1a** with a

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[1] For reviews, see: (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300. (b) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481.

[2] (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125−8126. (b) Sita, L. R.; Babcock, J. R. *Organometallics* **1998**, *17*, 5228−5230. (c) Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183−4190 and references therein.

[3] (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959. (b) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490−10491. (c) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197−6198.

[4] Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347−1376.

[5] Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: New York, 1982.

[6] For unexpected observations of metal-complexed ligand deprotonations by base, see: (a) Okeya, S.; Kusuyama, Y.; Isobe, K. Nakamura, Y.; Kawaguchi, S. *J. Organomet. Chem.* **1998**, *551*, 117−123. (b) Neculai, A. M.; Roesky, H. W.; Neculai, D.; Magull, J. *Organometallics* **2001**, *20*, 5501−5503.

[7] Keaton, R. J.; Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 21, 5932−5933.

[8] Kissounko, D. A.; Sita, L. R. To be submitted for publication.

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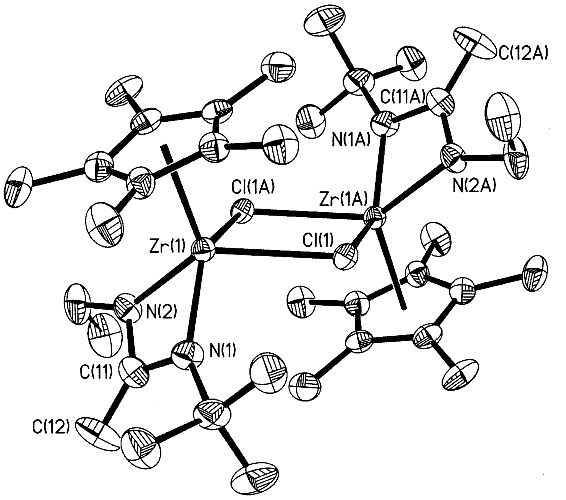
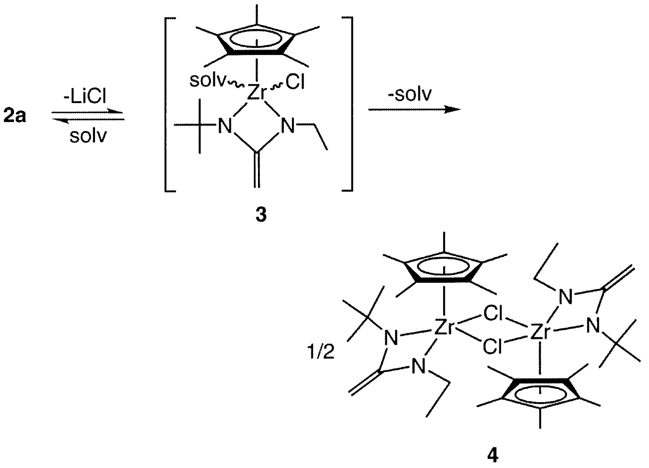


Figure 1. Molecular structure (30% thermal ellipsoids) of **4**. Hydrogen atoms have been removed for the sake of clarity.

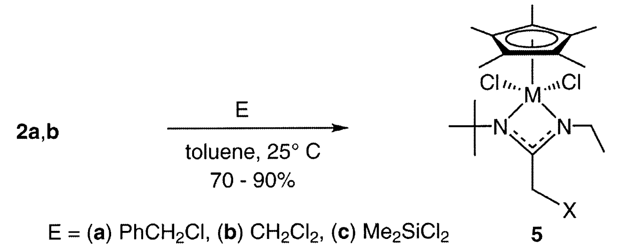
Scheme 2



slight excess of $LiSiPh_3$ in THF at 25 °C yielded, upon removal of the solvent after 2 h, a near-quantitative yield of complex **2a** which can be isolated as a purple powder that is analytically pure on the basis of chemical analysis.[10] Importantly, use of the less hindered base $LiSiMe_2Ph$ led to preferential nucleophilic attack at the metal center, rather than deprotonation, to provide a zirconium silyl complex.[11] Finally, in terms of reaction time and yield of product, deprotonation of the hafnium analogue **1b** to provide **2b** was best achieved using $KN(SiMe_3)_2$ rather than $LiSiPh_3$.[10]

^1H and ^{13}C NMR spectra taken in THF-d_8 support the enolate structure for **2** shown in Scheme 1, in which the deprotonated acetamidinate is now formally serving as a dianionic ligand. Thus, a ^1H NMR (400 MHz, 25 °C) spectrum of **2a** in this solvent displays a set of two resonances at δ 2.91 and 2.89 ppm for the diastereotopic methylene protons of the enolized acetamidinate fragment, and both of these were found to correlate, via a 2D $^{13}C-^1H$ HSQC NMR spectrum, with a ^{13}C NMR resonance at 55.6 ppm ($^1J(^{13}C-^1H) = 157$ Hz).[10] Observation that the $^2J(^1H-^1H)$ coupling constant between

Scheme 3



these protons is smaller than the line width of the resonances is consistent with the ^1H NMR data reported for other enolates.[12]

In aprotic polar coordinating solvents, such as diethyl ether (Et_2O), evidence exists to suggest that **2a** can undergo loss of LiCl to produce neutral, solvent-stabilized species such as **3**, shown in Scheme 2. Indeed, upon attempts to grow crystals of **2a** from a Et_2O/pentane solvent mixture, continual precipitation of LiCl was observed to occur and subsequent single-crystal X-ray analysis of the dark orange crystalline material that was obtained revealed it to be the dinuclear species **4** shown in Figure 1, which is presumed to arise from dimerization of **3** upon displacement of the weakly coordinated solvent molecule (see Scheme 2).[13] In **4**, the methylene carbon of the enolized amidinate, C12, is trigonal coplanar, as revealed by the sum of the bond angles about this atom, $\sum\theta_{C12}$, which is 360°, and the C11−C12 bond length of 1.332(8) Å supports full double-bond character for the interaction between these two carbon centers.

Regarding the reactivity of **2a** and **2b** toward electrophiles, a variety of transformations have been carried out which successfully place a substituent at the enolized carbon of the acetamidinate ligand according to Scheme 3.[10] The products of these reactions that are of most interest to us, however, are those that provide new types of amidinate ligands that are not accessible by conventional synthetic procedures, such as compounds

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(9) Woo, H. G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198−2205.

(10) Detailed information is provided in the Supporting Information.

(11) Zhang, Y.; Sita, L. R. Unpublished results.

(12) See for instance: Abiko, A. Inoue, T.; Masamune, S. *J. Am. Chem. Soc.* **2002**, *124*, 10759−10764.

(13) Crystal data for **4**: $C_{36}H_{62}Cl_2N_4Zr_2$, $M_r = 804.24$, monoclinic, *C2/c*, $a = 12.6867(13)$ Å, $b = 17.2867(18)$ Å, $c = 18.6795(19)$ Å, $\beta = 108.344(2)°$, $V = 3888.4(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.374$ mg/m^3, $\mu = 0.702$ mm^{-1}, $F(000) = 1680$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 293(2)$ K, $2\theta_{max} = 25°$, 9423 independent reflections collected, 6392 reflections in refinement, final *R* indices ($I > 2\sigma(I)$) R1 = 0.0763 and wR2 = 0.1795. Crystal data for **5a**·(tol): $C_{32}H_{46}Cl_2N_2Hf$, $M_r = 708.10$, monoclinic, $P2_1/c$, $a = 14.9125(4)$ Å, $b = 8.1333(2)$ Å, $c = 26.7677(8)$ Å, $\beta = 104.6570(10)°$, $V = 3140.94(15)$ Å^3, $Z = 4$, $D_{calcd} = 1.497$ mg/m^3, $\mu = 3.514$ mm^{-1}, $F(000) = 1432$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 293(2)$ K, $2\theta_{max} = 27.5°$, 7226 independent reflections collected, 5555 reflections in refinement, final R indices ($I > 2\sigma(I)$) R1 = 0.0250 and wR2 = 0.0535. Crystal data for **5b**: $C_{19}H_{33}Cl_3N_2Hf$, $M_r = 574.31$, orthorhombic, *Pbca*, $a = 13.8548(5)$ Å, $b = 15.9428(6)$ Å, $c = 20.4171(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4509.8(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.692$ mg/m^3, $\mu = 4.987$ mm^{-1}, $F(000) = 2272$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 193(2)$ K, $2\theta_{max} = 27.5°$, 5181 independent reflections collected, 4523 reflections in refinement, final R indices ($I > 2\sigma(I)$) R1 = 0.0200 and wR2 = 0.0459. Crystal data for **5c**: $C_{20}H_{37}Cl_3N_2HfSi$, $M = 618.45$, monoclinic, $P2_1/n$, $a = 11.7097(10)$ Å, $b = 14.6441(12)$ Å, $c = 15.1842(13)$ Å, $\beta = 101.8770(10)°$, $V = 2548.0(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.612$ mg/m^3, $\mu = 4.464$ mm^{-1}, $F(000) = 1232$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 293(2)$ K, $2\theta_{max} = 27.5°$, 39 099 independent reflections collected, 5123 reflections in refinement, final R indices ($I > 2\sigma(I)$) R1 = 0.0220, wR2 = 0.0536. Crystal data for **6**·OEt_2: $C_{44}H_{51}BClF_{15}N_2O_2Zr$, $M_r = 1062.35$, monoclinic, $P2_1/n$, $a = 12.7912(4)$ Å, $b = 16.2876(5)$ Å, $c = 22.7788(6)$ Å, $\beta = 92.3540(10)°$, $V = 4741.7(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.488$ mg/m^3, $\mu = 0.385$ mm^{-1}, $F(000) = 2168$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 293(2)$ K, $2\theta_{max} = 30.0°$, 13 661 independent reflections collected, 10 772 reflections in refinement, final R indices ($I > 2\sigma(I)$) R1 = 0.0358 and wR2 = 0.0959.

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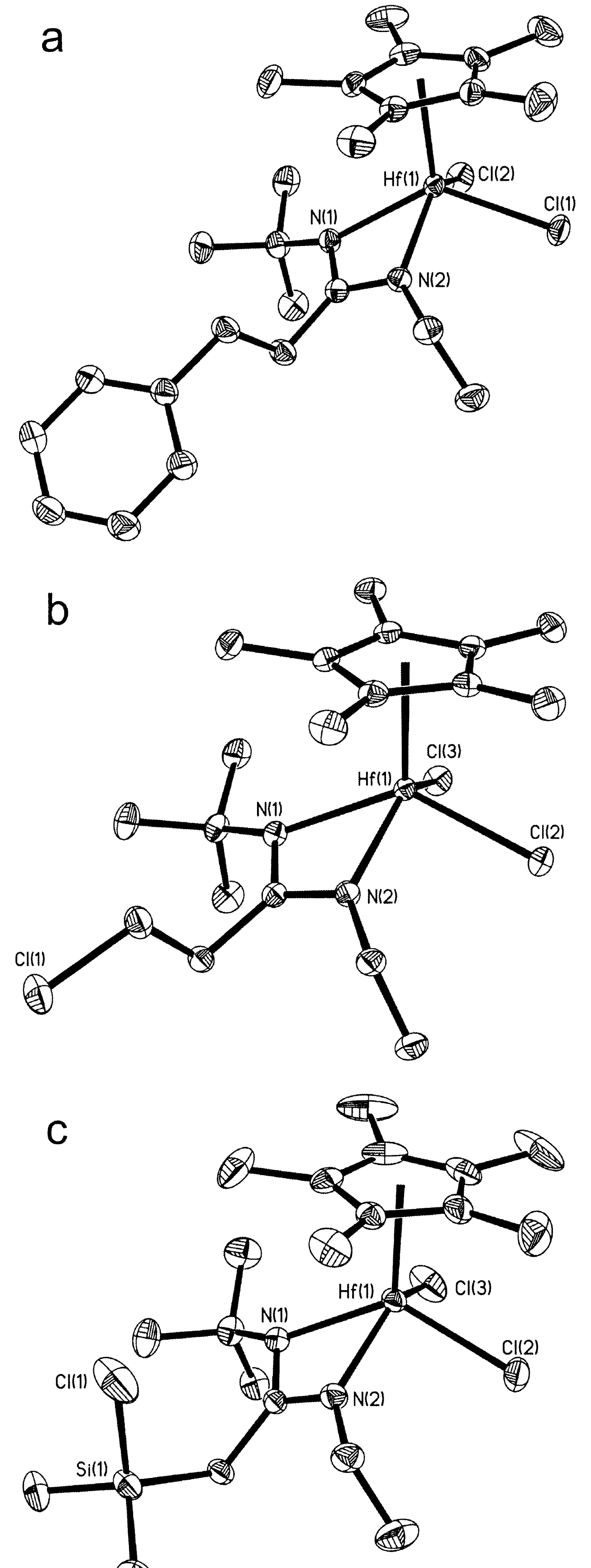

Figure 2. Molecular structure (30% thermal ellipsoids) of (a) **5a**, (b) **5b**, and (c) **5c**. Hydrogen atoms have been removed for the sake of clarity.

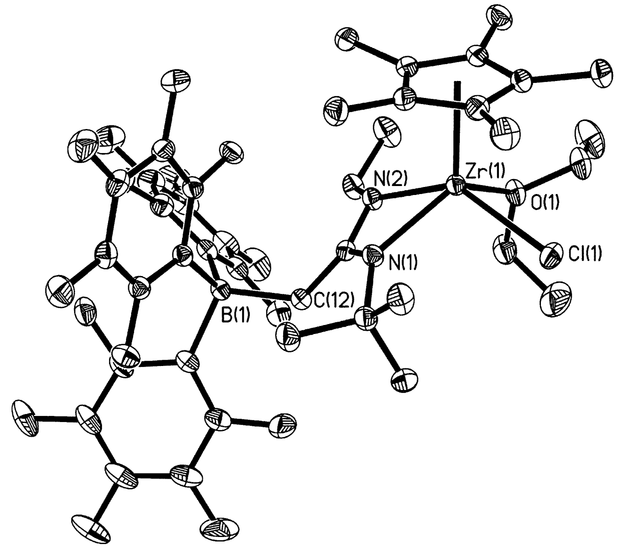

Figure 3. Molecular structure (30% thermal ellipsoids) of **6**. Hydrogen atoms have been removed for the sake of clarity.

5a−**c** (M = Hf), the molecular structures of which are shown in Figure 2.[10,13] While the chlorodimethylsilyl group of **5c** should now provide a convenient handle by which to anchor this species to solid inorganic oxide supports, we have also carried out the direct functionalization of chloromethylated polystyrene beads (1.3 meq/g) with **2a** in which 70% of the chloromethyl sites were found to have reacted.

As a final initial survey of reactivity, we were interested in determining whether the enolates **2a** and **2b** could be “remotely activated” through reaction with a group 13 Lewis acid to produce charge-neutral zwitterionic complexes that could then function as Ziegler−Natta polymerization initiators.[14] To our great satisfaction, treatment of a Et$_2$O solution of **2a** with 1 equiv of B(C$_6$F$_5$)$_3$ provided, in 66% yield, the Et$_2$O-coordinated zwitterionic complex **6** upon crystallization from solution at −30 °C. Figure 3 displays the molecular structure of **6** as obtained from crystallographic analysis, and it is interesting to note that the structural environment around the zirconium atom is very similar to that observed for the solid-state structure of an Et$_2$O complex of a cationic zirconium acetamidinate that is a known active initiator for olefin polymerization.[10,13,15]

In conclusion, we have demonstrated that deprotonation of group 4 metal acetamidinates can be achieved in high yield to provide enolate complexes that can subsequently be used to produce several new classes of metal amidinates that are not accessible by conventional routes. Further studies of the scope and utility of this new procedure are currently in progress.

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Supporting Information Available: Text and tables giving details of the synthesis and characterization of **2**−**6**, including crystallographic analysis of **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansee, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082−3084.

(15) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909−12910.