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Regarding the Stability of d^0 Monocyclopentadienyl Zirconium Acetamidinate Complexes Bearing Alkyl Substituents with β-Hydrogens

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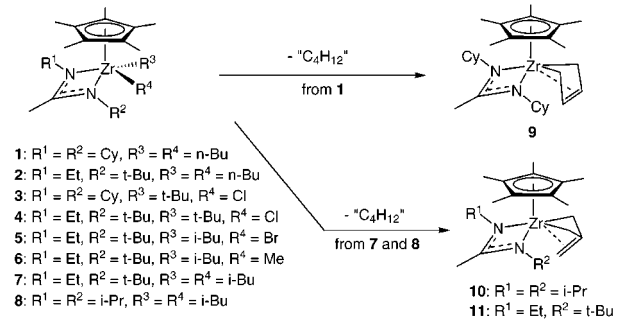
β-Hydrogen eliminations/abstractions within neutral and cationic zirconium d^0 dialkyl and alkyl complexes, respectively, play fundamental roles in a number of important chemical transformations that include the: (1) Ziegler−Natta polymerization of α-olefins,[1] (2) hydrozirconation of terminal and internal olefins,[2] and (3) metal-mediated cyclization of α,ω-nonconjugated enynes and diynes.[3] Accordingly, an elucidation of the steric and electronic factors that can be used to control β-hydrogen eliminations/abstractions is of paramount importance for the continued evolution of these, and possibly yet-to-be-discovered, synthetic methods.[4] Unfortunately, due to the generally low thermal stability of zirconium complexes bearing alkyl substituents with β-hydrogens, such information has been difficult and slow to come by. Herein, we now report the series of titled compounds, **1**−**8**, that are remarkably resistant to β-hydrogen eliminations/abstractions, including the *tert*-butyl derivatives **3** and **4**, the former of which is stable in solution to temperatures of at least 100 °C. We further document two striking examples of an apparent preference for alternative hydrogen atom abstractions in which complexes **1** and **7**/**8** that bear isomeric dibutyl substituents are transformed at elevated temperatures to complexes **9** and **10**/**11** that contain the isomeric butadiene and trimethylenemethane (TMM) C_4 fragments, respectively, according to Scheme 1.

Scheme 1



Compounds **1**−**8** were prepared by conventional methods using the dichlorides **12**−**14** ($R^3 = R^4 = Cl$ in **1**, **2**, and **8**, respectively) and either an alkyllithium or an alkyl Grignard reagent as the alkylating reagent.[5] In every instance, except for **2** and **8**, the crystallinity of the product allowed for analytically pure material to be obtained through recrystallization at −30 °C. This same crystallinity also allowed each compound to be structurally characterized by single-crystal X-ray analysis, and Figure 1 displays a subset of these structures that serves to highlight two of the different alkyl group classes (i.e., *n*-butyl, *iso*-butyl, and *tert*- butyl).[5] In all of these structures, no α-, β-, or γ- hydrogen agostic

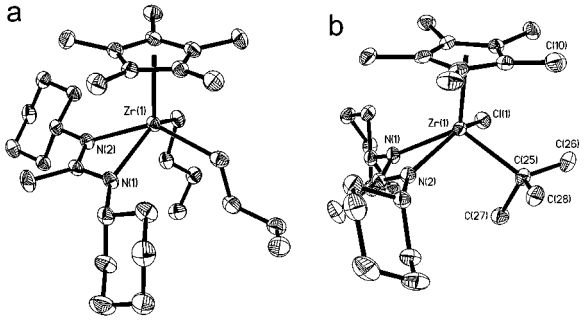


Figure 1. Molecular structures (30% thermal ellipsoids) of (a) **1** and (b) **3**. Hydrogen atoms have been removed for the sake of clarity.

interactions of the butyl substituents with the zirconium center are observed in the solid state.[6] For compounds **3** and **4**, strong nonbonded steric interactions between the ligands are manifested as a substantial tilting of the *tert*-butyl group away from the η^5-C_5Me_5 ring as indicated by the reduced Zr(1)−C(25)−C(27) bond angle of 92.6(2)° in **3** and a corresponding value of 96.73(15)° for **4**.[5] Not surprisingly, variable temperature ^{1}H NMR (500 MHz, toluene-d_8) studies also revealed the existence of a substantial barrier to rotation about the zirconium−carbon bond of the *tert*-butyl group as evidenced by three distinct methyl resonances being observed for this substituent in the slow exchange limit spectra recorded at 213 K (T_{coal} = 298 and 238 K for **3** and **4**, respectively).[5]

All the compounds **1**−**8** share the interesting property of being moderately to extremely robust in solution, thereby establishing the η^5-C_5Me_5/acetamidinate ligand set as one of the few geometrically unconstrained environments that have been found to impart such stability to alkyl zirconium complexes bearing β-hydrogens.[4a,b,j] Of particular interest are the *tert*-butyl complexes, **3** and **4**, that do not isomerize at elevated temperatures in solution to the corresponding *iso*-butyl derivatives.[4k,7] Indeed, compound **3** resists both isomerization and decomposition up to temperatures of 100 °C in toluene. Finally, C_1-symmetric **3** and **4**, and the less hindered *iso*-butyl bromide derivative, **5** [$t_{1/2}$(dec) = 365 min at 50 °C], were all found to be configurationally stable at zirconium on the NMR time frame even at elevated temperatures. Regarding the origin of the unexpected thermal stability of **3**−**5**, it is known that steric congestion within the ligand sphere of a complex can retard β-hydrogen abstraction/elimination of alkyl substituents.[8,9] It is also known that in zirconocenes, the order of stability is: Cp_2-ZrRCl > Cp_2ZrRR or Cp_2ZrRH (Cp = η^5-C_5H_5).[7b] We were surprised to find, however, that even the di(*n*-butyl) compounds **1** and **2** are moderately stable in solution, with similar half-lives of ~48 h at 30 °C. Further, the mixed methyl, *iso*-butyl complex **6** (prepared from **5** using methyllithium) and the di(*iso*-butyl) derivative **7** are even more robust in solution with the latter having a $t_{1/2}$(dec) value of 107 min at 50 °C. This increase in stability of

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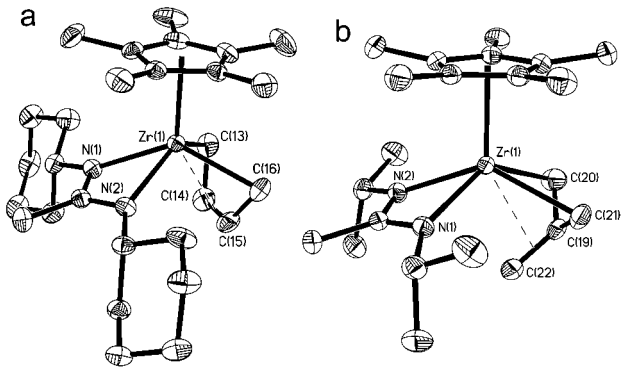
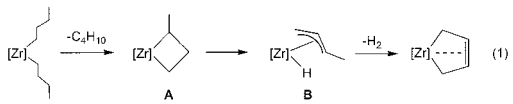


Figure 2. Molecular structures (30% thermal ellipsoids) of (a) **9** and (b) **10**. Hydrogen atoms have been removed for the sake of clarity.

the *iso*-butyl over that of the *n*-butyl compounds may be due, along with steric considerations, to the known trend in β-hydrogen stability of alkyl substituents where β-methine > β-methylene > β-methyl.[4c]

With the di(*n*-butyl) compounds **1** and **2** in hand, we were interested in determining whether they could shed any additional light on the still unsettled mechanism by which Negishi's in situ-formed $Cp_2Zr(n\text{-}Bu)_2$ reagent produces Zr(II) products that can engage in cyclization reactions.[3,10] Thus, the first-order decomposition of **1** was followed by ^{1}H NMR (toluene-d_8) in a flame-sealed tube at 50 °C with the quite unexpected result that it was observed to cleanly convert to the zirconacyclopentene **9** as the final product. Figure 2a presents the molecular structure of **9** as derived from a single-crystal X-ray analysis, and in this structure, the observed geometrical parameters are indicative that it is best represented as being a Zr(IV) metallacyclopentene of the σ^2, π-type.[5,11] Regarding a possible mechanism for its formation, we note that the addition of reagents that can potentially trap Zr(II) intermediates, such as alkynes, dienes, or PMe_3,[3,12] had no apparent effect on either the rate or the nature of the end product of this process. We have further never observed the production of free 1-butene under any conditions. On the other hand, growth of a singlet centered at 4.5 ppm was observed in the NMR spectrum that can be confidently assigned to the resonance for dihydrogen.[9b,c] On the basis of these facts, we suggest that formation of **9** proceeds through a mechanism that is based largely on that presented by Harrod and co-workers[10b] for the decomposition of $Cp_2Zr(n\text{-}Bu)_2$. Thus, as depicted in eq 1



a zirconacyclobutane intermediate (**A**) is first formed through γ-hydrogen abstraction and this subsequently undergoes deinsertion to produce an allyl hydride (**B**) that may then undergo direct hydrogen abstraction by the hydride to generate dihydrogen and **9**.[13] Intriguingly, during attempts to purify the di(*iso*-butyl) derivative **8** through crystallization, its solution in toluene became deep red in color, and X-ray analysis of the red crystalline material that was obtained upon cooling to −30 °C revealed it to be the TMM derivative **10** (see Figure 2b). Once more, the observed bond lengths of **10** are consistent with a σ^2, π-type of bonding interaction of the TMM moiety with the metal center.[14] In solution, however, a ^{1}H NMR spectrum revealed that all three CH_2 centers of the TMM ligand are equivalent at 25 °C, thereby presenting evidence for a facile dynamic process that serves to "rotate" the TMM fragment about the Zr(1)−C(19) "bond". With the identity of **10** established, a reinvestigation of the thermolysis of **7** revealed that it too produced the corresponding TMM derivative **11** that possesses a TMM-bonding pattern similar to that of **10** as revealed by single-crystal X-ray analysis.[5] Mechanistically, however, the pathway for decomposition of **7**/**8** appears to be quite different than that for **1** in that, while being first-order under identical conditions, the production of dihydrogen is never observed, generating instead only isobutane and a relatively small amount of isobutylene. Further, in both cases, **10** and **11** are not the final products of thermolysis, but rather, after reaching a maximum concentration, they are subsequently consumed with time through an as-of-yet unidentified process. Studies to further clarify and confirm the nature of these decomposition pathways are currently in progress.

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Supporting Information Available: ^{1}H NMR spectra of **1**−**10** and details of the crystallographic analyses of **1**, **3**−**7**, **9**−**11**. This material is free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Brintzinger, H. H.; Fischer, D.; Müllhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Gladysz, J. A., Ed. *Chem. Rev.* **2000**, *100*, special issue devoted to Frontiers in Metal-Catalyzed Polymerization.
(2) (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc*. **1974**, *96*, 8115−8116 (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl*. **1976**, *15*, 333−340.
(3) (a) Negishi, E.; Takahashi, T. *Acc. Chem. Res*. **1994**, *27*, 124−130. (b) Nitschke, J. R.; Zürcher, S.; Tilley, T. D. *J. Am. Chem. Soc*. **2000**, *122*, 10345−10352 and references therein.
(4) (a) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16−20. (b) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc*. **1989**, *111*, 9113−9114. (c) Negishi, E.; Nguyen, T.; Maye, J. P.; Choueiri, D.; Suzuki, N.; Takahashi, T. *Chem. Lett*. **1992**, 2367−2370. (d) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655−3665. (e) Amor, F.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4765−4767. (f) Paolucci, G.; Pojana, G.; Zanon, J.; Lucchini, V.; Avtomonov, E. *Organometallics* **1997**, *16*, 5312−5320. (g) Fernandez, F. J.; Gomez-Sal, P.; Manzanero, A.; Royo, P.; Jacobsen, H.; Berke, H. *Organometallics* **1997**, *16*, 1553−1561. (h) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649−3670. (i) Mehrkhodavandi, P.; Bonitatebus, P. J.; Schrock, R. R. *J. Am. Chem. Soc*. **2000**, *122*, 7841−7842. (j) Wendt, O. F.; Bercaw, J. E. *Organometallics* **2001**, *20*, 3891−3895. (k) Pool, J. A.; Bradley, C. A.; Chirik, P. J. *Organometallics* **2002**, *21*, 1271−1277.
(5) Detailed information is provided in the Supporting Information.
(6) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem*. **1988**, *36*, 1−124.
(7) (a) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825−826. (b) Chirik, P. J.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc*. **1999**, *121*, 10308−10317.
(8) Kruse, W. *J. Organomet. Chem*. **1972**, *42*, C39−C42.
(9) (a) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K. Y.; O'Donoghue, M. B.; Davis, W. M.; Reiff, W. M. *J. Am. Chem. Soc*. **1997**, *119*, 11876−11893. (b) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Dobbs, D. A.; Shih, K. Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195−5209. (c) Seidel, S. W.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 1058−1068.
(10) (a) Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun*. **1990**, 1254−1255. (b) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 1452−1464.
(11) Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem*. **1985**, *24*, 1−39 and references therein.
(12) Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber*. **1989**, *122*, 1035−1042.
(13) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem*. **1981**, *218*, 383−393.
(14) Bazan, G. C.; Rodriguez, G.; Cleary, B. P. *J. Am. Chem. Soc*. **1994**, *116*, 2177−2178.

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