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Facile Formation of a μ-[σ^2,η^3-C_4H_5], μ-Hydrido Dizirconium Complex through Multiple Intra- and Intermolecular C−H Bond Activations of an Isobutyl Group

Richard J. Keaton and Lawrence R. Sita*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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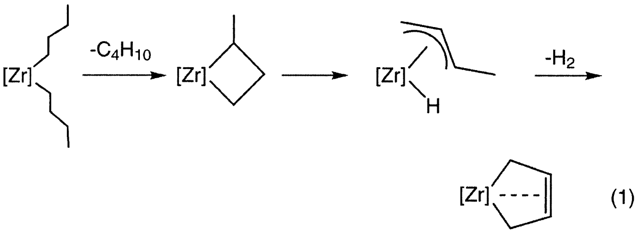
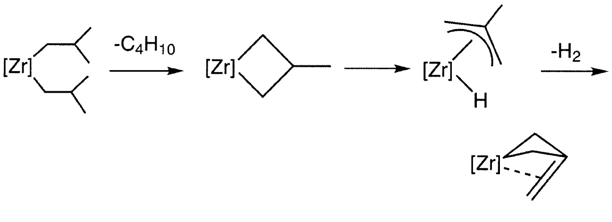
Summary: Thermolysis of (η^5-C_5Me_5)Zr(i-Bu)$_2$[N(t-Bu)C(Me)N(Et)] (**3**) *at 50 °C in benzene ultimately produces, in high yield, the* μ*-hydrido dizirconium complex* **6** *that bears a novel* μ-[σ^2,η^3-C_4H_5] *fragment arising from multiple intra- and intermolecular C−H bond activations of an isobutyl group.*

It is well known that group 4 metal complexes bearing alkyl substituents with β-hydrogens have generally poor thermal stability that leads to their decomposition in solution at low, to moderately low, temperatures.[1,2] Surprisingly, though, few products of these decompositions have ever been structurally characterized, and as a result, there remains much uncertainty and speculation regarding the nature of the decomposition pathways that are involved. In this regard, the thermal decomposition of $Cp_2Zr(n\text{-}Bu)_2$ (Cp = η^5-C_5H_5) has, by far, received the most attention, as the solution-characterized Zr(II) product, Cp_2Zr(η^2-1-butene), can engage in a number of synthetically useful cyclization reactions.[3] Even in this case, however, two competing mechanisms have been proposed to account for formation of this species: one involving an initial β-hydrogen abstraction process,[2a,b] and one involving an initial γ-hydrogen abstraction.[2c] Recently, we reported that the moderately stable di(n-butyl) complex Cp*Zr(n-Bu)$_2$[N(Cy)C(Me)N(Cy)] (Cp* = η^5-C_5Me_5) (**1**), which can be isolated in pure form, quantitatively decomposes in solution at 50 °C to produce the σ^2,π-butadiene derivative **2** as shown in Scheme 1.[4] Observation of concomitant dihydrogen production led us to propose the mechanism provided by eq 1 to account for formation



(1)

of this unexpected product. Importantly, the first two steps shown, initial γ-hydrogen abstraction followed by deinsertion to produce a zirconium allyl hydride intermediate, were adopted from the mechanism proposed by Harrod and co-workers[2c] for the decomposition of $Cp_2Zr(n\text{-}Bu)_2$. The final step, hydrogen atom abstraction from an η^3-allyl ligand to form a σ^2,π-butadiene complex, also has precedent.[5] Related to these observations, in the same report, we further documented that the analogous di(isobutyl) complex Cp*Zr(i-Bu)$_2$[N(t-Bu)C(Me)N(Et)] (**3**) produced the σ^2,π-trimethylenemethane (TMM) derivative **4** upon thermolysis in benzene at 50 °C according to Scheme 1.[4] Given the isomeric relationship between the σ^2,π-butadiene and σ^2,π-trimethylenemethane fragments of **2** and **4**, respectively, and the prior observation of formation of a zirconium TMM complex through hydrogen atom abstraction of an η^3-allyl precursor,[6] our first assumption was that **4** was being produced from **3** through the path shown by eq 2,



(2)

which is mechanistically quite similar to the **1** → **2** conversion. Upon further investigation, however, we were able to unequivocally rule out the formation of dihydrogen as a coproduct, thereby, eliminating eq 2 as

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[1] (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* **1999**, *18*, 3649−3470. (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.

[2] (a) Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254−1255. (b) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035−1042. (c) Diomaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 1452−1464.

[3] For a review, see: Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124−130.

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

[5] Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383−393.

[6] Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343−352.

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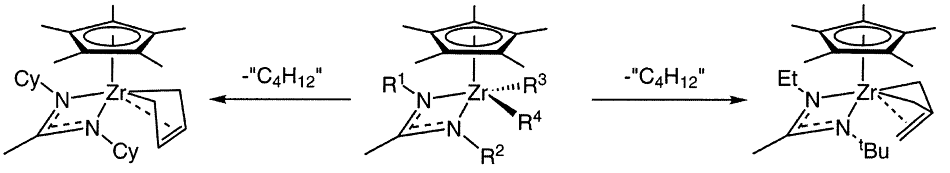
Scheme 1



2

1: R^1 = R^2 = Cy, R^3 = R^4 = ^{n}Bu
3: R^1 = Et, R^2 = ^{t}Bu, R^3 = R^4 = ^{i}Bu

4

a possible route to **4**. These studies further revealed that, unlike **2**, compound **4** is not the final product of thermolysis of **3**, but rather, after reaching a maximum concentration, it is consumed upon further heating. The ultimate product(s) of this extended thermolysis of **3**, however, remained cloaked in mystery due to the absence of any structurally distinguishing ^{1}H NMR resonances that could be observed after the disappearance of both **3** and **4** in solution. Herein, we now report the results of a continued investigation of the thermolysis of **3** in which it is revealed that both intra- and intermolecular C−H bond activations contribute to dramatically convert an initial isobutyl (C$_4$H$_9$) group of **3** to a novel μ-[σ^2,η^3-C$_4$H$_5$] fragment that resides within a dinuclear complex. This observation serves to highlight how complex the decomposition of early transition metal alkyl compounds can be, and it raises the suggestion that intermolecular C−H activations may be more common in these decomposition pathways than presently thought.

Thermolysis of **3** in benzene-d_6 at 50 °C was observed to proceed in a first-order fashion as determined by following the disappearance of **3** over time by ^{1}H NMR spectroscopy performed in a flame-sealed tube. From an Eyring analysis conducted over the temperature range 30−70 °C (five points), the following activation parameters were obtained: $\Delta H^{\ddagger} = 20.8(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.2(3)$ eu.[7] A negative entropic term is consistent with an intramolecular α-, β-, or γ-hydrogen abstraction being the rate-determining process; however, we are unable to discern which of these processes is operative at the present time. With respect to formation of the TMM complex **4**, careful inspection of the sequence of timed ^{1}H NMR spectra taken at a given temperature revealed that no dihydrogen was formed as the resonances of **4** grew in along with those for isobutane, the other expected coproduct for a hydrogen atom abstraction. We also observed another isobutyl-containing product that qualitatively formed at the same rate of **4** as evidenced by the growth of a distinctive high-field resonance for one of a pair of diastereotopic methylene protons on the carbon of an isobutyl fragment bonded to zirconium [cf. δ −0.29 (dd, ^2J 13.3 Hz, ^3J 4.9 Hz)]. Unfortunately, all attempts to isolate this compound have so far failed. Upon extended thermolysis, however, it was observed that the resonances for both **4** and this unknown compound, **5**, qualitatively disappeared at the same rate after having reached a maximum concentration. In their place, a set of new resonances appeared that were consistent with a single new product, **6**, being formed, and indeed, after the resonances for **3**−**5** had finally disappeared completely, **6** essentially became the sole species in solution.

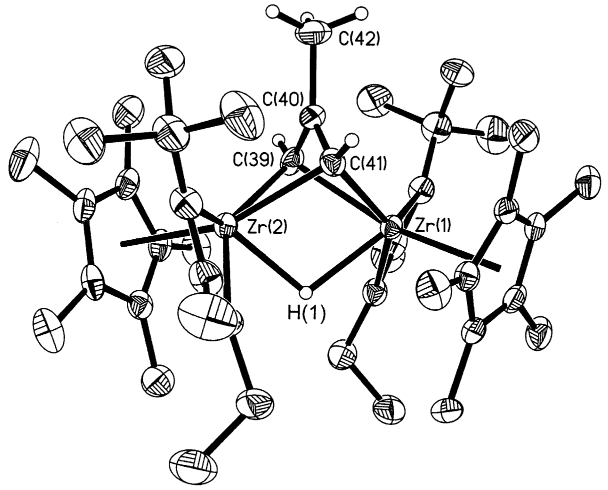


Figure 1. Molecular structure (30% thermal ellipsoids) of compound **6**. Hydrogen atoms, except those for the crystallographically located bridging hydride and the μ-[σ^2,η^3-C$_4$H$_5$] fragment, have been removed for the sake of clarity.

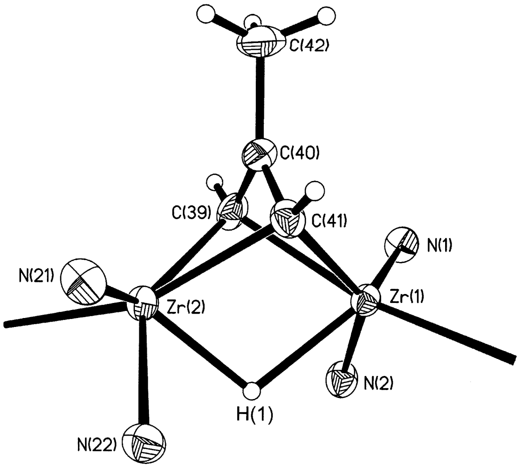


Figure 2. Partial molecular structure (30% thermal ellipsoids) of **6** showing the dizirconium core. Selected distances (Å) and angles (deg): Zr(1)−H(1) 2.04(4), Zr(1)−N(1) 2.299(3), Zr(1)−N(2) 2.256(3), Zr(1)−C(39) 2.279(4), Zr(1)−C(41) 2.310(4), Zr(1)−C(40) 2.557(4), Zr(2)−H(1) 1.99(4), Zr(2)−N(21) 2.326(3), Zr(2)−N(22) 2.260(3), Zr(2)−C(39) 2.309(4), Zr(2)−C(41) 2.293(4), Zr(1)−Zr(2) 3.2096(5), Zr(2)−C(40) 2.558(4), C(39)−C(40) 1.398(6), C(40)−C(41) 1.408(6), C(40)−C(42) 1.532(6), C(39)−C(40)−C(41) 109.4(4), C(39)−C(40)−C(42) 125.1(4), C(41)−C(40)−C(42) 125.6(4).

In an attempt to isolate both **5** and **6**, the thermolysis of **3** was conducted on a preparative scale at 50 °C using 250 mg of starting material in 10 mL of benzene. After

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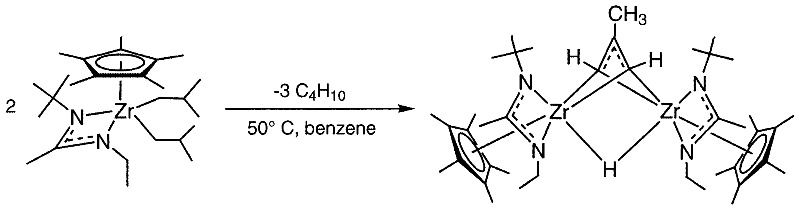
(7) Detailed information is provided in the Supporting Information.

Scheme 2



3 **6**

10 h, a deep red solution was obtained that was cooled to −30 °C within a glovebox, and after 3 days, 100 mg of a brick red crystalline material was obtained. After recrystallization from pentane, single-crystal X-ray analysis revealed the species to be the novel dinuclear species, [μ-(σ^2,η^3-C_4H_5)](μ-H)[Cp*Zr[N(t-Bu)C(Me)N-(Et)]]$_2$ (**6**).[7−9] Figures 1 and 2 display the molecular structure of **6** as obtained from this analysis along with selected distances and angles. Of immediate interest is the nature of the bridging molecular moieties in **6**. To begin, the bridging hydride atom was crystallographically located with Zr(1)−H(1) and Zr(2)−H(1) bond distances of 2.04(4) and 1.99(4) Å, respectively. Further support for this entity was found in the ^{1}H NMR spectrum that revealed a singlet at 2.42 ppm that integrates for one hydrogen.[8] In contrast to the hydride, observation of the bridging C_4H_5 fragment in **6** was much more of a surprise given that it must be derived from a C_4H_9 isobutyl group through four hydrogen atom abstractions. Once more, the ^{1}H NMR spectrum of **6** provides additional evidence for this bridging C_4H_5 group with the occurrence of singlets at 7.20 and 1.76 ppm that integrate for two (2 CH) and three (CH_3) hydrogens, respectively. A ^{13}C−^{1}H HSQC (500 MHz) NMR spectrum revealed that the former of these carbon centers (^{13}C δ 181.7 ppm) has an associated $^1J(^{13}C-^1H)$ coupling constant of 147 Hz, signifying that it has substantial sp^2 character. This same spectrum provided a ^{13}C NMR resonance at 140 ppm that has no attached protons and is therefore assigned to the central carbon of the bridging C_4H_5 group. The zirconium−carbon bond distances for this bridging C_4H_5 fragment fall within the range 2.279(4)−2.310(4) Å, and for a given zirconium atom, there is only a small difference in the two values for the bond distances to C(39) and C(41) [cf., [(C(39)−C(40)) − (C(41)−C(40))] = −0.031 Å for Zr(1) and 0.016 Å for Zr(2)]. Interestingly, all of these zirconium−carbon bonds are significantly shorter than those observed for bonding to terminal carbon atoms in η^3-allyl zirconium complexes [cf., the Zr−C$_t$ bond distances of 2.443(7) Å within the η^3-allyl fragment of CpZr(η^3-allyl)(η^4-butadiene)[10]]. In contrast, the distance between each of the metal centers and C(40) is significantly longer at 2.557(4) for Zr(1) and 2.558(4) Å for Zr(2), and both of these values are elongated relative to the Zr−C$_c$ bond distance of 2.446(8) Å within the η^3-allyl fragment of CpZr(η^3-allyl)(η^4-butadiene).[10] Within the C_4H_5 fragment of **6** itself, the carbon−carbon bond distances are indicative of substantial partial double bond character between C(39) and C(40) and between C(40) and C(41) [cf., 1.398(6) and 1.408(6) Å, respectively, vs 1.532(6) Å for C(40)−C(42)]. On the other hand, the C(39)−C(40)−C(41) bond angle of 109.4(4)° is considerably more acute than that expected for a trigonal coplanar carbon atom. The reduction in this bond angle, however, is most likely a result of structural constraints, and the sum of all angles about C(40), $\sum\theta_{C(40)} = 360°$, indicates that this carbon atom is indeed not pyramidalized to any extent. Collectively then, the structural features presented by the molecular structure of **6** suggest that the bridging organic group is best represented as being a σ^2,η^3-C_4H_5 fragment, which in terms of formal charge and electron donation is a −3, 8 electron donor. This formal charge designation then sets a Zr(IV) oxidation state for each of the zirconium centers.[11]

The mechanisms by which the TMM derivative **3**, and ultimately, the dizirconium complex **6**, are formed await further clarification through the synthesis of selectively deuterated derivatives of **1** and the isolation and full characterization of the intermediate **5**. Clearly, the **3** → **6** conversion, which is shown as a balanced equation in Scheme 2, must involve both intra- and intermolecular C−H bond activations of an isobutyl group that proceed with high efficiency (cf., yield of **6**: 90% by ^{1}H NMR, 40% isolated) to radically change the nature of this original alkyl substituent. It is more than likely that the present observations are not unique, however, and that such complex decomposition paths may prove to be the norm for early transition metal alkyl complexes. With the discovery that the Cp*/acetamidinate ligand set lends considerable stability to zirconium dialkyl complexes,[4] we are now poised to undertake systematic investigations that may serve to clarify further the range of available decomposition paths.

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Supporting Information Available: Details of the Eyring analysis for decomposition of **3** and the crystallographic analysis of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) For **6**: ^{1}H NMR (400 MHz, benzene-d_6) δ 1.18 (t, 6 H, J = 7.2 Hz), 1.35 (br s, 18 H), 1.76 (s, 3 H), 1.98 (s, 6 H), 2.03 (s, 30 H), 2.42 (s, 1 H), 3.48 (dq, 2 H, J_{AB} = 13.7, Hz, J_{AC} = 7.2 Hz), 3.15 (dq, 2H, J_{AB} = 13.7, Hz, J_{AC} = 7.2 Hz), 7.20 (s, 2 H). Anal. Calcd. for $C_{40}H_{70}N_4Zr_2$: C, 60.86; H, 8.94; N, 7.10. Found: C, 60.67; H, 8.77; N, 7.00.

(9) Crystal data for **6**: $C_{45}H_{82}N_4Zr_2$, M = 861.59, monoclinic, $P2_1/c$, a = 13.9080(4) Å, b = 16.5816(5) Å, c = 20.6416(6) Å, β= 102.6930(10)°, V = 4644.0(2) Å^3, Z = 4, D_{calcd} = 1.232 mg/m^3, μ = 0.481 mm^{-1}, F(000) = 1840, Mo Kα radiation (λ = 0.71073 Å), T = 193 K, $2\theta_{max}$ = 25°, 57 418 independent reflections collected, 8184 reflections in refinement, final R indices [$I > 2\sigma(I)$; R_1 = 0.0427, wR_2 = 0.1045.[7]

(10) Erker, G.; Berg, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 4455−4456.

(11) It should be noted that these particular charge and electron count of the C_4H_5 fragment and the oxidation states of the zirconium atoms are only one possible set of formal designations.