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Reversible Haptotropic Shift in Zirconocene−Hexapentaene Complexes

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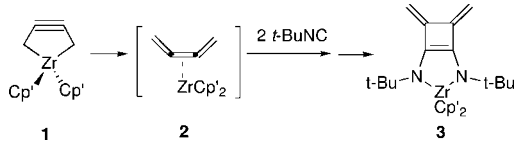
Haptotropic shift in organometallic species of π-ligands has been extensively studied in cyclic polyenes, such as cyclopentadienyl, indenyl, and anthracenyl ligands.[1] A reversible haptotropic shift has been applied for molecular switches.[1a] Fewer studies have been carried out for linear polyenes and polyynes.[2] For example, the "chain walk" of a metal atom along conjugated polyynes by η^2-/η^4-haptotropic shift was reported, although only one of the η^2- or η^4-species was detected.[3] We recently reported that 1,2,3-butatrienes react with group 4 metallocenes to form 1-metallacyclopent-3-ynes, five-membered cycloalkynes.[4] On the other hand, many examples of η^2-π-coordinated [*n*]cumulene ($n \geq 3$) complexes are known.[5] Haptotropic interconversion between these two types of cumulene complexes, however, has not been reported. Rosenthal and co-workers suggested the possibility of η^2-butatriene complexes **2** as intermediates in the insertion reactions of isocyanide into 1-zirconacyclopent-3-ynes **1**,[6] although these species **2** were not detected (Scheme 1). Herein we report on zirconocene−hexapentaene complexes that show haptotropic behavior.

We previously reported the synthesis of a 1-zirconacyclopent-3-yne compound of 2,5-bisalkylidene moieties **5a** from $Cp_2Zr(PMe_3)_2$ and hexapentaene **4a**[7] (R = 4-ethylphenyl).[8] In this study, we found that the reaction of 1,1,6,6-tetrakis(*tert*-butyl)-1,2,3,4,5-hexapentaene (**4b**),[9] under similar conditions, afforded the phosphine-coordinated η^2-π-complex **6b** (92%) selectively, instead of the 1-zirconacyclopent-3-yne **5b** (Scheme 2).[10,11] Prolonged stirring did not result in the formation of **5b**. Complex **6b** was also prepared from low-valent zirconocene species generated by Cp_2ZrCl_2 and Mg in the presence of PMe_3. Note that **5b** could be prepared from **4b** and Cp_2ZrCl_2/Mg in the *absence* of PMe_3 (76%).

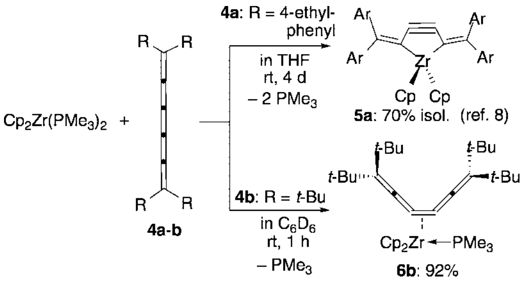
Treatment of **5b** with an excess of trimethylphosphine in benzene-d_6 afforded **6b** in 73% yield (Scheme 3). On the other hand, addition of triethylborane to **6b** afforded **5b** (60%). This is the first example of haptotropic interconversion between an η^2-cumulene complex and a 1-metallacyclopent-3-yne.[12] The molecular structures of both **5b** and **6b** were unequivocally determined (Figure 1).

These molecular structures show that the ligand is rotated perpendicularly during the interconversion between **5b** and **6b**. Bond lengths and angles around the Zr, C3, and C4 atoms in **6b** resemble those in zirconium−alkene complexes.[13] It is noteworthy that the distances Zr−C3 in **5b** and Zr−C3, Zr−C4 in **6b** are in the same range.

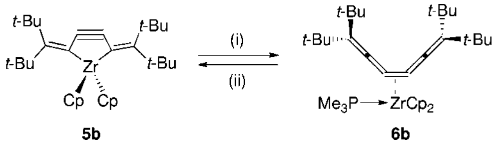
Scheme 1. Insertion of Isocyanide into 1-Zirconacyclopent-3-ynes



Scheme 2. Reactions of Hexapentaenes and $Cp_2Zr(PMe_3)_2$



Scheme 3. Reversible Haptotropic Conversion in **5b** and **6b**[a]



[a] (i) In C_6D_6, 20 equiv of PMe_3, rt, 20 h, 73%; (ii) in C_6D_6, BEt_3, rt, 1 h, 60%.

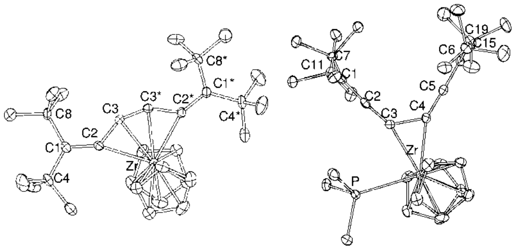


Figure 1. Molecular structures of **5b** (left) and **6b** (right). Drawn with 50% probability. H-atoms are omitted. Selected bond lengths (Å) and angles (deg): **5b**, Zr−C2 2.393(2), Zr−C3 2.307(2), C2−C3 1.390(3), C3−C3* 1.258(2), C2−Zr−C2* 100.3(1), Zr−C2−C3 69.4(1), C2−C3−C3* 150.3(2); **6b**, Zr−P 2.6916(7), Zr−C3 2.305(2), Zr−C4 2.246(2), C1−C2 1.326(3), C2−C3 1.303(3), C3−C4 1.445(3), C4−C5 1.303(3), C5−C6 1.318(3), C1−C2−C3 174.6(2), C2−C3−C4 128.5(2), C3−C4−C5 131.6(2), C4−C5−C6 178.3(2).

These findings lead us to reexamine the reaction of **4a**. ^{1}H and ^{13}C NMR observation at −40 °C revealed that, in the beginning of the reaction (1 h), the η^2-π-complexes **6a** and **6a′** were formed in 50% and 26% yield, respectively, accompanied by a small amount of **5a** (4%) (Scheme 4). Two Cp ^{1}H NMR doublets were observed at 5.39 and 5.29 ppm in toluene-d_8, and these coalesced at 20 °C. They disappeared with time and **5a** formed quantitatively in 4 days.

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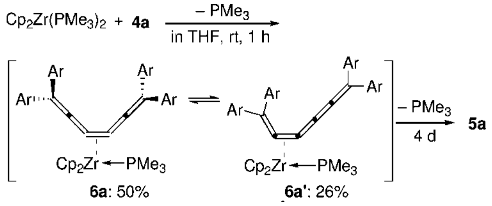
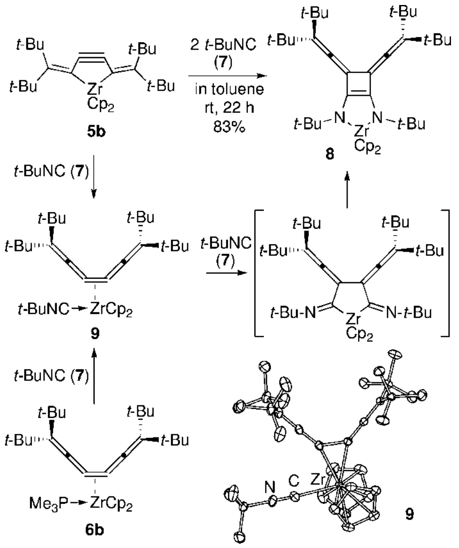
Scheme 4. Formation of η^2-Complexes of **4a**



Scheme 5. Insertion of *tert*-Butylisocyanide and the Molecular Structure of **9**



This indicates that **6a** and **6a′** were in equilibrium in solution and that they released PMe_3 to transform into **5a**. The equilibrium probably proceeded by "ligand sliding", not via **5a**.[14] Complexes **6a** and **6a′** were identified by using ^{13}C-enriched products. To our surprise, **5a** remained unreacted by the addition of PMe_3 and so did complex **1** ($Cp' = C_5H_5$). These facts indicate that the equilibrium lies toward the right in (**5b** + PMe_3)/**6b** (Scheme 3), while it lies far toward the left in (**5a** + PMe_3)/**6a** and in (**1** + PMe_3)/**2**. This is probably due to the steric demand of *tert*-butyl groups.

Complexes **5b** and **6b** reacted with 2 equiv of *tert*-butylisocyanide (**7**) at rt to give the inserted product **8** in good yields, although **5a** did not give any inserted products even at 80 °C.[15,16] It was interesting that the η^2-complex isocyanide adduct **9** was formed during the reaction of **6b** with **7** (Scheme 5). The molecular structure of **9** was unambiguously characterized.[17] Treatment of **9** with 1 equiv of **7** gave **8** in 42% yield.

The reaction of **5b** and 2 equiv of **7** was observed in ^1H NMR spectra. Formation of **9** (24%) and **8** (29%) was observed after 3 h. Complex **8** increased as the amount of **9** decreased, reaching 82% in 18 h. These results clearly indicate that a ligand-induced haptotropic shift from **5b** to **9** was the first step in the insertion of isocyanides.

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Supporting Information Available: Preparation and spectroscopic data for **4**−**6**, **8**, and **9**; the reactions of **5b** and **6b** with **7**; details on X-ray diffraction studies on **5b**, **6b**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **6b**: ^1H NMR (C_6D_6): δ 0.92 (d, $^2J_{P\text{-}H} = 6.9$ Hz, 9H), 1.43 (s, 18H), 1.57 (s, 18H), 5.45 (d, $^3J_{P\text{-}H} = 1.8$ Hz, 10H). ^{13}C NMR (C_6D_6): δ 16.77 (d, $J = 17.3$ Hz), 34.00, 34.25, 36.03 (q), 36.65 (q), 97.38 ($J = 23.0$ Hz), 102.99, 103.32 (d, $J = 9.6$ Hz), 109.68, 112.59, 195.66, 200.95. IR (neat, ATR): 2948, 2906, 1870, 1355, 1208, 791 cm^{-1}. Anal. calcd for $C_{35}H_{55}PZr$: C, 70.30; H, 9.27. Found: C, 70.06; H, 9.32. Crystallographic data: $C_{35}H_{55}PZr$, FW = 598.01, $P2_12_12_1$ (#19), $a = 8.306(2)$, $b = 18.527(5)$, $c = 21.323(5)$ Å, $V = 3281.4(14)$ Å^3, 90 K, $Z = 4$, $R_1 = 0.043$, wR (all data) = 0.052 (CCDC-699032).

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(17) **9**: ^1H NMR (C_6D_6, Me_4Si): δ 1.00 (s, 9H), 1.44 (s, 18H), 1.57 (s, 18H), 5.60 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si): δ 30.26, 34.10, 34.12, 35.95 (q), 36.61 (q), 56.70 (q), 97.55, 98.36, 102.81 (Cp), 109.62, 112.05, 189.36 (*C*N), 196.13, 198.05. IR (ATR, neat): 2946, 2861, 2175, 1891, 1476, 1355, 1208, 1177, 1011, 787 cm^{-1}. Anal. calcd for $C_{37}H_{55}NZr$: C, 73.45; H, 9.16; N, 2.31. Found: C, 73.20; H, 9.34; N, 2.14 (CCDC-699034).

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