η^3-Bonding of Phenylallenyl in a Zirconocene Complex

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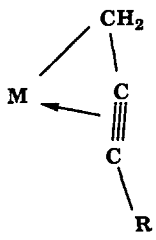
The chemistry of transition-metal propargyls and allenyls continues to grow at a rapid pace stimulated by the intriguing structural features[1-5] and unusual reactivities[1-8] of these complexes. Such compounds have proven versatility as reagents in organic synthesis[6] and as synthons for mixed-metal clusters.[6a] Notwithstanding these developments, the chemistry in point has shown a conspicuous absence of the early transition metals. In fact, a general synthetic route to the early transition-metal d^0 complexes of this type is still lacking. Several reports of d^0 complexes containing propargyl or allenyl ligands synthesized by various methods have recently appeared in the literature,[9] but, owing to the lack of structural data, the nature of the bonding of the hydrocarbyl ligand in these mononuclear complexes remains an issue of conjecture. Herein we report the syntheses, through ligand substitution reactions, of two zirconocene d^0 complexes: $Cp_2Zr(CH_3)(\eta^3\text{-}C(Ph){=}C{=}CH_2)$ (**1**), which is shown by X-ray crystallography to contain η^3-bonded phenylallenyl, and $Cp_2Zr(CH_2CCPh)_2$ (**2**), which displays a dynamic solution behavior that apparently involves rapid interconversion of η^1- and η^3-CH_2CCPh ligands. Given the role of Ziegler–Natta-type catalysts in the activation of unsaturated hydrocarbons toward polymerization,[10] the novel bonding modes of the hydrocarbyl ligands in **1** and **2** are of considerable general interest.

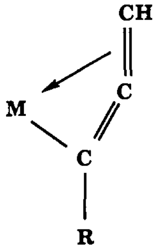
1 was prepared by the reaction of $Cp_2Zr(CH_3)Cl$[11] with $PhC{\equiv}CCH_2MgBr$[12] in diethyl ether at 0 °C, followed by stirring at room temperature for 3 h. Removal of ether and concentration of hexane extracts of the residue yields the air-sensitive tan solid in high (>96%) yield. The CH_2 resonance at δ 3.37 in the ^1H NMR spectrum of **1**[13] is downfield of that expected for a 3-phenylpropargyl ligand[8] and upfield of that expected for an η^1-1-phenylallenyl ligand[14] but is comparable to values observed for the CH_2 protons of the η^3-propargyl ligand in the complexes $[(\eta^5\text{-}C_5Me_5)(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)]PF_6$ and $[(\eta^6\text{-}C_6Me_6)(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)]BF_4$ prepared by Casey[3] and Krivykh,[1] respectively. However, the ^{13}C NMR chemical shifts of the quaternary and methylene carbons of the CH_2CC unit of **1** at δ 120.5, 114.1, and 55.5, respectively, are not in complete agreement with those reported for η^1-propargyl,[8] η^3-propargyl,[1,3] or η^1-allenyl[2,7a,8b] (including η^1-1-phenylallenyl[14]) complexes.

A single-crystal X-ray analysis of **1**[15] resolved these spectroscopic ambiguities and revealed an unusual η^3-bonding mode for the phenylallenyl ligand, as shown in Figure 1. **1** adopts a normal bent metallocene structure in which the methyl and C(1), C(2), C(3), and C(4) atoms of the phenylallenyl ligand lie roughly in the plane that bisects the Cp_2Zr fragment. For the phenylallenyl ligand, the Zr—C bonds lengthen upon going from C(3) to C(2) to C(1). This trend deviates significantly from the relative bond distances in $[(\eta^6\text{-}C_6Me_5H)(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)]BF_4$[1], in which the central Mo—C bond is the shortest, but is consistent with the trend in Zr—C bond distances in the d^0–d^0 dizirconium allenediyl complex $(Cp_2ZrEt)_2(\mu_2\text{-}\eta^1,\eta^2\text{-}CCC(CH_3)_2)$.[5] The latter complex is remarkably similar to **1** if one Cp_2ZrEt fragment is replaced by Ph.

The best bonding description of the CH_2CCPh ligand in **1** is a combination of η^3-propargyl (**A**) and η^3-allenyl (**B**) resonance structures. The sum of the bond angles around C(1) (359(6)°), the value of $^1J_{CH}$ for the CH_2 group (167 Hz), and the bond distances C(1)–C(2) (1.344(5) Å) and C(2)–C(3) (1.259(4) Å) of **1** compared to those of $[(\eta^6\text{-}C_6Me_5H)(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)]BF_4$ (1.380(4) and 1.236(4) Å, respectively)[1] all suggest a greater importance of the resonance structure **B** than of **A**.



A



B

The reaction of Cp_2ZrCl_2 with $PhC{\equiv}CCH_2MgBr$ in Et_2O/CH_2Cl_2 affords $Cp_2Zr(CH_2CCPh)_2$ (**2**), which is isolated as an air-sensitive brown-red solid by removal of solvent from the reaction mixture and cooling of the hexane extracts to −78 °C.

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[13] Spectroscopic data for **1**: IR (KBr) $\nu_{C=C}$ 2176 (m), 1924 (m); ^1H NMR (300 K, CD_2Cl_2) δ 7.67–7.37 (m, 5 H, Ph), 5.64 (s, 10 H, Cp), 3.37 (s, 2 H, CH_2), 0.34 (s, 3 H, CH_3); ^{13}C NMR (300 K, CD_2Cl_2) δ 133–127 (Ph), 120.5 and 114.1 (-*C*(Ph)=C= and -C(Ph)=*C*=), 107.2 (Cp), 55.5 (t, $^1J_{CH}$ = 167 Hz, CH_2), 4.8 (q, $^1J_{CH}$ = 123 Hz, CH_3); mass spectrum (EI), ^{90}Zr isotope, *m/z* (ion, relative intensity) 350.060 (exact M^+, 0.7; calcd for $C_{20}H_{20}Zr$ 350.061), 335 ($M^+ - CH_3$, 73), 220 ($M^+ - CH_3 - C_3H_2Ph$, 52), 115 ($C_3H_2Ph^+$, 100).

[14] Blosser, P. W.; Schimpff, D. G.; Wojcicki, A.; Calligaris, M.; Faleschini, P., to be submitted for publication.

[15] Crystal data for **1**: $C_{20}H_{20}Zr$, monoclinic, $P2_1/c$ (No. 14); $a = 8.147(2)$ Å, $b = 8.766(2)$ Å, $c = 22.672(3)$ Å, $\beta = 97.10(2)°$, $V = 1607(1)$ Å^3, $Z = 4$, $d_{calc} = 1.45$ g cm^{-3}. The data were collected at 296 K on a colorless almost cubic-shaped specimen (0.31 × 0.35 × 0.38 mm) mounted in an argon-filled glass capillary with Mo Kα radiation, $\mu = 6.63$ cm^{-1}, 2θ limits 4–55°, 211 variables refined with 2692 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ to $R(F) = 0.029$ and $R_w(F) = 0.035$, GOF = 1.30. The hydrogen atoms bonded to C(1) and C(10) were refined isotropically.

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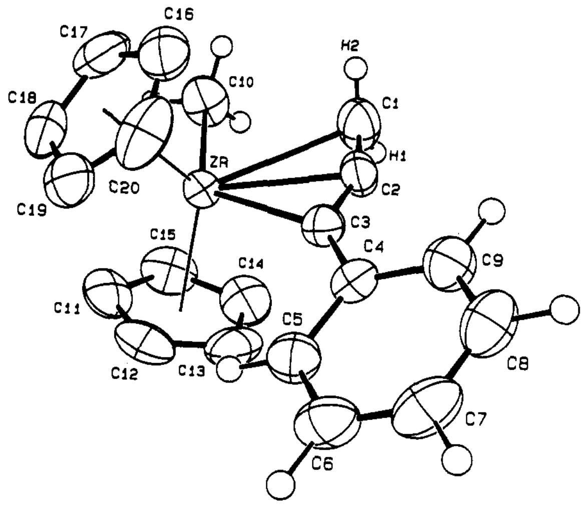
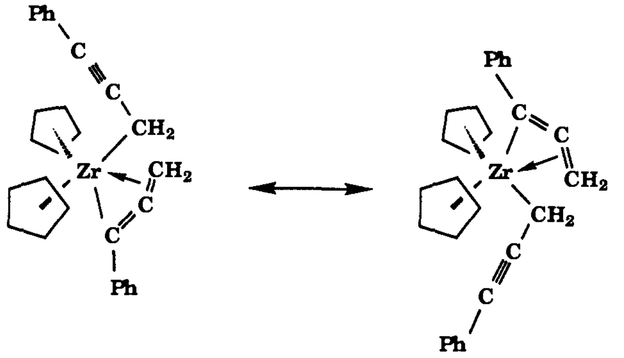


Figure 1. Ortep plot of **1**. Selected bond distances (Å) and angles (deg): Zr–C(1) 2.658(4), Zr–C(2) 2.438(3), Zr–C(3) 2.361(3), Zr–C(10) 2.364(4), C(1)–C(2) 1.344(5), C(2)–C(3) 1.259(4), C(3)–C(4) 1.462(4), C(1)–C(2)–C(3) 155.4(3), C(2)–C(1)–H(1) 116(3), C(2)–C(1)–H(2) 119(3), H(1)–C(1)–H(2) 124(4).

Ambient-temperature ^1H and ^{13}C NMR spectra of **2**[16] indicate apparent equivalence of both CH_2CCPh ligands.

Unlike **1**, which shows no change in the ^1H NMR over the temperature range 223–303 K, **2** is fluxional. When the temperature is lowered to 240 K, the CH_2 signal at δ 2.80 broadens, while the Ph and Cp signals remain essentially unchanged. At 180 K, the CH_2 resonance splits into two equal-intensity broad resonances centered at δ 3.3 and 1.9. Based upon their positions, these signals are consistent with the presence of one η^3-CH_2CCPh ligand (δ 3.3) and one η^1-$CH_2C{\equiv}CPh$ ligand (δ 1.9).[8] At ambient temperature, these two ligands apparently interconvert as illustrated below. **2** represents the first example of a transition-metal complex that contains both η^1-propargyl and η^3-propargyl/allenyl ligands. For comparison, complexes incorporating both η^1- and η^3-allyl ligands are known;[17] some exhibit fluxional behavior that results in the η^1–η^3 interchange of the two hydrocarbyl groups.[17b,c]



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Supplementary Material Available: Variable-temperature ^1H NMR spectra of **2**; details of the structure determination of **1**, including data collection and refinement, positional parameters, anisotropic thermal parameters, and complete bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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[16] (16) Spectroscopic data for **2**: ^1H NMR (300 K, CD_2Cl_2) δ 7.58–7.30 (m, 10 H, Ph), 5.80 (s, 10 H, Cp), 2.80 (s, 4 H, CH_2); ^{13}C NMR (300 K, CD_2Cl_2) δ 132–127 (Ph), 112.9 and 98.8 (quaternary C's of CH_2CC unit), 108.0 (Cp), 30.7 (t, $^1J_{CH}$ = 151 Hz, CH_2); mass spectrum (EI), ^{90}Zr isotope, m/z (ion, relative intensity) 450.093 (exact M^+, 8.8; calcd for $C_{28}H_{24}Zr$ 450.093), 335 ($M^+ - C_3H_2Ph$, 74), 220 ($M^+ - 2C_3H_2Ph$, 100), 115 ($C_3H_2Ph^+$, 59).

[17] (17) Selected examples: (a) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 583. (b) Martin, H. A.; Lemaire, P. J.; Jellinek, F. *J. Organomet. Chem.* **1968**, *14*, 149. (c) Henc, B.; Jolly, P. W.; Sabz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449.