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Factors Determining Allyl Hapticity in Early-Transition-Metal Allyl Complexes: Synthesis, Structure, and Dynamics of $Cp_2(\eta^3\text{-}1,2,3\text{-}Me_3allyl)ZrBr$ and $Cp_2(\eta^1\text{-}1,1,2\text{-}Me_3allyl)ZrBr$

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The reaction of Cp_2ZrCl_2 with (1,1,2-Me_3allyl)MgBr or (1,2,3-Me_3allyl)MgBr and excess $MgBr_2$ yields $Cp_2(\eta^1$-1,1,2-Me_3allyl)ZrBr and $Cp_2(\eta^3$-1,2,3-Me_3allyl)ZrBr. X-ray crystallography of these compounds shows a bent-metallocene geometry, with steric congestion in the η^3-allyl compound causing the most distortion toward η^1-coordination yet observed for an η^3-allyl early-transition-metal complex. For $Cp_2(\eta^1$-1,1,2-Me_3allyl)ZrBr: cell constants $a = 18.683$ (18) Å, $b = 7.552$ (6) Å, $c = 11.272$ (10) Å, $\beta = 101.02$ (5)°, space group $P2_1/a$; $R = 0.046$, $R_w = 0.042$. For $Cp_2(\eta^3$-1,2,3-Me_3allyl)ZrBr: cell constants $a = 13.843$ (7) Å, $b = 7.544$ (3) Å, $c = 14.054$ (9) Å, $\beta = 100.86$ (3)°, space group $P2_1/c$; $R = 0.064$, $R_w = 0.064$. A variable-temperature ^1H NMR study indicates that the allyl ligand in $Cp_2(\eta^3$-1,2,3-Me_3allyl)ZrBr undergoes η^3–η^1 isomerization [$\Delta G^\ddagger = 37.3 \pm 2.0$ kJ/mol].

Introduction

It has been known for some time that methylation of the cyclopentadienyl (Cp) ligands in early-transition-metal Cp complexes enhances the stability of these compounds. This increased stability has been attributed to both increased ligand size and increased ligand donor ability upon methylation.[1] The relative importance of these factors is not known, and the Cp ligand is ill-suited to answer this question since it yields stable compounds without methylation. The allyl ligand [C_3H_5], being smaller, a weaker electron donor, and nonaromatic, is borderline in its ability to yield stable early-transition-metal compounds. Thus, the allyl ligand should be a more effective probe as to how methylation influences the properties of an electron-deficient (<18-electron) early-transition-metal complex. The allyl ligand also demonstrates *two* common modes of binding to a metal, η^1 and η^3. Generally speaking, the *steric* preference is for η^1-allyl binding, since an η^3-mode brings more of the allyl ligand into the inner coordination sphere. The *electronic* preference is for η^3-binding (four-electron donation) rather than η^1-binding (two-electron donation). This should make it possible upon ligand methylation to sort out the relative importance of steric versus electronic effects in determining the mode of allyl binding to an electron-deficient early transition metal. For example, can allyl ligand donor ability be increased via methylation to the point that an η^3-binding mode is favored over η^1 even in the face of sever steric congestion? Unfortunately, relatively few early-transition-metal allyl compounds have been prepared from which to draw these types of conclusions. Most of those known possess an unsubstituted allyl ligand(s),[2-7] although there are a few examples having a mono-,[7-11] di-,[7,12] or trimethylated[7,13] allyl ligand. Before our work, only a few unsubstituted allyl complexes of the early transition metals had been structurally characterized via X-ray crystallography.[2,5,6,11] Furthermore, no studies had been undertaken to establish the role of allyl methylation in influencing either the mode of allyl binding (η^3 versus η^1), the activation barrier for η^3–η^1 isomerization, or the thermal stability of these complexes. We report here on the preparation, X-ray structural characterization, and dynamics of $Cp_2(\eta^3$-1,2,3-Me_3allyl)ZrBr (**3**) and $Cp_2(\eta^1$-1,1,2-Me_3allyl)ZrBr (**4**). We will show that steric congestion brought about by allyl methylation in these compounds outweighs increased donor ability and significantly effects the mode of allyl binding and the barrier to η^3–η^1 isomerization.

Experimental Section

General Comments. Solutions of the allyl Grignards (1,2,3-Me_3allyl)MgBr (**1**) and (1,1,2-Me_3allyl)MgBr (**2**) were prepared as described elsewhere (the solutions also contained $MgBr_2$).[13] Ether, tetrahydrofuran, and hexane were distilled from sodium/benzophenone under argon. Zirconocene dichloride was purchased from the Aldrich Chemical Co. and used without further purification. All syntheses and subsequent handling of compounds were conducted under anhydrous conditions in a dry argon atmosphere.

$Cp_2(\eta^3$-1,2,3-Me_3allyl)ZrBr (3). A THF solution of (1,2,3-Me_3allyl)MgBr (**1**) [0.0225 M (330 mL, 7.42 mmol), the solution also contained $MgBr_2$] was added via cannula to a stirred solution of Cp_2ZrCl_2 (2.28 g, 7.79 mmol) in 50 mL of THF. The solvent was removed from the clear orange reaction solution via trap to trap distillation immediately after addition of the Grignard, yielding an orange solid. The product was extracted with 20-mL

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portions of ether (collected and combined via cannula) leaving behind white magnesium salts. Successive crops of air-sensitive yellow crystals were obtained upon cooling the cannulate to −14 °C in a freezer (1.26 g, 44%). The crystals could be stored for long periods under argon in a freezer (−14 °C). However, the crystals darkened considerably within 1 month when stored in the dark under argon at room tempertaure. Anal. Calcd for $C_{16}H_{21}ZrBr$: C, 49.98; H, 5.50. Found: C, 50.10; H, 5.54. ^1H NMR [80 MHz, 22 °C] ($CDCl_3$/TMS 2%): δ 5.81 (Cp, 10 H); 2.94 (CH, allyl, q, 2 H, $J[^1H-^1H] = 6.4$ Hz); 1.80 1.72 (terminal CH_3, allyl, d, 6 H, $J[^1H-^1H] = 6.4$ Hz); 1.76 (central CH_3, allyl, 3 H). ^1H NMR [300 MHz, 22 °C] (toluene-d_8): δ 5.46 (Cp, 10 H); 2.68 (CH, allyl, q, 2 H, $J[^1H-^1H] = 6.3$ Hz); 1.66, 1.63 (terminal CH_3, allyl, d, 6 H, $J[^1H-^1H] = 7.2$ Hz); 1.38 (central CH_3, allyl, 3 H). ^1H NMR [300 MHz, −99 °C] (toluene-d_8): δ 5.50 (Cp, 5 H); 5.29 (Cp, 5 H); 3.32 (CH, allyl, br, 1 H); 2.13 (terminal CH_3, allyl, br, 3 H); 1.91 (CH, allyl, br, 1 H); 1.34 (terminal CH_3, allyl, br, 3 H); 1.27 (central CH_3, allyl, 3 H). IR (cm^{-1}, Nujol mull): 3136 w, 3083 w, 1571 w, 1542 w, 1233 m, 1139 w, 1129 w, 1090 w, 1075 w, 1067 w, 1016 s, 978 w, 933 m, 907 m, 870 m, 853 m, 844 s, 825 s, 806 vs, 787 vs, 773 sh, 725 s, 612 w, 603 m, 553 m, 532 m, 475 m, 364 m, 334 s. IR (cm^{-1}, halocarbon mull): 3136 w, 3104 w, 3096 w, 3083 m, 3071 w, 2985 w, 2961 w, 2932 w, 2891 m, 2859 m, 1571 w, 1542 m, 1450 s, 1440 s, 1378 s, 1373 s, 1365 s.

$Cp_2(\eta^1$-1,1,2-Me_3allyl)ZrBr (4). An ether solution of (1,1,2-Me_3allyl)MgBr (**2**) [0.0270 M (280 mL, 7.56 mmol), the solution also contained $MgBr_2$] was added via cannula to a stirred slurry of Cp_2ZrCl_2 (2.21 g, 7.56 mmol) in 50 mL of ether, yielding a dark red solution. The reaction solution was stirred for 8 h, after which all but 10 mL of solvent was removed via trap to trap distillation. Hexane (50 mL) was then added, and the solution was filtered, yielding a red precipitate and a dark red filtrate. The precipitate was washed with 50 mL of hexane until it was white; the wash was collected with the filtrate. The volume of the filtrate was then reduced via trap to trap distillation, and successive crops of air-sensitive red crystals were recovered upon cooling to −14 °C in a freezer (1.62 g, 56%). Anal. Calcd for $C_{16}H_{21}ZrBr$: C, 49.98; H, 5.50. Found: C, 49.37; H, 5.61. ^1H NMR ($CDCl_3$/TMS 2%): δ 6.23 (Cp, 10 H); 1.80, 1.65, 1.57 (CH_2 and CH_3, 11 H). IR (cm^{-1}, Nujol mull): 3117 w, 1740 w, 1637 w, 1264 w, 1187 m, 1159 m, 1014 s, 889 w, 841 sh, 832 sh, 817 vs, 811 vs, 738 m, 723 m, 558 w, 486 w, 426 w, 348 s. IR (cm^{-1}, halocarbon mull): 3108 s, 2969 s, 2929 m, 2903 s, 2851 s, 1737 w, 1636 w, 1437 vs, 1381 m, 1368 s. The fourth crop of crystals yielded a mixture of **4** and a darker red solid (0.35 g) which was manually separated from **4**. ^1H NMR showed this dark red solid to be almost pure Cp_2-(η^1-1,1,2-Me_3allyl)$_2$Zr (**5**) (contaminated by 2–3% with **4**). ^1H NMR ($CDCl_3$/TMS 2%): δ 5.99 (Cp, 10 H); 1.76 (CH_3, allyl, 6 H); 1.63 (CH_3, allyl, 6 H); 1.54 (CH_3, allyl, 6 H); 1.12 (CH_2, allyl, 4 H). IR (cm^{-1}, Nujol mull): 3096 w, 3077 m, 1819 w, 1731 w, 1640 m, 1364 s, 1309 vw, 1265 m, 1184 s, 1158 s, 1076 w, 1030 w, 1018 s, 982 m, 952 m, 917 wv, 888 m, 835 m, 808 vs, 738 m, 722 m, 707 m, 615 w, 568 w, 554 m, 485 m, 410 w, 387 vw, 338 s. IR (cm^{-1}, halocarbon mull): 3097 w, 3078 m, 2971 m, 2907 s, 2850 s, 1820 vw, 1729 w, 1638 m, 1443 s, 1379 w, 1364 s.

Nuclear Magnetic Resonance Spectra. Ambient-probe temperature (22.0 °C) proton chemical shifts were measured with a Varian FT-80A 80-MHz spectrometer as $CDCl_3$ solutions; peak positions are reported as δ in parts per million relative to TMS at 0. Variable-temperature (+22 to −99 °C) proton chemical shifts were measured with a Varian XL-300-MHz spectrometer as toluene-d_8 solutions; peak positions are reported as δ in parts per million relative to the residual toluene methyl resonance at δ 2.09. Temperatures, determined by using a methanol standard, are estimated to be accurate to ±0.5 °C.

Infrared Spectra. Infrared spectra were measured in the region 4000–300 cm^{-1} with a Nicolet 20-DX spectrophotometer equipped with a CsI beam splitter. The compounds were studied as mineral oil mulls and as Halocarbon 25-5S grease mulls (polychlorotrifluoroethylene oils thickened with silica gel, Halocarbon Products Corp., NJ, has no absorptions between 1300 and 4000 cm^{-1}) between CsI plates. The estimated uncertainty in reported frequencies is ±2 cm^{-1}.

X-ray Structural Determination. Pertinent data for the structures of compounds **3** and **4** are presented in Table I. The crystals were mounted on a Picker computer controlled four-circle diffractometer equipped with a Furnas Monochromator (HOG crystal) and cooled by a gaseous nitrogen cooling system. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with systematic absences and symmetry consistent with the monoclinic space group $P2_1/c$ for **3** and $P2_1/a$ for **4**. Orientation matrices and accurate unit cell dimensions were determined at low temperature from least-squares fits of 32 reflections (20° < 2θ < 30°) for both **3** and **4**. Intensity data were collected by using the $\theta/2\theta$ scan method; four standard reflections, monitored every 300 reflection measurements, showed only statistical fluctuations for both compounds. On the basis of the cited dimensions of the crystals and moderate values for the linear absorption coefficients, absorption corrections were judged unnecessary. The intensities were then corrected for Lorentz and polarization factors and scaled to give the numbers of independent F_{hkl} values for $I > 3\sigma(I)$ indicated in Table I.

Table I. Summary of Crystal Data and Intensity Collection for $Cp_2(\eta^3$-1,2,3-Me_3allyl)ZrBr (3) and $Cp_2(\eta^1$-1,1,2-Me_3allyl)ZrBr (4)

	3	4
formula	$C_{16}H_{21}ZrBr$	$C_{16}H_{21}ZrBr$
fw	384.47	384.47
a, Å	13.843 (7)	18.683 (18)
b, Å	7.544 (3)	7.552 (6)
c, Å	14.054 (9)	11.272 (10)
β, deg	100.86 (3)	101.02 (5)
V, $Å^3$	1441.45	1560.99
Z	4	4
d, g cm^{-3}	1.772	1.636
space group	$P2_1/c$	$P2_1/a$
cryst dimens, mm	0.18 × 0.18 × 0.23	0.16 × 0.22 × 0.33
temp, °C	−155	−153
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
linear abs coeff	34.775 cm^{-1}	32.112 cm^{-1}
receiving aperture	3.0 × 4.0 mm; 22.5 cm from xtal	3.0 × 4.0 mm; 22.5 cm from xtal
takeoff angle, deg	2.0	2.0
scan speed	4° in 2θ/min	4° in 2θ/min
scan width	2° + dispersion	2° + dispersion
bkgd counts	6 s at each end	6 s at each end
2θ limits, deg	6–60	6–45
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
unique data	4217	2052
unique data with $F_o^2 > 3\sigma(F_o^2)$	3478	1558
$R(F)$	0.0642	0.0465
$R_w(F)$	0.0643	0.0419

Both structures were solved by a combination of direct methods (MULTAN78) and Fourier techniques. All atoms, including hydrogens, were located for compound **3**. All but two hydrogen atoms were located for compound **4**; these were included at their calculated positions. All atoms, including hydrogens, were refined. Full-matrix least-squares refinement included anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms; refinements converged to values for the conventional *R* indices shown in Table I. The final difference Fourier syntheses were essentially featureless, the largest residuals being 0.3 and 0.7 e/$Å^3$ for **3** and **4**, respectively. The weighting scheme used in the final calculations was of the form $w = 1/\sigma_F^2$. Scattering factors for the atoms were taken from ref 14. The scattering factor for the Zr and Br atoms were corrected for the real and imaginary parts of anomalous dispersion by using values from ref 14. All computations were carried out on a CDC Cyber 170-855 computer using programs described elsewhere.[15] The positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II, the atom–numbering schemes being shown in Figure 1 for compounds **3** and **4**, respectively. Anisotropic thermal parameters for the non-hydrogen atoms are listed in Table III (supplementary ma-

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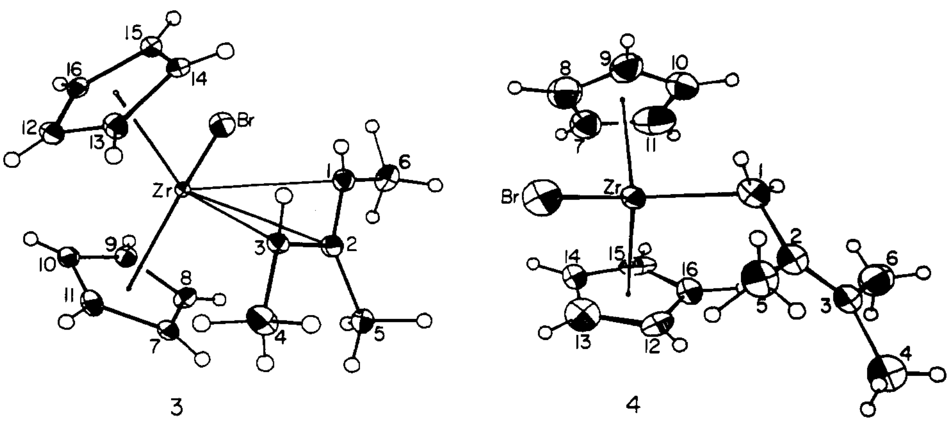
Table II. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for 3 and 4[a]

3					4				
atom	x	y	z	B(eq), Å^2	atom	x	y	z	B(eq), Å^2
Zr	2889.4 (4)	952 (1)	7751.4 (4)	0.6	Zr	6316.8 (5)	654 (1)	2039 (1)	1.8
Br	3782 (1)	44 (1)	6237 (1)	2.0	Br	5795 (1)	−2430 (1)	1251 (1)	3.1
C(1)	1753 (5)	−1462 (9)	6701 (5)	1.3	C(1)	7223 (6)	−276 (19)	3632 (10)	2.8
C(2)	1125 (4)	−440 (8)	7124 (4)	1.1	C(2)	7899 (5)	−1153 (14)	3406 (8)	2.4
C(3)	1353 (4)	−174 (8)	8152 (4)	1.0	C(3)	8553 (5)	−421 (14)	3600 (8)	2.6
C(4)	686 (5)	721 (9)	8739 (5)	1.5	C(4)	9215 (7)	−1344 (19)	3301 (12)	3.4
C(5)	293 (5)	528 (9)	6478 (5)	1.3	C(5)	7754 (7)	−3009 (16)	2932 (10)	3.0
C(6)	1628 (6)	−1844 (11)	5643 (5)	1.9	C(6)	8732 (7)	1387 (18)	4131 (12)	3.4
C(7)	1730 (5)	3600 (8)	7501 (5)	1.2	C(7)	5300 (6)	2709 (19)	2096 (11)	3.6
C(8)	2140 (5)	3477 (9)	6655 (5)	1.4	C(8)	5029 (5)	1091 (18)	2317 (10)	3.5
C(9)	3152 (5)	3851 (9)	6924 (5)	1.3	C(9)	5415 (6)	492 (15)	3441 (10)	3.2
C(10)	3369 (5)	4179 (8)	7912 (5)	1.3	C(10)	5904 (6)	1794 (17)	3913 (10)	3.4
C(11)	2488 (5)	3995 (9)	8281 (5)	1.4	C(11)	5840 (7)	3194 (16)	3083 (12)	3.6
C(12)	4021 (5)	1310 (8)	9365 (4)	1.2	C(12)	7345 (5)	654 (16)	879 (8)	2.8
C(13)	3345 (5)	−3 (9)	9492 (4)	1.3	C(13)	6705 (5)	606 (16)	7 (9)	3.1
C(14)	3534 (4)	−1504 (8)	8957 (4)	1.2	C(14)	6330 (6)	2184 (16)	102 (8)	3.0
C(15)	4302 (5)	−1108 (9)	8480 (4)	1.3	C(15)	6765 (6)	3194 (15)	1009 (10)	2.9
C(16)	4592 (4)	689 (8)	8711 (4)	1.1	C(16)	7388 (5)	2285 (15)	1514 (9)	2.6

[a] Estimated standard deviations are given in parentheses. Equivalent isotropic temperature factors are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.



3 4

Figure 1.

terial), hydrogen atom coordinates and isotropic thermal parameters in Table IV (supplementary material), and structure factors in Tables V and VI (supplementary material), for compounds 3 and 4, respectively.

Results and Discussion

The compounds $Cp_2ZrBr(\eta^3\text{-}1,2,3\text{-}Me_3allyl)$ (**3**) and $Cp_2ZrBr(\eta^1\text{-}1,1,2\text{-}Me_3allyl)$ (**4**) were prepared at room temperature via addition of a single equivalent of allyl Grignard to a solution of Cp_2ZrCl_2 (solutions of allyl Grignard contained $MgBr_2$). The bis(allyl) complex

$$Cp_2ZrCl_2 + \underset{1,\,2}{(allyl)MgBr} + \text{excess } MgBr_2 \rightarrow \underset{3,\,4}{Cp_2ZrBr(allyl)}$$

1, 3: 1,2,3-Me$_3$allyl (solvent THF)

2, 4: 1,1,2-Me$_3$allyl (solvent ether)

$Cp_2Zr(\eta^1\text{-}1,1,2\text{-}Me_3allyl)_2$ (**5**) was also isolated during the preparation of **4** (see Experimental Section; the analogous $Cp_2Zr(\eta^1\text{-}1,2,3\text{-}Me_3allyl)_2$ was not formed during the preparation of **3**). It is of interest to note that **3** is thermally unstable (yellow crystals of **3** sealed in an ampule under argon and stored in the dark at room temperature darkened considerably within one month). This instability is likely due to the large degree of steric congestion within the molecule (vide infra).

Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of **3** and **4** are presented in Table II; bond distances and angles for both compounds are given in Table VII. Perspective views showing the molecular geometry and the atom numbering schemes are presented in Figure 1. The molecules of **3** and **4** occupy general positions of the space groups $P2_1/c$ and $P2_1/a$, respectively, and are not required to have any symmetry. The molecular structures of **3** and **4** are that of a bent metallocene, with the plane defined by the Zr, Br, and either the allyl centroid (for **3**) or allyl C(1) atom (for **4**) and the plane defined by the Zr atom and the two Cp centroids being nearly orthogonal for **3** (91.1°) and **4** (90.1°). The Cp(centroid)–Zr–Cp(centroid) angles of 125.4° and 130.5° for **3** and **4**, respectively, are within the range expected for bent metallocenes.[16]

The Cp rings of both **3** and **4** are planar, with displacements of the C atoms from the mean planes of the ligands being ≤ 0.023 Å. The normals to the Cp planes are essentially colinear with their respective Zr–Cp(centroid) vectors (angles for **3** and **4** of 1.8° and 1.9° [C(7)–C(11)] and of 3.0° and 2.0° [C(12)–C(16)], respectively). The unique aspects of these structures involves the metal–allyl bonding. The allyl ligands of both complexes (including the methyl carbons) are planar, with displacements of the C atoms from the mean planes of the ligands being ≤ 0.089

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Table VII. Bond Distances and Angles in 3 and 4

	distance, Å			angle, deg	
atoms	3	4	atoms	3	4
Zr-Br	2.741 (2)	2.614 (1)	Br-Zr-C(1)	72.8 (2)	99.4 (4)
Zr-C(1)	2.663 (7)	2.328 (11)	Br-Zr-Ct(al)	101.5 (2)	
Zr-C(2)	2.652 (5)		Ct(Cp)-Zr-Ct(Cp′)	125.4 (2)	130.5 (4)
Zr-C(3)	2.452 (6)		Zr-C(1)-C(2)		121.2 (7)
Zr-Ct(Cp)[a]	2.212 (6)	2.204 (11)	C(6)-C(1)-C(2)	125.0 (6)	
Zr-Ct(Cp′)[a]	2.231 (7)	2.210 (12)	C(1)-C(2)-C(3)	118.4 (5)	124.9 (10)
Zr-Ct(al)	2.372 (7)		C(1)-C(2)-C(5)	118.8 (5)	111.9 (9)
C(1)-C(2)	1.378 (10)	1.490 (16)	C(3)-C(2)-C(5)	122.4 (5)	123.1 (10)
C(1)-C(6)	1.493 (10)		C(2)-C(3)-C(4)	124.9 (5)	122.7 (10)
C(2)-C(3)	1.434 (8)	1.322 (13)	C(2)-C(3)-C(6)		125.0 (10)
C(2)-C(5)	1.513 (8)	1.506 (16)	C(4)-C(3)-C(6)		112.3 (9)
C(3)-C(4)	1.509 (10)	1.513 (17)	C(8)-C(7)-C(11)	108.2 (6)	109.0 (11)
C(3)-C(6)		1.502 (17)	C(7)-C(8)-C(9)	107.3 (6)	107.9 (9)
C(7)-C(8)	1.413 (11)	1.364 (19)	C(8)-C(9)-C(10)	108.7 (6)	107.8 (10)
C(7)-C(11)	1.399 (9)	1.399 (16)	C(9)-C(10)-C(11)	108.0 (6)	108.3 (10)
C(8)-C(9)	1.409 (10)	1.407 (15)	C(7)-C(11)-C(10)	107.7 (6)	106.9 (11)
C(9)-C(10)	1.387 (10)	1.378 (16)	C(13)-C(12)-C(16)	108.7 (5)	108.8 (9)
C(10)-C(11)	1.418 (10)	1.402 (18)	C(12)-C(13)-C(14)	107.8 (6)	107.6 (9)
C(12)-C(13)	1.396 (10)	1.408 (12)	C(13)-C(14)-C(15)	108.6 (6)	106.8 (9)
C(12)-C(16)	1.401 (9)	1.420 (16)	C(14)-C(15)-C(16)	107.5 (6)	110.9 (10)
C(13)-C(14)	1.411 (9)	1.398 (17)	C(15)-C(16)-C(12)	107.3 (5)	105.8 (8)
C(14)-C(15)	1.393 (9)	1.404 (14)			
C(15)-C(16)	1.433 (9)	1.377 (14)			

[a] The centroid of the Cp ligand [C(12)–C(16)], the centroid of the Cp ligand [C(7)–C(11)], and the centroid of the allyl ligand are represented as Ct(Cp), Ct(Cp′), and Ct(al), respectively.

and ≤0.040 Å for **3** and **4**, respectively. However, the 1,2,3-trimethylallyl ligand in **3** is η^3-bound, while the 1,1,2-trimethylallyl ligand in **4** is η^1-bound. As a consequence, the steric congestion between the allyl ligand and the rest of the molecule is far greater for **3** than for **4**. For compound **3**, every allyl carbon atom experiences at least one significant repulsive interaction with either a Cp ring or the Br atom [C(1)–Br, 0.341 Å; C(2)–C(7), 0.222 Å; C(3)–C(13), 0.365 Å; C(3)–C(7), 0.335 Å; C(3)–C(14), 0.220 Å; C(4)–C(7), 0.417 Å; C(5)–C(8), 0.337 Å; C(6)–Br, 0.583 Å; values represent how much the nonbonded contact is within the sum of the van der Waals radii].[17a] The result is that **3** exhibits the longest bond lengths [Zr–C(1), 2.663 (7) Å; Zr–C(2), 2.652 (6) Å] yet observed between a Zr atom and an η^3-allyl ligand [these are slightly longer than the previous longest length of 2.648 (11) Å observed in Cp*(η^3-1,1,2-Me$_3$allyl)ZrBr$_2$ which is also distorted toward η^1 [Cp* = (η^5-C$_5$Me$_5$)];[13] typical Zr–C(η^3-allyl) bond lengths are in the range of 2.36–2.52 Å[5,6]]. In contrast, only the bound carbon atom of the η^1-allyl ligand in **4** experiences significant repulsive interactions [C(1)–C(10), 0.714 Å; C(1)–C(16), 0.567 Å; C(1)–C(12), 0.463 Å; C(1)–C(9), 0.308 Å; values represent how much the nonbonded contact is within the sum of the van der Waals radii].[17b]

Infrared spectroscopy has often been used to assign an η^1- or an η^3-bound configuration to allyl ligands in metal complexes [1650–1580 cm^{-1} for η^1-bound allyl; 1550–1450 cm^{-1} for η^3-bound allyl].[7,18] Accordingly, η^1-1,1,2-trimethylallyl compound **4** has a moderate absorption at 1636 cm^{-1}, whereas η^3-1,2,3-trimethylallyl complex **3** has a strong absorption at 1450 cm^{-1}. However, **3** displays additional weak absorptions at 1571 and 1542 cm^{-1}. This is consistent with the X-ray observation that the η^3-bound 1,2,3-trimethylallyl ligand in **3** is significantly distorted toward an η^1-bound configuration (there is a wide variation in the C–C bond lengths within the allyl ligand of **3** [C(1)–C(2), 1.378 (10) Å; C(2)–C(3), 1.434 (8) Å] significantly lengthening the C(2)–C(3) bond that would be a single bond in the η^1-form). Finally, Cp$_2$Zr(η^1-1,1,2-Me$_3$allyl)$_2$ (**5**) exhibits a moderate absorption at 1638 cm^{-1}, indicative of η^1-binding only.

The ^{1}H NMR spectra for **4** and **5** are consistent with η^1-attachment of the allyl ligands (see Experimental Section). The room-temperature ^{1}H NMR spectrum of **3** consists of a single Cp singlet, a single allyl CH quartet, a single allyl terminal CH$_3$ doublet, and an allyl central CH$_3$ singlet. Since molecules of **3** possess no symmetry, the inferred conclusion is that the 1,2,3-trimethylallyl ligand exhibits dynamic behavior in which the ends of the allyl ligand become equivalent and, as a consequence, the two Cp ligands also become equivalent. This was confirmed by variable-temperature ^{1}H NMR spectroscopy. Spectra were measured from −99 to 22 °C (see Experimental Section), yielding a $\Delta G^{\ddagger}$ = 37.3 ± 2.0 kJ/mol [this represents an average of $\Delta G^{\ddagger}$ (−91 °C) = 36.3 ± 2.0 kJ/mol from Cp; $\Delta G^{\ddagger}$ (−78 °C) = 36.9 ± 1.0 kJ/mol from allyl terminal CH$_3$; $\Delta G^{\ddagger}$ (−67 °C) = 38.1 ± 1.0 kJ/mol from allyl CH; as estimated from the respective coalescences]. A mechanism for **3**, whereby the η^3-1,2,3-trimethylallyl ligand becomes η^1 via rupture of the two longest Zr–C bonds, followed by rotation about the remaining Zr–C bond and return to the η^3-bonding mode is consistent with this. Such a mechanism must also give the enantiomeric form (i.e., the C(2) atom of the allyl ligand must point toward the other Cp ring) so as to equilibrate the Cp rings. Such η^3–η^1 isomerization for allyl complexes is well-known.[4,5,19–21] However, this is the lowest barrier yet observed for η^3–η^1 isomerization involving a Zr–allyl complex. This is consistent with the X-ray observation that the η^3-bound 1,2,3-trimethylallyl ligand in **3** is significantly distorted toward an η^1-bound configuration. Indeed, the barrier for isomerization in **3** is 14.2 kJ/mol lower than the abnor-

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(17) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260. (a) We use the following values for van der Waals radii: allyl or Cp carbon, 1.7 Å; allyl methyl, 2.0 Å; Br, 1.85 Å. (b) We use the following values for van der Waals radii: Cp carbon, 1.7 Å; allyl carbon C(1), 2.0 Å.

(18) Hendrik, M. A.; Lemaire, P. J.; Jellinek, F. *J. Organomet. Chem.* **1968**, *14*, 149.

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mally low barrier reported for $Cp^*(\eta^3\text{-}1,1,2\text{-}Me_3allyl)ZrBr_2$ [$\Delta G^* = 51.5$ kJ/mol], which is also distorted toward an η^1-allyl configuration due to steric crowding.[13] A much greater barrier to η^3–η^1 allyl isomerization was observed for $(\eta^3\text{-}C_3H_5)(\eta^4\text{-butadiene})CpZr$ [$\Delta G^* = 79.9$ kJ/mol] in which the allyl ligand does not exhibit any distortion toward η^1.[5] Considered together, the X-ray and variable temperature ^1H NMR data for **3** depict a distortion toward η^1 and a degree of steric congestion unsurpassed by any other η^3-allyl zirconium compound.

Conclusions

Knowing how an allyl ligand will bind to an electron deficient (<18-electron) early transition metal and how easily it will undergo η^3 to η^1 isomerization is important in attempting to understand the reactivity of early-transition-metal allyl complexes. Under what circumstances will an allyl ligand bind η^3 versus η^1? We have previously shown that the $Cp^*(allyl)ZrBr_2$ compounds (allyl = 1,1,2-trimethylallyl and 1,2,3-trimethylallyl) have η^3-bound allyls, although severe distortion toward η^1 did occur for the 1,1,2-trimethylallyl complex.[13] The Cp^*ZrBr_2 portion of these complexes provides a relatively uncrowded environment for the allyl ligand, and so the electronic desire for η^3 outweighs the sterically favored η^1 mode. The Cp_2ZrBr moiety, on the other hand, provides a relatively crowded environment for an allyl ligand. Infrared studies have shown $Cp_2ZrCl(C_3H_5)$ and $Cp_2ZrCl(2\text{-Meallyl})$ to have η^1-bound allyls.[7] We have shown that $Cp_2ZrBr(1,1,2\text{-}Me_3allyl)$, while somewhat crowded, also possesses an η^1-bound allyl. However, $Cp_2ZrBr(1,2,3\text{-}Me_3allyl)$ was severely crowded, with its allyl ligand bound η^3. The question arises, have we increased donor ability via trimethylation to the point where electronic effects outweigh steric considerations to yield a crowded η^3 complex? We believe the answer to be no, and that the 1,2,3-trimethylallyl ligand binds η^3 not because donor ability is significantly enhanced but because η^3 is the more sterically favored mode in this case. This is supported by molecular modeling calculations, which reveal more congestion in the minimized η^1 geometry than in the minimized η^3 form of $Cp_2(1,2,3\text{-}Me_3allyl)ZrBr$.[22] Presumably, the 1,1,2-trimethylallyl ligand is η^1 bound since the bulk at the disubstituted end is too great to allow η^3 in complexes of this type no matter how good a donor the ligand is.

In conclusion, the allyl ligand appears to be an effective probe for determining the relative effect on the donor and steric properties of a ligand upon its methylation. We are continuing with work in this area, with particular interest being directed at the extent of allyl methylation necessary to achieve thermally stable electron-deficient early-transition-metal allyl halide compounds.

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Supplementary Material Available: Tables of thermal parameters (Table III) and hydrogen atom coordinates (Table IV) (3 pages); listings of observed and calculated structure factors (Tables V and VI) (15 pages). Ordering information is given on any current masthead page.

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[22] Modeling calculations were carried out by using an extended version of Allinger's MM2 force field which includes transition metals. The programs were obtained from Serena Software Inc., P.O. Box 3076, Bloomington, IN 47402.

Electrophilic Substitution with Allylic Rearrangement (S_E') Stereochemistry of Trifluoroacetolysis of Some Cyclohex-2-enylmetal Compounds

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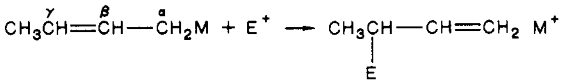
A range of (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)silanes, (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)germanes, and (4-alkylcyclohex-2-enyl)-, (5-alkylcyclohex-2-enyl)-, and (6-alkylcyclohex-2-enyl)stannanes were cleaved to the cycloalkene (and R_3MX) with trifluoroacetic acid-*d* in various solvents. Complete allylic rearrangement (γ-attack) was observed, and the preferred direction of delivery of the electrophile (formally D^+) to the γ-carbon of the allylic triad was determined by detailed ^1H, ^{13}C, and ^2H NMR analyses of the derived dibromides of the various alkyl-substituted cyclohexenes or by direct ^2H NMR analysis and comparisons with ^2H-substituted alkylcyclohexenes of established relative configurations. A highly preferred γ-anti mode of acidolysis is established for all systems, except for the *trans*-4-*tert*-butylcyclohex-2-enyl derivatives, such exception being ascribed to steric impedance of electrophile approach, promoting syn attack. Thus, overall, highly γ-regioselective and anti-stereoselective substitutions (S_E') are observed.

Introduction

Early studies of electrophilic substitutions (with simple protic acid electrophiles) of allyl groups bound to main-group metals such as silicon, tin, or mercury established their facility and high regioselectivity, resulting in essentially complete allylic rearrangement, i.e. attack at the γ-carbon of the allylic triad. Along with kinetic and other data, these facts indicated such demetalations to display the characteristics of S_E' (S_E2' or S_Ei') processes[1-6] (Scheme

Scheme I



$$\overset{\gamma}{CH_3CH}{=}\overset{\beta}{CH}{-}\overset{\alpha}{CH_2}M + E^+ \longrightarrow CH_3\underset{\substack{|\\E}}{CH}{-}CH{=}CH_2\ \ M^+$$

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