Submitted to Organometallics

Synthesis, Structure, and Reactions of \( (\eta^5-C_5H_5)_3Zr \)

W.W. Lukens, Jr. and R.A. Andersen

January 1995
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Lawrence Berkeley Laboratory is an equal opportunity employer.
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Synthesis, Structure, and Reactions of (η⁵-C₅H₅)₃Zr

Wayne W. Lukens, Jr. and Richard A. Andersen*

Department of Chemistry
University of California, Berkeley

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

January 1995

*Address correspondence to this author at
Chemistry Department, University of California, Berkeley, California 94720

This work was partially supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Abstract. $\text{Cp}_3\text{Zr}$ was synthesized by the reduction of $\text{Cp}_4\text{Zr}(\text{where } \text{Cp} = \text{C}_5\text{H}_5)$. $\text{Cp}_3\text{Zr}$ is monomeric in the solid state with three $\text{Cp}$ rings bonded to zirconium and an $\eta^5$-fashion. The nineteen electron metallocene has a single unpaired electron and an axial EPR spectrum in frozen solution. It does not appear to form base adducts but does react by atom abstraction. The observed spectra and reactions are explained using the MO model for $\text{Cp}_3\text{M}$ developed by Bursten and Strittmatter and previously by Lauher and Hoffmann.
Introduction. Only a few tris(cyclopentadienyl) compounds of the d-transition metals have been described and, with the exception of the "pseudolanthanides" Cp3Y1 and Cp3La2, none of them have all three cyclopentadienyl ligands bound in an η5-manner. The crystal structure of Cp3Sc shows that it is a dimer with the two (η5-Cp)2Sc fragments bridged by a pair of C5H5 groups that are η1-bound to each Cp2Sc fragment.3 The crystal structure of the d1 Cp3Ti shows that two rings are bound in an η5-manner and that the third is bound as η2.4 While the crystal structure of the d2 Cp3V is not known, the 1H NMR spectrum of this paramagnetic compound shows two resonances in a 2:1 ratio.5 The spectrum was interpreted as being due two η5-Cp ligands and an η1-Cp ligand which is fluxional making all of the protons of the η1-ligand equivalent. The solid state and solution structure of Cp3Tc and Cp3Re also show that two rings are η5 and one is η1.6-8 Curiously, the two η5-rings are not rotating on the NMR time scale since all 5 protons are inequivalent, and the η1-ring is not fluxional since it has 3 inequivalent protons which are distinct at all temperatures studied.

In contrast to the d-metal complexes, the tris(cyclopentadienyl) compounds of the f-metals (except for lutetium) all have 3 η5-Cp ligands9 and unlike the d-block complexes, the f-block complexes form base adducts.10 As noted by Bursten, two factors are responsible for the difference in reactivity between the f and d metal complexes.11,12 First, the f metals have larger radii reducing steric congestion enough to allow all three Cp ligands to coordinate in an η5-manner. Second, the presence of the low lying f orbitals prevents these complexes from becoming electronically saturated by allowing the metal electrons to fill their f orbitals. The MO description of tris-η5-cyclopentadienyl compounds has been described by Bursten and previously by Lauher and Hoffmann.13-15 For d-transition metals, the three ligands contribute 13 electrons since one ligand-based orbital of a2' symmetry, shown in Figure 1, has no overlap with s, p, or d orbitals. This orbital is entirely ligand based and therefore relatively high in energy. Only one Cp to metal non-bonding metal based orbital is available, and it is largely dz2. Any d-metal complex with more than two electrons is forced to place electrons in high lying antibonding orbitals, and therefore forcing the third cyclopentadienyl ligand to be something other than η5. As previously noted, the f-block metallocenes fill the f orbitals rather than the d orbitals leaving the dz2 orbital empty and available to interact with a Lewis base allowing these metallocenes to form base adducts.
An interesting anomaly among the f-block metallocenes is \([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Th}\).\(^{16}\) This complex has a d\(^1\) rather than an f\(^1\) electronic ground state and unlike the other f-block metallocenes does not appear to form base adducts.\(^{17,18}\) The analogous lanthanide metallocene, tris(cyclopentadienyl)cerium, has an f\(^1\) electronic ground state and forms base adducts.\(^{19}\) We were interested in comparing the reactions of this 6d\(^1\) actinide metallocene to that of a transition metallocene with a d\(^1\) electronic ground state to assess the influence of the electronic ground state upon the reactivity. In order to do this, we had to prepare a compound with three \(\pi^5\)-Cp ligands. Since zirconium(IV) complexes which have three \(\pi^5\)-Cp ligands were known,\(^{14,20,21}\) and since \(\text{Cp}_3\text{Ti}\) was also known\(^{22}\), it seemed likely that \(\text{Cp}_3\text{Zr}\) could be synthesized.

**Results and Discussion.** \(\text{Cp}_3\text{Zr}\) was synthesized by reducing \(\text{Cp}_4\text{Zr}\)\(^{20}\) with potassium graphite\(^{23}\) in toluene from which it was crystallized as shiny, brown, hexagonal plates. In this reaction, only the zirconium reactant and product are soluble allowing for easy separation. \(\text{Cp}_3\text{Zr}\) was also made by reducing \(\text{Cp}_4\text{Zr}\) with sodium naphthalide in tetrahydrofuran. However, while it was possible to prepare \(\text{Cp}_3\text{Zr}\) pure by the former method, the latter always gave \(\text{Cp}_3\text{Zr}\) contaminated with 5-10\% \(\text{Cp}_3\text{ZrH}\).\(^{24}\) The purity was estimated by treating a \(\text{C}_6\text{D}_6\) solution with \(\text{CCl}_4\) and comparing the integration of the cyclopentadienyl resonance before addition of \(\text{CCl}_4\), i.e. due to \(\text{Cp}_3\text{ZrH}\), to the integration of the cyclopentadienyl resonance after addition due to \(\text{Cp}_3\text{ZrCl}\) from the reaction of \(\text{Cp}_3\text{Zr}\) with \(\text{CCl}_4\). The purity could not be determined directly \(\text{Cp}_3\text{Zr}\) is NMR silent. Attempts to reduce \(\text{Cp}_4\text{Zr}\) with t-BuLi analogously to the reduction of \(\text{Cp}_3\text{UCl}\)\(^{25-28}\) or \(\text{Cp}_2\text{ZrX}_2\)\(^{29}\) gave only \(\text{Cp}_3\text{ZrH}\).

The EPR spectrum of \(\text{Cp}_3\text{Zr}\) at room temperature in 2-methyltetrahydrofuran was observed at \(g_{\text{iso}} = 1.977\) with six satellites having \(A_{\text{iso}} = 115\) MHz (41 Gauss) presumably due to coupling to \(^{91}\text{Zr}\). As a frozen glass, the spectral parameters were \(g_{||}=1.999\) and \(g_{\perp}=1.970\); the spectrum is shown in Figure 2. These \(g\) values are consistent with the MO model since an electron in a \(d_{z^2}\) orbital cannot change the value of \(g_{\parallel}\) from that of a free electron by spin-orbit coupling but spin-orbit coupling to the \(d_{xz}\) and \(d_{yz}\) orbitals can lower \(g_{\perp}\).\(^{30}\) The magnetic moment of \(\text{Cp}_3\text{Zr}\) was determined by variable temperature
magnetic susceptibility and was found to be 1.64 B. M. from 5 to 300 K with $\theta = -3.5$ K.

Insert Figures 2 and 3 Here
Insert Tables 1, 2, and 3 Here

The solid state structure of \( \text{Cp}_3\text{Zr} \) is shown in Figure 3. The data collection parameters are given in Table 1, the atomic positions in Table 2, and the distances and angles in Table 3. The molecule possess crystallographic $\overline{6} (C_3h)$ symmetry and is monomeric. The nearest intermolecular Zr-H and Zr-C distances are 4.29 Å and 5.00 Å, respectively. Surprisingly, the average Zr-C distance is 2.58 Å, the same as the average Zr-C distance for the three $\eta^5$-Cp ligands in \( \text{Cp}_4\text{Zr} \).\(^{20}\) As noted above, the Cp rings of \( \text{Cp}_3\text{Zr} \) are postulated to have a high lying non-bonding orbital of $a_2'$ symmetry which is not stabilized by the metal center.\(^{14}\) The Cp rings of \( \text{Cp}_3\text{Zr} \) are distorted in the manner consistent with this lack of stabilization. This orbital, Figure 1, possess a node between C1 and C2, the presence of which is reflected in the longer C1-C2 distance of 1.420(5) Å relative to the shorter C2-C3 and C1-C1' distances of 1.395(5) Å and 1.376(7) Å, respectively. In the analogous \( \text{Cp}^*_3\text{Sm} \)\(^{31} \) (Cp* is MesCs) which crystallizes in the same space group also at a site of $\overline{6}$ symmetry, this the Cp* ligands are not distorted in this manner, consistent with stabilization of this orbital by the \( f_y(3x^2-y^2) \) orbital as predicted by Bursten and Strittmatter.\(^{13,14}\) While other tris-cyclopentadienyl compounds have been characterized by crystallography, these compounds do not have pentasubstituted Cp rings;\(^{32}\) substitution of the Cp removes the degeneracy in the $E_2$ orbital of the ligand also causing a distortion of the ligand.\(^{33,34}\)

Insert Scheme 1 Here

Some reactions of \( \text{Cp}_3\text{Zr} \) are shown in Scheme 1. We were unable to isolate or obtain evidence for the existence of base adducts of \( \text{Cp}_3\text{Zr} \) with THF, pyridine, or \( \text{OP(OCH}_2\text{)}_3\text{CEt} \). In addition, \( \text{Cp}_3\text{Zr} \) did not appear to react with carbon monoxide or ethylene. In all cases, only \( \text{Cp}_3\text{Zr} \) was recovered as determined by EPR spectroscopy, and NMR spectroscopy showed no evidence of dimagnetic zirconium species. While \( \text{Cp}_3\text{Zr} \) did not form base adducts, it did
react with CCl₄ and t-BuNC to form the oxidation products Cp₃ZrCl and Cp₃ZrCN, respectively. When treated with one equivalent of water in benzene, Cp₃Zr gave [Cp₂ZrO]₃ and CpH. When treated with half an equivalent of water, Cp₃Zr gave a mixture of [Cp₂ZrO]₃ and Cp₃ZrH, presumably by the series of steps shown in Equation 1.

\[
2 \text{Cp₃Zr} + \text{H₂O} \rightarrow \text{Cp₃ZrH} + \{\text{Cp₃ZrOH}\}
\]

\[
\{\text{Cp₃ZrOH}\} \rightarrow \frac{1}{3} [\text{Cp₂ZrO}]₃ + \text{CpH}
\]

Steric effects cannot account for the inability of Cp₃Zr to form base adducts since compounds of Zr(IV) exist which have three η⁵-Cp ligands plus an additional ligand coordinated to the Zr center. In addition, Zr(III) should be larger than Zr(IV) for a given coordination number. Rather, the lack of reactivity is most likely due to its electronic structure. When a Lewis base interacts with Cp₃Zr, the d₂2 orbital is destabilized becoming the σ* orbital with respect to the incoming ligand. Since the unpaired electron occupies this orbital, the interaction with the incoming ligand becomes less favorable. However, the unpaired electron does not prevent single-electron reactions. When the ligand is a one electron donor, as is the case for OH, CN, and Cl, the unpaired electron in the a₁ (d₂2 parentage) orbital can share this bonding orbital with the electron from the one electron ligand while the antibonding orbital remains unoccupied.

In order to compare the reactivity of Cp₃Zr to that of a transition metal complex in which all three Cp rings are not η⁵-coordinated Cp rings, the behavior of Cp₃Ti was briefly examined.

Insert Scheme 2 Here

The reactivity of Cp₃Ti as shown in Scheme 2 is quite different from that of Cp₃Zr. While Cp₃Zr does not react with CO, Cp₃Ti forms Cp₂Ti(CO)₂ when treated with CO. Additionally, although Cp₃Ti reacts with CCl₄ and t-BuNC, the products are Cp₂TiCl₂ and [Cp₂TiCN]₄, respectively. Treatment of Cp₃Ti with one-half of an equivalent of water produced (Cp₂Ti)₂(μ-O) cleanly. The reactivity of Cp₃Ti is consistent with a bent metallocene in which the η²-Cp ligand behaves somewhat analogously to a weakly bound alkyl group.
Conclusion. The synthesis, structure, and chemical behavior of Cp₃Zr have been described. Its reactivity is controlled by the presence of an electron in the d₂₂ orbital. Since [(Me₃Si)₂C₅H₃]₃Th behaves similarly,¹⁸ and since its electronic ground state is 6d¹, it seems likely that the electronic structure controls the reactivity in this case as well. Cp₃Ti, which also has a single d electron but does not have the same molecular structure, reacts differently. In light of the similarity of the reactivity of Cp₃Zr to that of the thorium metallocene, perhaps in this case, it is useful to think of zirconium as "a little thorium".

Experimental. All reactions and manipulations were carried out in an inert atmosphere using standard Schlenk and dry box techniques as described previously.⁴⁰

Cp₃Zr. a) From Cp₄Zr²⁰ and KC₈²³. Cp₄Zr (1.00 g, 2.84 mmol), dissolved in 200 mL of toluene, was added slowly to a slurry of KC₈ (0.42 g, 3.1 mmol) in 10 mL of toluene using a cannula. The reaction mixture was allowed to stir overnight. The solution was filtered giving a deep brown solution. The volume of the filtrate was reduced to ca. 175 mL, and the solution was heated to 80 °C to redissolve the solid. The solution was placed in a -20 °C freezer. After three days, the mother liquor was removed yielding Cp₃Zr (0.46 g, 56%) as thin hexagonal plates. The compound did not melt to 300 °C. IR: 3130 (m), 1023 (s), 1012 (s), 912 (s), 845 (s), 819 (s), 790 (s) 730 (m, sh), 285 (s), 250 (s) cm⁻¹. MS(found, calc) 285 (100,100), 286 (85,39), 287 (80,38), 288 (28,6), 289 (75,34). Anal. Calc. for C₁₅H₁₅Zr: C, 62.9; H, 5.28; Found: C, 63.1; H, 5.32.

b) From Cp₄Zr²⁰ and NaC₁₀H₈. Naphthalene (0.37 g, 2.8 mmol) was added to a flask with a large excess of sodium slices followed by the addition of 50 mL of tetrahydrofuran. The solution quickly became green and the contents of the flask were stirred for 12 hours. The NaC₁₀H₈ solution was added using a cannula to Cp₄Zr (1.00 g, 2.84 mmol) dissolved in 100 mL of tetrahydrofuran. The reaction mixture became red-brown and it was allowed to stir for 12 hours. The tetrahydrofuran was removed under reduced pressure and the naphthalene was removed by heating the Schlenk tube to 80 °C under dynamic vacuum for 4 hours. The solid residue was suspended in 200 mL of toluene then filtered and cooled to -20 °C. After 10 days, brown plates were isolated (0.40 g), but they were contaminated with 12 % Cp₃ZrH²⁴ as judged by the following method.

Reaction of Cp₃Zr with CCl₄. In an NMR tube, a benzene solution of Cp₃Zr was treated with an excess of CCl₄ using a syringe. The color immediately...
changed from green-brown to yellow-orange. The $^1$H NMR spectrum of the reaction mixture showed it to be Cp$_3$ZrCl.\textsuperscript{41} In this way, the purity of the Cp$_3$Zr was estimated by comparing the integrations of the Cp peaks relative to benzene before and after the addition of CCl$_4$. It must be noted that the chemical shift of the protons of Cp$_3$ZrCl was reported as $\delta = 6.05$ ppm in CDCl$_3$.\textsuperscript{41} We find the resonance of Cp$_3$ZrCl, prepared as described in ref. \textsuperscript{41}, at 5.67 ppm in C$_6$D$_6$.

**Reaction of Cp$_3$Ti with CCl$_4$.** In an NMR tube, a benzene solution of Cp$_3$Ti\textsuperscript{22,36,37} was treated with an excess of CCl$_4$ added using a syringe. The color immediately changed from dark green to dark red. The $^1$H NMR spectrum of the reaction mixture showed it to be Cp$_2$TiCl$_2$.

**Reaction of Cp$_4$Zr with t-BuLi.** Cp$_4$Zr(0.50 g, 1.4 mmol) was dissolved in 125 mL of hot toluene and the solution was cooled to room temperature. t-BuLi (0.64 mL, 2.24 M in hexane) was added by syringe. The solution became viscous and a colorless precipitate appeared. After 1 hour, the mixture was filtered giving a pale yellow solution out of which white needles formed on standing. The solution was cooled to -80 °C to complete the crystallization. After three days, the mother liquor was removed from the small white needles using a cannula (0.29 g, 71 %). $^1$H-NMR(not previously reported):$\delta = 5.28$ (15H), 2.83 (1H). The IR spectrum was identical to that previously reported.\textsuperscript{24}

**Cp$_3$ZrCN • 1/3C$_7$H$_8$:** Cp$_3$Zr (0.30 g, 1.0 mmol) was dissolved in 100 mL of warm toluene. t-BuNC (0.10 g, 1.2 mmol) was added using a syringe. The solution instantly became dark then lightened to red and finally to orange-red. The solution was filtered although no precipitate was evident and the volume was reduced to ca. 25 mL. The solution was cooled to -20 °C. After two weeks, the slightly cloudy solution was refiltered and cooled to -80 °C. After 3 weeks, the mother liquor was removed yielding orange-red microcrystals (0.04 g, 12 %). MP 220 °C (dec.). $^1$H NMR:$\delta = 5.39$($^{15}$H, C$_5$H$_5$), 2.10($^{1}$H,$^{1}$H,$^{3}$CC$_6$H$_5$). IR: 3100 (m), 3080 (w), 2130 (w), 1260 (w), 1020 (m), 1010 (m), 840 (m), 825 (s), 810 (s), 800 (s), 730 (w), 605 (w), 375 (w), 290 (m), 235 (m) cm$^{-1}$. MS(found, calc.): 311(100,100), 312 (43,38), 313 (38,37), 315 (34,32). Anal. Calc. for C$_{55}$H$_{53}$N$_2$Zr$_3$: C, 64.2; H, 5.19; N, 4.08; Found: C, 63.7; H, 5.37; N, 3.81.

**Reaction of Cp$_3$Ti with t-BuNC.** Cp$_3$Ti\textsuperscript{22,36,37}(0.50 g, 2.1 mmol) was dissolved in 80 mL of toluene, t-BuNC (0.25 mL, 2.3 mmol) was added using a syringe. The green solution immediately became deep purple. The solution was allowed to stand for 4 hours then filtered and cooled to -20 °C. After 2 weeks, the mother liquor was removed using a cannula leaving a purple powder. The IR spectrum,
color, and solubility matched that reported for [Cp2TiCN]4. MS(found, calc.): 814(36,40), 815(55,53), 816(100,100), 817(68,71), 818(42,47), 819(16,21).

Reactions of Cp3Zr with water. a) With 1 equivalent of water. Cp3Zr (1.8 mg, 6.4 μmol) was dissolved in 0.25 mL of C6D6. Water (0.1 μmol, 6 μmol) was added using a syringe. The initially green-brown solution became cloudy and a white precipitate formed. The only species present in solution were [Cp2ZrO]3 (δ = 6.21(s) ppm) and C5H6 (δ = 6.40(m), 2.68(m) ppm).

b) With 0.5 equivalents of water. Cp3Zr (0.26 g, 0.91 mmol) was dissolved in 40 mL of tetrahydrofuran and cooled to -78 °C. Water (8.2 μL, 0.45 mmol) was dissolved in 30 mL tetrahydrofuran and slowly added to the solution of Cp3Zr. The solution was allowed to warm to room temperature and became pale and cloudy as the temperature increased. After stirring for 12 hours, the tetrahydrofuran was removed under reduced pressure and 100 mL toluene was added. The mixture was heated to 90 °C then allowed to cool to room temperature and settle which gave a clear solution and a white precipitate which was removed by filtration. The white solid was almost insoluble in benzene and its IR and 1H NMR spectra matched those reported for [Cp2ZrO]3. Cooling to -80 °C caused the precipitation of a white solid which was found to be a mixture of Cp3ZrH24 and [Cp2ZrO]3 by IR and 1H NMR spectroscopy.

Attempted reactions of Cp3Zr with ligands. Cp3Zr was dissolved in toluene. Ligands were added as toluene solution (OP(OCH2)3CET), neat (pyridine), or as a gas in a thick-walled pressure bottle (CO, and C2H4). After stirring for 12 hr, no color change was noted. The solutions were filtered and the volume of the mother liquor was reduced. Cooling to -20 °C produced the characteristic thin, brown, hexagonal crystals of Cp3Zr. The spectra were identical to that of Cp3Zr.

Solid State Structure of Cp3Zr: Small, brown, hexagonal prisms were grown by slowly cooling a diethyl ether solution of the compound. The crystals were placed in a petri dish and covered with Paratone N. A crystal measuring 0.20 x 0.20 x 0.40 mm was placed on the end of a 0.2 mm quartz capillary tube with a drop of Paratone N. The crystal was transferred to an Enraf-Nonius CAD-4 automated diffractometer and cooled to -108 °C under a cold stream of nitrogen previously calibrated by a thermocouple placed in the sample position. The crystal was centered in the beam. Automatic peak search and indexing procedures indicated that the crystal had a trigonal cell and yielded the unit cell parameters. The cell parameters and data collection parameters are given in Table I.
The data collected was \((\pm h, \pm k, \pm l)\). The 851 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz-polarization effects. Inspection of the intensity standards showed a very severe decay at the middle of the data collection, so the last half of the data was discarded (it was redundant). No decay correction was applied to the remaining 532 data. Reflection condition \((0, 0, I) I=2n\) was observed and the 5 \((0,0,I) I=2n+1\) reflections were discarded. Azimuthal scan data showed a difference of \(I_{\text{min}}/I_{\text{max}} = 0.78\). An empirical absorption was applied. Finally, redundant data were averaged yielding 266 unique data of which 245 data had \(F_0 > 3\sigma(F_0)\).

The cell volume of 570 cm\(^3\) indicated that \(Z = 2\) by comparison with the known structure of \(\text{Cp}_3\text{Ti}\). Systematic absences suggested that the space group was either \(P6_3\) of \(P6_3/m\) with the molecule sitting on a site with 3 or \(\bar{6}\) symmetry. The zirconium position was obtained by solving the Patterson map. Initially, the solution was attempted in \(P6_3\). The carbon positions were obtained by difference Fourier searches after refining on the zirconium position. With the carbon atoms refined isotropically and the zirconium atom refined anisotropically, the \(R\) value was 0.051. However, when the carbon atoms were refined anisotropically, the thermal parameters seemed to be highly correlated, and the carbon atoms went non-positive definite. Since the molecule appeared to have \(\bar{6}\) symmetry, the space group was changed to \(P6_3/m\). With the carbon atoms refined isotropically and the zirconium atom refined anisotropically, the \(R\) value was 0.052. In addition, the carbon atoms could be refined anisotropically. After the anisotropic refinement of the carbon and zirconium atoms had converged, a difference Fourier search located the three hydrogen atom positions. The hydrogen atoms were refined isotropically. Toward the end of the refinement, an examination of the extinction test listing showed that secondary extinction was occurring, so a secondary extinction coefficient was included and refined upon.

The final residuals for 39 variables refined against the 245 data with \(F_0 > 3\sigma(F_0)\) were \(R = 2.9\%\), \(R_W = 3.25\%\), and \(\text{GOF} = 1.179\). The \(R\) value for all data (including unobserved reflections) was 3.2\%. The quantity minimized by the least squares refinements was \(w(I(F_0 - I_C)^2)\), where \(w\) is the weight given to a particular reflection. The \(p\)-factor, used to reduce the weight of intense reflections, was set to 0.03 initially, but later changed to 0.04. The analytical forms of the scattering factors for neutral atoms were used. All non-hydrogen
scattering factors were corrected for both real and imaginary components of anomalous dispersion.

Inspection of the residuals in the range of \(\sin(\theta/\lambda), |F_o|\), and parity and value of the individual indexes showed no trend other than the one previously mentioned in correction with secondary extinction. Three reflections had anomalously high values of \(w x \Delta^2\), and were weighted to zero toward the end of the refinement. The largest positive and negative peaks in the final difference Fourier map had electron densities of 0.58 and -0.65 respectively and were associated with the zirconium atom.

**Acknowledgment.** The authors would like to thank Dr. Fred Hollander for assistance with the crystallography and Drs. Norman Edelstein and Wing Kot for helpful discussions and for making the data on the reactivity of \([(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Th}\) available. W. L. would like to thank the National Science Foundation for a graduate fellowship. This work was partially supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

**Supplementary Material Available:** A listing of all data reduction formulas, bond lengths, angles, and anisotropic thermal parameters along with a table of \(F_o\) and \(F_c\) for \(\text{Cp}_3\text{Zr}\) (6 pages). Ordering information is given on any current masthead page.
Table 1: Crystal Data for Cp3Zr

<table>
<thead>
<tr>
<th>Space group:</th>
<th>P63/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>8.003(1)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>8.003(1)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>10.276(2)</td>
</tr>
<tr>
<td>α(deg)</td>
<td>90</td>
</tr>
<tr>
<td>β(deg)</td>
<td>90</td>
</tr>
<tr>
<td>γ(deg)</td>
<td>120</td>
</tr>
<tr>
<td>Cell Volume (cm³)</td>
<td>570.0</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>d(calc.) g/cm³</td>
<td>1.668</td>
</tr>
<tr>
<td>μ(calc) 1/cm</td>
<td>9.148</td>
</tr>
<tr>
<td>radiation</td>
<td>MoKα</td>
</tr>
<tr>
<td>monochrometer</td>
<td>highly oriented graphite</td>
</tr>
<tr>
<td>scan range, type</td>
<td>3°≤2θ≤45°, θ-2θ</td>
</tr>
<tr>
<td>scan speed (deg/min)</td>
<td>2.8</td>
</tr>
<tr>
<td>scan width, deg.</td>
<td>Δθ=0.90 + 0.35tan(θ)</td>
</tr>
<tr>
<td>reflections collected</td>
<td>851(±h,+k,+l), 532 used</td>
</tr>
<tr>
<td>unique reflections</td>
<td>266</td>
</tr>
<tr>
<td>reflections F_0^2&gt;3σ(F_0^2)</td>
<td>245</td>
</tr>
<tr>
<td>R, %</td>
<td>2.97</td>
</tr>
<tr>
<td>Rw, %</td>
<td>3.25</td>
</tr>
<tr>
<td>R_all, %</td>
<td>3.20</td>
</tr>
<tr>
<td>GOF</td>
<td>1.179</td>
</tr>
<tr>
<td>Largest Δ/σ in final least squares cycle</td>
<td>0</td>
</tr>
</tbody>
</table>
**Table 2: Atomic Coordinates and Isotropic Thermal Parameters for Cp₃Zr**

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>-0.333</td>
<td>0.333</td>
<td>0.25</td>
<td>1.33(1)</td>
</tr>
<tr>
<td>C1</td>
<td>0.0168(3)</td>
<td>0.5827(3)</td>
<td>0.3170(3)</td>
<td>1.44(5)</td>
</tr>
<tr>
<td>C2</td>
<td>-0.1032(4)</td>
<td>0.6551(3)</td>
<td>0.3607(3)</td>
<td>1.66(6)</td>
</tr>
<tr>
<td>C3</td>
<td>-0.1683(5)</td>
<td>0.7062(5)</td>
<td>0.25</td>
<td>1.47(8)</td>
</tr>
<tr>
<td>H1</td>
<td>0.088(4)</td>
<td>0.538(3)</td>
<td>0.366(3)</td>
<td>2.1(6)</td>
</tr>
<tr>
<td>H2</td>
<td>-0.125(4)</td>
<td>0.670(3)</td>
<td>0.452(2)</td>
<td>2.4(6)</td>
</tr>
<tr>
<td>H3</td>
<td>-0.245(4)</td>
<td>0.749(5)</td>
<td>0.25</td>
<td>1.0(8)</td>
</tr>
<tr>
<td>Bond</td>
<td>Distance (Å)</td>
<td>Bond</td>
<td>Distance (Å)</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Zr - C1</td>
<td>2.592(3)</td>
<td>C1 - C2</td>
<td>1.420(5)</td>
<td></td>
</tr>
<tr>
<td>Zr - C2</td>
<td>2.564(3)</td>
<td>C2 - C3</td>
<td>1.395(5)</td>
<td></td>
</tr>
<tr>
<td>Zr - C3</td>
<td>2.590(4)</td>
<td>C1 - C1'</td>
<td>1.376(7)</td>
<td></td>
</tr>
<tr>
<td>C1 - H1</td>
<td>0.95(4)</td>
<td>C1' - C1 - C2</td>
<td>108.4(2)°</td>
<td></td>
</tr>
<tr>
<td>C2 - H2</td>
<td>0.97(3)</td>
<td>C1 - C2 - C3</td>
<td>106.8(3)°</td>
<td></td>
</tr>
<tr>
<td>C3 - H3</td>
<td>0.84(5)</td>
<td>C2 - C3 - C2</td>
<td>109.2(4)°</td>
<td></td>
</tr>
</tbody>
</table>
References.
(38) Fischer, E. O.; Löchner, A. Z. *Naturforsch.* 1960, 15b, 266.
Figure 1: The non-bonding a_2^" orbital of Cp_3Zr. The shadings represent opposite signs of the π-bonding p orbitals of the Cp ligands.
Figure 2: The EPR spectrum of Cp₃Zr in 2-methyltetrahydrofuran at 100 K.
Figure 3: An ORTEP drawing of $\text{Cp}_3\text{Zr}$ with 50% thermal ellipsoids.
Scheme 1: Some reactions of Cp₃Zr

Cp₄Zr + KC₈ → Cp₃Zr

THF, pyridine, or O=P O → N. R.

CO, C₂H₄ → N. R.

CCl₄ → Cp₃ZrCl

t-BuNC → Cp₃ZrCN

1 H₂O → [Cp₂ZrO]₃

1/2 H₂O → [Cp₃ZrH]₉ → [Cp₂ZrO]₉
Scheme 2: Some reactions of $\text{Cp}_3\text{Ti}$