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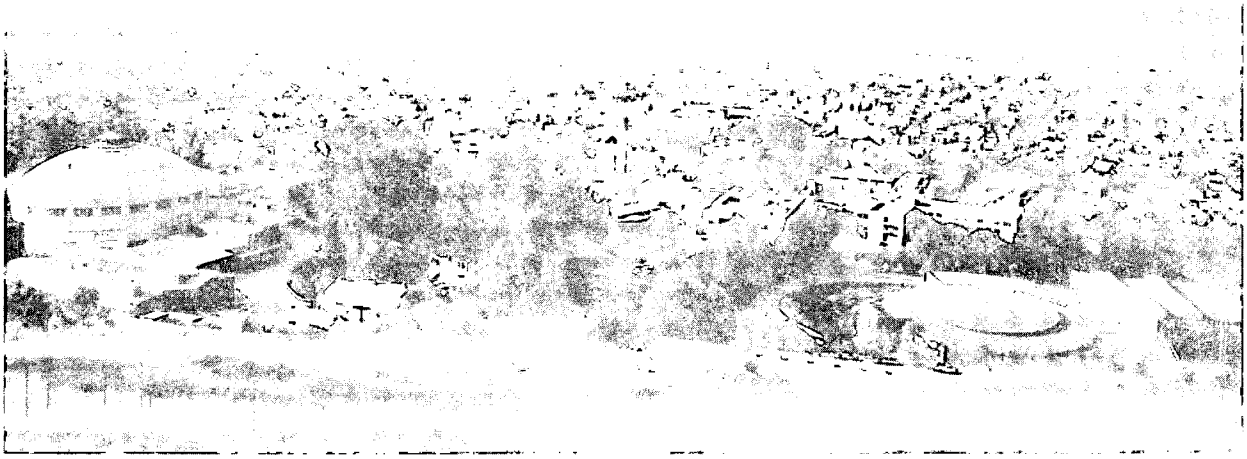

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Synthesis, Structure, and Reactions of $(\eta^5\text{-}C_5H_5)_3Zr$

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Abstract. Cp_3Zr was synthesized by the reduction of Cp_4Zr(where Cp = C_5H_5). Cp_3Zr is monomeric in the solid state with three Cp rings bonded to zirconium and an η^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 Cp_3M 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" Cp_3Y[1] and Cp_3La[2], none of them have all three cyclopentadienyl ligands bound in an η^5-manner. The crystal structure of Cp_3Sc shows that it is a dimer with the two $(\eta^5\text{-}Cp)_2Sc$ fragments bridged by a pair of C_5H_5 groups that are η^1-bound to each Cp_2Sc fragment.[3] The crystal structure of the d^1 Cp_3Ti shows that two rings are bound in an η^5-manner and that the third is bound as η^2.[4] While the crystal structure of the d^2 Cp_3V 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 η^5-Cp ligands and an η^1-Cp ligand which is fluxional making all of the protons of the η^1-ligand equivalent. The solid state and solution structure of Cp_3Tc and Cp_3Re also show that two rings are η^5 and one is η^1.[6-8] Curiously, the two η^5-rings are not rotating on the NMR time scale since all 5 protons are inequivalent, and the η^1-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 η^5-Cp ligands[9] 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 η^5-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-η^5-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 a_2' 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 d_z2. 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 η^5. As previously noted, the f-block metallocenes fill the f orbitals rather than the d orbitals leaving the d_z2 orbital empty and available to interact with a Lewis base allowing these metallocenes to form base adducts.

Insert Figure 1 here

An interesting anomaly among the f-block metallocenes is $[(Me_3Si)_2C_5H_3]_3Th$.[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 states 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 η^5-Cp ligands. Since zirconium(IV) complexes which have three η^5-Cp ligands were known,[14,20,21] and since Cp_3Ti was also known[22], it seemed likely that Cp_3Zr could be synthesized.

Results and Discussion. Cp_3Zr was synthesized by reducing Cp_4Zr[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. Cp_3Zr was also made by reducing Cp_4Zr with sodium naphthalide in tetrahydrofuran. However, while it was possible to prepare Cp_3Zr pure by the former method, the latter always gave Cp_3Zr contaminated with 5-10 % Cp_3ZrH.[24] The purity was estimated by treating a C_6D_6 solution with CCl_4 and comparing the integration of the cyclopentadienyl *resonance before addition of CCl_4, i.e. due to Cp_3ZrH, to the integration of the cyclopentadienyl resonance after addition due to Cp_3ZrCl from the reaction of Cp_3Zr with CCl_4. The purity could not be determined directly Cp_3Zr is NMR silent.* Attempts to reduce Cp_4Zr with *t*-BuLi analogously to the reduction of Cp_3UCl[25-28] or Cp_2ZrX_2[29] gave only Cp_3ZrH.

The EPR spectrum of Cp_3Zr at room temperature in 2-methyltetrahydrofuran was observed at $g_{iso} = 1.977$ with six satellites having $A_{iso} = 115$ MHz (41 Gauss) presumably due to coupling to ^{91}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 $g_{||}$ 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 Cp_3Zr was determined by variable temperature

magnetic susceptibility and was found to be 1.64 B. M. from 5 to 300 K with θ = -3.5 K.

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

The solid state structure of Cp_3Zr 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 $\bar{6}$ (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 η^5-Cp ligands in Cp_4Zr.[20] As noted above, the Cp rings of Cp_3Zr 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 Cp_3Zr 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 Cp^*_3Sm[31] (Cp^* is Me_5C_5) which crystallizes in the same space group also at a site of $\bar{6}$ symmetry, this the Cp^* ligands are not distorted in this manner, consistent with stabilization of this orbital by the $f_{y(3x2-y2)}$ 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 Cp_3Zr are shown in Scheme 1. We were unable to isolate or obtain evidence for the existence of base adducts of Cp_3Zr with THF, pyridine, or $OP(OCH_2)_3CEt$. In addition, Cp_3Zr did not appear to react with carbon monoxide or ethylene. In all cases, only Cp_3Zr was recovered as determined by EPR *spectroscopy,* and NMR spectroscopy *showed no evidence of dimagnetic zirconium species.* While Cp_3Zr did not form base adducts, it did

react with CCl_4 and *t*-BuNC to form the oxidation products Cp_3ZrCl and Cp_3ZrCN, respectively. When treated with one equivalent of water in benzene, Cp_3Zr gave $[Cp_2ZrO]_3$[35] and CpH. When treated with half an equivalent of water, Cp_3Zr gave a mixture of $[Cp_2ZrO]_3$[35] and Cp_3ZrH[24] presumably by the series of steps shown in Equation 1.

$$2\ Cp_3Zr + H_2O \rightarrow Cp_3ZrH + \{Cp_3ZrOH\}$$
$$\{Cp_3ZrOH\} \rightarrow 1/3\ [Cp_2ZrO]_3 + CpH \qquad (1)$$

Steric effects cannot account for the inability of Cp_3Zr to form base adducts since compounds of Zr(IV) exist which have three η^5-Cp ligands plus an additional ligand coordinated to the Zr center. In addition, Zr(III) should be larger than Zr(IV) for a give coordination number. Rather, the lack of reactivity is most likely due to its electronic structure. When a Lewis base interacts with Cp_3Zr, the d_z2 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 a_1 (d_z2 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 Cp_3Zr to that of a transition metal complex in which all three Cp rings are not η^5-coordinated Cp rings, the behavior of Cp_3Ti was briefly examined.

Insert Scheme 2 Here

The reactivity of Cp_3Ti[22,36,37] as shown in Scheme 2 is quite different from that of Cp_3Zr. While Cp_3Zr does not react with CO, Cp_3Ti forms $Cp_2Ti(CO)_2$ when treated with CO.[38] Additionally, although Cp_3Ti reacts with CCl_4 and *t*-BuNC, the products are Cp_2TiCl_2 and $[Cp_2TiCN]_4$,[39] respectively. Treatment of Cp_3Ti with one-half of an equivalent of water produced $(Cp_2Ti)_2(\mu\text{-}O)$ cleanly.[40] The reactivity of Cp_3Ti is consistent with a bent metallocene in which the η^2-Cp ligand behaves somewhat analogously to a weakly bound alkyl group.

Conclusion. The synthesis, structure, and *chemical behavior* of Cp_3Zr have been described. Its reactivity is controlled by the presence of a electron in the d_z2 orbital. Since $[(Me_3Si)_2C_5H_3]_3Th$ *behaves similarly*,[18] and since its electronic ground state is $6d^1$, it seems likely that the electronic structure controls the reactivity in this case as well. Cp_3Ti, 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 Cp_3Zr 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]

Cp_3Zr. a) From Cp_4Zr[20] and KC_8[23]. Cp_4Zr(1.00g, 2.84 mmol), dissolved in 200 mL of toluene, was added slowly to a slurry of KC_8 (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 Cp_3Zr (0.46g, 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 $C_{15}H_{15}Zr$: C, 62.9; H, 5.28; Found: C, 63.1; H, 5.32.

b) From Cp_4Zr[20] and $NaC_{10}H_8$. 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 $NaC_{10}H_8$ solution was added using a cannula to Cp_4Zr (1.00g, 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 % Cp_3ZrH[24] as judged by the following method.

Reaction of Cp_3Zr with CCl_4. In an NMR tube, a benzene solution of Cp_3Zr was treated with an excess of CCl_4 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_3ZrCl.[41] In this way, the purity of the Cp_3Zr 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_3ZrCl was reported as $\delta = 6.05$ ppm in $CDCl_3$.[41] We find the resonance of Cp_3ZrCl, prepared as described in ref. [41], at 5.67 ppm in C_6D_6.

Reaction of Cp_3Ti with CCl_4. In an NMR tube, a benzene solution of Cp_3Ti[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_2TiCl_2.

Reaction of Cp_4Zr with *t*-BuLi. Cp_4Zr(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.[24]

$Cp_3ZrCN \cdot 1/3C_7H_8$: Cp_3Zr (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:$\delta = 5.39$(15H, C_5H_5), 2.10(1H,$H_3CC_6H_5$). 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 $C_{55}H_{53}N_3Zr_3$: C, 64.2; H, 5.19; N, 4.08; Found: C, 63.7; H, 5.37; N, 3.81.

Reaction of Cp_3Ti with *t*-BuNC. Cp_3Ti[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 $[Cp_2TiCN]_4$.[39,42] MS(found, calc.): 814(36,40), 815(55,53), 816(100,100), 817(68,71), 818(42,47), 819(16,21).

Reactions of Cp_3Zr with water. a) With 1 equivalent of water. Cp_3Zr(1.8 mg, 6.4 μmol) was dissolved in 0.25 mL of C_6D_6. 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 $[Cp_2ZrO]_3$ (δ = 6.21(s) ppm)[35], and C_5H_6 (δ = 6.40(m), 2.68(m) ppm).

b) With 0.5 equivalents of water. Cp_3Zr (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 Cp_3Zr. 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 $[Cp_2ZrO]_3$.[35] Cooling to -80 °C caused the precipitation of a white solid which was found to be a mixture of Cp_3ZrH[24] and $[Cp_2ZrO]_3$ [35] by IR and ^1H NMR spectroscopy.

Attempted reactions of Cp_3Zr with ligands. Cp_3Zr was dissolved in toluene. Ligands were added as toluene solution ($OP(OCH_2)_3CEt$), neat (pyridine), or as a gas in a thick-walled pressure bottle (CO, and C_2H_4). 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 Cp_3Zr. The spectra were identical to that of Cp_3Zr.

Solid State Structure of Cp_3Zr: 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 (±h, +k, +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, l) l=2n was observed and the 5 (0,0,l) l=2n+1 reflections were discarded. Azimuthal scan data showed a difference of $I_{min}/I_{max} = 0.78$. An empirical absorption was applied. Finally, redundant data were averaged yielding 266 unique data of which 245 data had $F_o > 3\sigma(F_o)$.

The cell volume of 570 cm^3 indicated that Z = 2 by comparison with the known structure of Cp_3Ti. 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 $F_o > 3\sigma(F_o)$ were R = 2.9 %, $R_w = 3.25$ %, and GOF =1.179. The R value for all data (including unobserved reflections) was 3.2 %. The quantity minimized by the least squares refinements was $w(|F_o|-|F_c|)^2$, 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 $w \times \Delta^2$, 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.

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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 Cp_3Zr (6 pages). Ordering information is given on any current masthead page.

Table 1: Crystal Data for Cp3Zr

Space group:	$P6_3/m$
a(Å)	8.003(1)
b(Å)	8.003(1)
c(Å)	10.276(2)
α(deg)	90
β(deg)	90
γ(deg)	120
Cell Volume (cm^3)	570.0
Z	2
d(calc.) g/cm^3	1.668
μ(calc) 1/cm	9.148
radiation	MoKα
monochrometer	highly oriented graphite
scan range, type	$3° \leq 2\theta \leq 45°$, θ-2θ
scan speed (deg/min)	2.8
scan width, deg.	$\Delta\theta = 0.90 + 0.35\tan(\theta)$
reflections collected	851($\pm$h,+k,+l), 532 used
unique reflections	266
reflections $F_o^2 > 3\sigma(F_o^2)$	245
R, %	2.97
R_w, %	3.25
R_{all}, %	3.20
GOF	1.179
Largest Δ/σ in final least squares cycle	0

Table 2: Atomic Coordinates and Isotropic Thermal Parameters for Cp_3Zr

Atom	X	Y	Z	B(Å^2)
Zr	-0.333	0.333	0.25	1.33(1)
C1	0.0168(3)	0.5827(3)	0.3170(3)	1.44(5)
C2	-0.1032(4)	0.6551(3)	0.3607(3)	1.66(6)
C3	-0.1683(5)	0.7062(5)	0.25	1.47(8)
H1	0.088(4)	0.538(3)	0.366(3)	2.1(6)
H2	-0.125(4)	0.670(3)	0.452(2)	2.4(6)
H3	-0.245(4)	0.749(5)	0.25	1.0(8)

Table 3: Selected Distances and Angles in Cp_3Zr

Zr - C1	2.592(3) Å	C1 - C2	1.420(5) Å
Zr - C2	2.564(3) Å	C2 - C3	1.395(5) Å
Zr - C3	2.590(4) Å	C1 - C1'	1.376(7) Å
C1 - H1	0.95(4) Å	C1'-C1-C2	108.4(2) °
C2 - H2	0.97(3) Å	C1-C2-C3	106.8(3) °
C3 - H3	0.84(5) Å	C2-C3-C2	109.2(4) °

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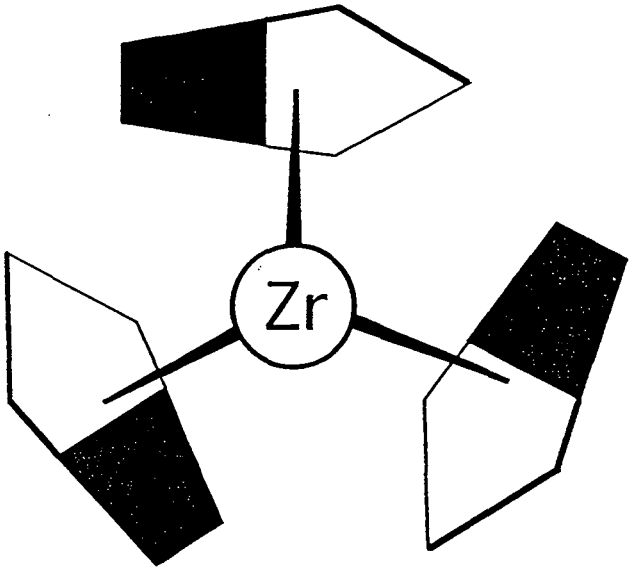


Figure 1: The non-bonding a_2'' orbital of Cp_3Zr. The shadings represent opposite signs of the π-bonding p orbitals of the Cp ligands.

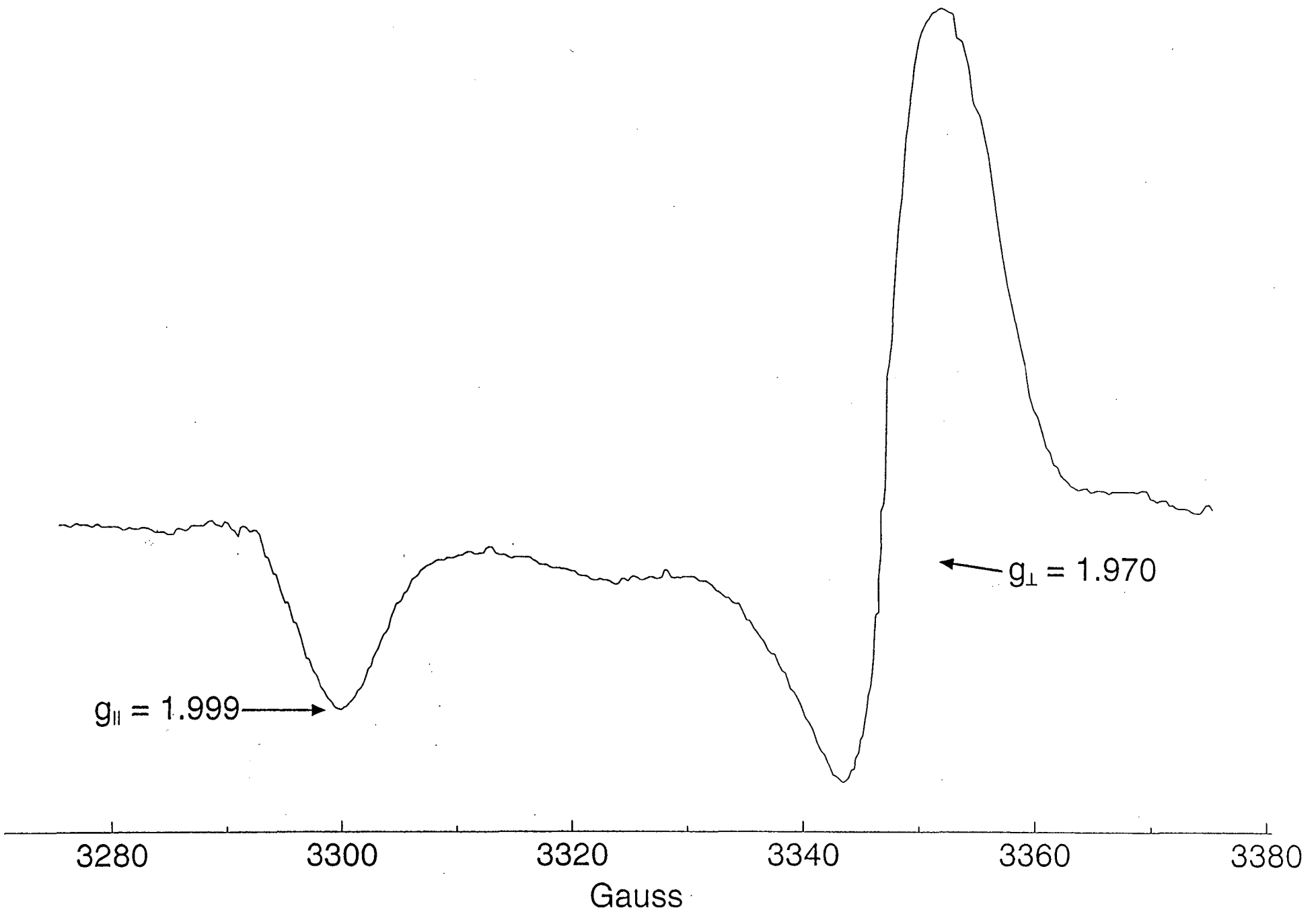


Figure 2: The EPR spectrum of Cp_3Zr in 2-methytetrahydrofuran at 100 K.

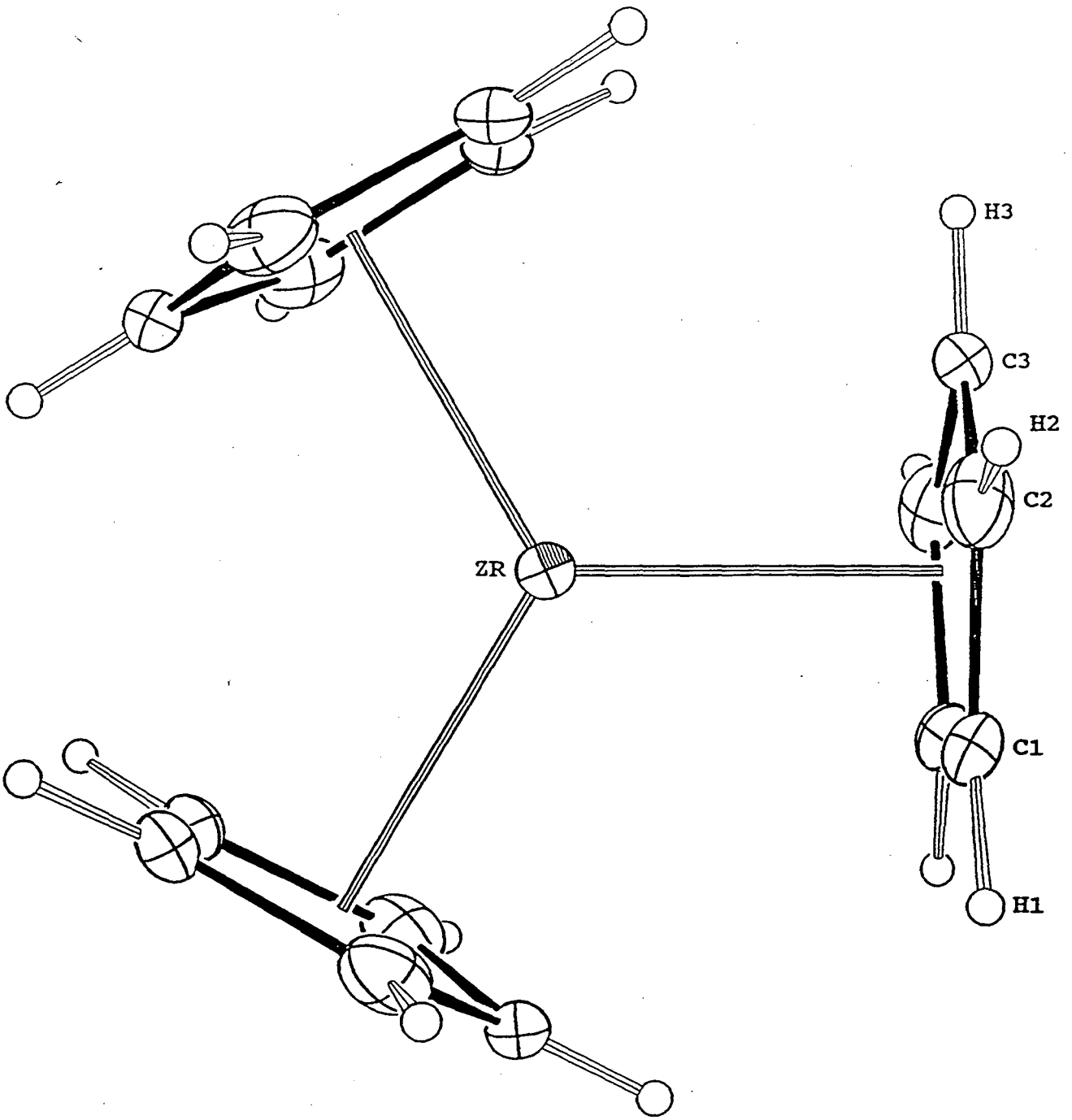
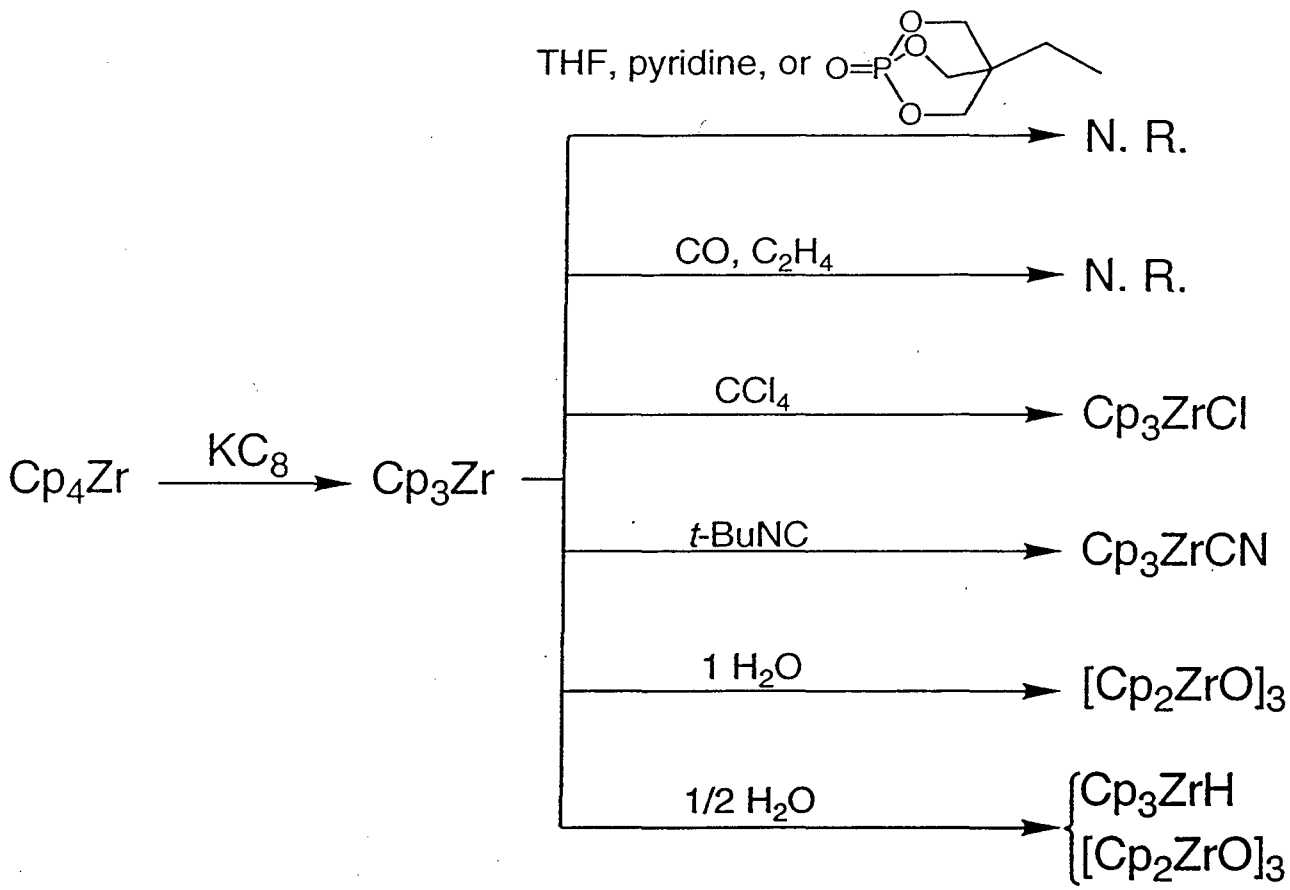
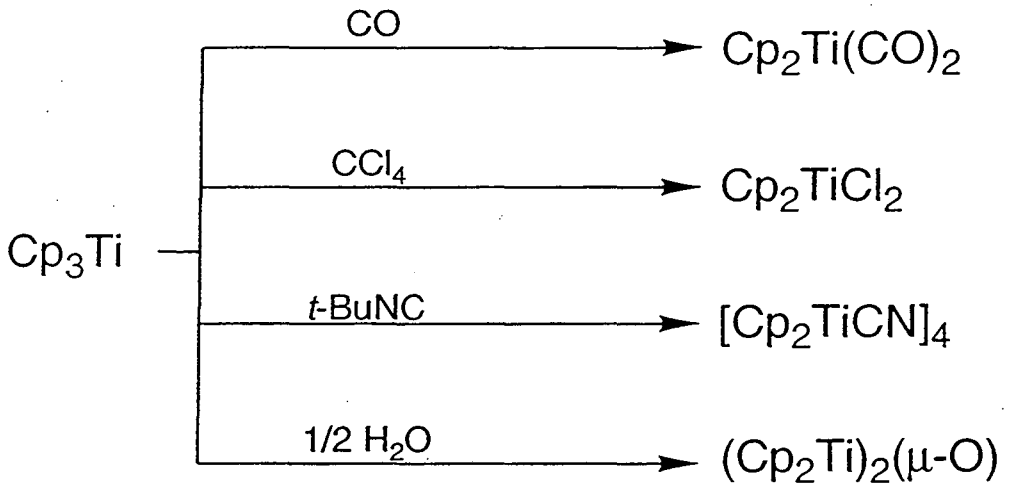


Figure 3: An ORTEP* drawing of Cp_3Zr with 50 % thermal ellipsoids.



Scheme 1: Some reactions of Cp_3Zr



Scheme 2: Some reactions of Cp_3Ti

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