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The preparation of the 2,4-di(t-butyl)pentadienyl anion and its Ti(II), Cr(II), and Zn(II) complexes

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Abstract

The potassium salt of the 2,4-di(t-butyl)pentadienyl anion may be prepared by metallation of the corresponding 1,3-diene. This anion reacts readily with titanium, chromium, and zinc dichloride complexes to yield the appropriate $M[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$ species, which display significant differences relative to their 2,4-dimethylpentadienyl analogs.

While pentadienyl ligands have been attracting growing attention [1], little effort has thus far been devoted to systematically probing the effects brought about by the placement of various substituents on the pentadienyl skeleton [2]. Although the incorporation of methyl substituents has been quite common, few other substituents have been investigated. One can readily note that the utilization of highly substituted cyclopentadienyl ligands has led to some extremely dramatic differences relative to the chemistry of the unsubstituted cyclopentadienyl ligand [3], and it must be assumed that much could be gained from similar exploitation of pentadienyl ligands. We now report the synthesis of the potassium salt of the 2,4-di(t-butyl)pentadienyl anion, and its utilization for the preparation of $M[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$ complexes (M = Ti, Cr, Zn). In all cases major differences have been found relative to the $M(2,4\text{-}C_7H_{11})_2$ counterparts (C_7H_{11} = dimethylpentadienyl).

Experimental

All operations involving organometallic compounds were carried out under prepurified nitrogen in Schlenk apparatus or in a glovebox. $CDCl_3$ was purified by vacuum transfer from P_4O_{10}. Other nonaqueous solvents were dried and degassed by distillation from benzophenone ketyl under nitrogen. Spectroscopic data were recorded as previously described [4]. For the ^{13}C NMR spectroscopic data, the indicated number of carbon atoms derives from the assignments of the resonances rather than from actual integrations. Elemental analyses were obtained from Galbraith Laboratories or Desert Analytics.

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2,4-di-t-butyl-1,3-pentadiene, 2,4-(t-C_4H_9)$_2$-1,3-C_5H_6. The first step involves the preparation of 2,2,5,6,6-pentamethyl-4-hepten-3-one [5], and was carried out in a hood due to the ammonia fumes produced. A mixture of 67.3 g (0.64 mmol) of pinacolone, 16.0 g (0.41 mmol) of sodium amide, and 135 mL of benzene in a 500 mL flask equipped with a reflux condenser and a magnetic stir bar was heated at reflux for 6 h. The mixture was allowed to cool and was then carefully hydrolyzed with 32 mL of glacial acetic acid. The mixture was extracted with three 75 mL portions of ether, the organic extracts combined, washed with 100 mL of water and dried over magnesium sulfate. The ether and benzene were distilled off at atmospheric pressure. The residue was then distilled under vacuum, yielding 37.0 g (60%) of colorless liquid (bp 43–45 °C at 0.25 Torr [5]). ^{1}H NMR ($CDCl_3$): δ 6.48 (s, 1H), 2.12 (s, 3H), 1.18 (s, 9H), 1.11 (s, 9H). A mixture of 35.7 g (0.196 mmol) of the above enone in 100 mL of ether in a 500 mL flask equipped with an addition funnel, nitrogen inlet, and a magnetic stir bar was cooled to 0 °C with an ice bath. Next, 80 mL of a 2.7 *M* solution (0.22 mmol) of methylmagnesium bromide in ether was placed in the addition funnel and then added dropwise to the enone solution. The ice bath was removed and the solution allowed to stir overnight. The milky-white solution was then hydrolyzed with ca. 2 mL of water and then washed successively with 50 mL of saturated aqueous sodium bicarbonate, and 50 mL of saturated aqueous sodium chloride. The aqueous washings were combined and extracted with two 50 mL portions of ether. The organic phases were combined and dried over magnesium sulfate. The ether was distilled off at atmospheric pressure, leaving behind the crude 2,2,3,5,6,6-hexamethyl-4-hepten-3-ol. ^{1}H NMR ($CDCl_3$): δ 5.52 (s, 1H), 1.92 (d, 3H, $J = 2.0$ Hz), 1.30 (s, 3H), 1.05 (s, 9H), 0.97 (s, 9H) (the hydroxyl proton ws not observed). IR data (neat): 3623(m), 3500(s,br), 2955(vs), 2908(sh), 2870(vs), 1675(m), 1643(m), 1603(m), 1470(s), 1363(vs), 1301(m), 1256(w), 1220(sh), 1210(m), 1195(w), 1170(sh), 1160(m), 1135(sh), 1082(s), 1065(sh), 1033(w), 1000(m), 980(w), 930(m), 895(s), 860(w), 837(m), 806(m), 770(w), 755(w). The crude alcohol was dehydrated to the diene by heating in a flask with ca. 0.1 g of iodine until water was seen to form inside. The mixture was cooled and then distilled under reduced pressure (ca. 5 Torr) using a 6″ Vigreaux column. The diene fraction was collected at 40–43 °C. After the diene was removed from some accompanying water, it was dried over magnesium sulfate and finally purified by distillation (bp 171–173 °C). A yield of 24.6 g (70% yield from the enone) of colorless diene was obtained. ^{1}H NMR ($CDCl_3$): δ 5.87 (s, 1H), 5.00 (d, 1H, $J = 1.8$ Hz), 4.58 (t, 1H, $J = 1.2$ Hz), 1.69 (d, 3H, $J = 1.2$ Hz), 1.08 (s, 9H), 1.04 (s, 9H). IR data (neat): 3095(m), 2970(vs), 2910(s), 2875(s), 1807(w), 1685(w), 1640(sh), 1622(s), 1480(s), 1465(s), 1443(sh), 1378(s), 1360(s), 1255(m), 1210(sh), 1203(m), 1163(m), 1123(s), 1092(w), 1038(m), 990(m), 900(s), 862(s), 837(m), 772(w), 715(w), 697(w), 622(w) cm^{-1}.

Potassium (2,4-di(t-butyl)pentadienide, K[2,4-(t-C_4H_9)$_2$$C_5H_5$]. To a slurry of 7.7 g (6.9 mmol) of potassium t-butoxide in a solution of 17.3 g (9.6 mmol) of the above diene in 100 mL of hexane was added 28 mL of a 2.6 *M* solution of n-butyllithium at room temperature. The solution became warm, and was subsequently stirred and/or refluxed for 8–19 hours. The resulting yellow precipitate was filtered off, washed with two 20 mL portions of benzene and a similar portion of hexane, and dried in vacuo, yielding 5.3 g (35% yield) of the salt as a very pyrophoric light yellow solid.

Bis(2,4-di(t-butyl)pentadienyl)zinc, $Zn[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$. To a 0.16 g (2.5 mmol) sample of zinc dust in 20 mL of ether was added 0.64 g (2.5 mmol) of iodine. The resulting solution was stirred at room temperature for about 3 h, by which time all the iodine had reacted. The ether was then removed in vacuo, 30 mL of THF were added, and the resulting solution of zinc iodide was cooled to −78 °C. A 1.2 g (5.5 mmol) portion of $K[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]$ was then added via a solid addition funnel and the resulting solution was stirred for two hours at −78 °C. The mixture was warmed slowly to room temperature, and allowed to stir an additional 6 hours. The solvent was removed in vacuo and the residue extracted with three 10 mL portions of pentane. The extracts were filtered and concentrated to ca. 5 mL, leading to the separation of a yellow oil. The solution was cooled to −80 °C for two hours and the supernatant was syringed away and transferred to a second flask under nitrogen. The supernatant was cooled to −80 °C for 1–2 days, during which time the product separated as white crystals with a slight yellow coloration from small amounts of the yellow oil. The product was recrystallized from pentane under similar conditions, after which the solvent was removed by syringe. The solid was dried in vacuo, leading to 0.36 g (34% yield) of product (mp 62–63 °C). Anal.: Calcd. for $C_{26}H_{46}Zn$: C, 73.65; H, 10.93. Found: C, 73.02; H, 11.19%. ^1H NMR (C_6D_6): δ 5.91 (s, 1H), 3.24 (s, 4H), 1.16 (s, 18H). ^{13}C NMR (C_6D_6): δ 158.4 (s, 2C), 115.1 (d of q, 1C, $J = 150.9$, 7.7 Hz), 64.2 (t of d, 2C, $J = 140.4$, 6.9 Hz), 37.8 (s, 2C), 29.8 (q of t, 6C, $J = 124.9$, 9.5 Hz). Mass spectrum (EI, 17 eV) m/z (rel. int.): 426(2), 425(1), 424(3), 422(5), 179(100), 123(43), 109(33), 57(35). IR (Nujol mull): 3115(w), 3065(w), 1620(sh), 1605(s), 1580(m), 1560(s), 1477(s), 1359(s), 1300(sh), 1275(w), 1243(m), 1205(m), 1199(m), 1165(s), 1137(m), 1057(m), 1305(m), 1021(m), 1007(m), 953(w), 930(w), 921(w), 888(s, br), 852(s), 791(m), 720(m), 700(w), 687(w), 640(m) cm^{-1}.

Bis(2,4-di(t-butyl)pentadienyl)titanium, $Ti[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$. A mixture of 0.41 mL (3.0 mmol) of titanium tetrachloride and 0.11 g (4.5 mmol) of magnesium powder in 40 mL of THF was refluxed for 1.5 hours, yielding a blackish "$TiCl_2(THF)_x$" suspension. This mixture was cooled to −80 °C, after which 1.3 g (6.0 mmol) of $K[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]$ in 60 mL of THF was added slowly, leading to a greenish solution. After being slowly warmed to room temperature, the solution was stirred overnight, and the THF was removed in vacuo. The residue was extracted with 10 mL portions of hexane until the extracts were nearly colorless. After filtration, the solution volume was reduced to 5–10 mL, and the solution cooled to −90 °C, yielding a mixed precipitate of the desired product and 2,4,7,9-tetra(t-butyl)deca-1,3,7,9-tetraene. These could best be separated by careful sublimation of the tetraene in vacuo, after which the remaining green titanium compound could be extracted with hexane. This solution was then filtered as before, and the bright green titanium compound crystallized on cooling to −90 °C. The air sensitivity of this compound is far lower than that of $Ti(2,4\text{-}C_7H_{11})_2$. Anal. Calcd for $C_{26}H_{46}Ti$: C, 76.81; H, 11.41. Found: C, 76.81; H, 11.09. ^1H NMR (C_6D_6, ambient): δ 7.83 (s, 1H), 3.80 (s, 1H), 1.96 (s, 1H), 1.85 (s, 1H), 1.37 (s, 9H), 1.01 (s, 9H), −1.19 (s, 1H). ^{13}C NMR (C_6D_6, 5 °C): δ 138.5 (s), 129.1 (s), 108.4 (d), 70.8 (t), 65.4 (t), 40.4 (s), 40.1 (s), 32.7 (q), 32.2 (q).

The tetraene (mp 94–95 °C) may be purified by recrystallization from hexane and/or vacuum sublimation at 90 °C. Anal. Calcd. for $C_{26}H_{46}$: C, 87.07; H, 12.93. Found: C, 86.83, 13.22%. ^1H NMR ($CDCl_3$): δ 5.86 (s, 2H), 4.98 (t, 2H, $J = 2.0$

Table 1

Crystallographic data for $Zn[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$

(a) Crystal parameters			
formula	$C_{26}H_{46}Zn$	β, deg.	110.46(2)
formula wt.	424.03	V, Å^3	1307.7(6)
crystal system	monoclinic	Z	2
space group	$P2_1/n$	D(calc), g cm^{-3}	1.077
a, Å	9.748(2)	T, K	295
b, Å	11.444(3)	color	colorless
c, Å	12.511(3)	size, mm	0.30×0.30×0.15
(b) Data collection			
diffractometer	Rigaku AFC6R	reflections collected	1408
radiation	Mo-$K\alpha$	observed reflections	1311
wavelength, Å	0.71069	independent reflections	764
scan range, deg.	$3 \leq 2\theta \leq 40$	R(merge)	0.037
μ(Mo-$K\alpha$), cm^{-1}	9.68	DIFABS trans. factors	0.65–1.26
(c) Refinement			
$R(F)$	0.047	N_o/N_v	6.16
$R(wF)$	0.057	max ρ, e Å^{-3}	0.30
GOF	1.88	min ρ, e Å^{-3}	−0.32

Hz), 4.79 (s, 2H, $J = 2.0$ Hz), 2.25 (s, 4H), 1.07 (s, 18H), 1.05 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 155.3 (s, 2C), 149.6 (s, 2C), 123.2 (d, 2C, $J = 146.7$ Hz), 109.5 (t, 2C, $J = 154.8$ Hz), 37.5 (s, 2C), 36.0 (s, 2C), 30.2 (q, 6C, $J = 125.6$ Hz), 29.5 (q, 6C,

Table 2

Positional and thermal parameters for $Zn[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$

Atom	x	y	z	B(eq)
Zn(1)	0	0	0	5.69(7)
C(1)	0.063(1)	0.1130(8)	0.1265(7)	5.5(5)
C(2)	0.066(1)	0.0518(7)	0.2338(6)	3.9(4)
C(3)	−0.0494(9)	−0.0084(8)	0.2389(5)	4.0(4)
C(4)	−0.1849(9)	−0.0391(7)	0.1505(7)	3.7(4)
C(5)	−0.252(1)	0.0287(8)	0.0631(8)	6.0(5)
C(6)	0.211(1)	0.0626(8)	0.3339(7)	4.8(4)
C(7)	0.246(1)	0.1906(8)	0.3675(7)	6.3(5)
C(8)	0.334(1)	0.009(1)	0.3034(8)	8.2(5)
C(9)	0.202(1)	0.000(1)	0.4387(7)	10.0(6)
C(10)	−0.2449(9)	−0.1593(8)	0.1597(7)	4.6(4)
C(11)	−0.373(1)	−0.1970(8)	0.0541(9)	7.7(5)
C(12)	−0.300(1)	−0.160(1)	0.259(1)	10.1(7)
C(13)	−0.127(1)	−0.2532(8)	0.1797(8)	7.7(6)

Table 3

Pertinent distances (Å) and angles (°) for Zn[2,4-(t-$C_4H_9)_2C_5H_5]_2$

Zn–C(1)	1.969(8)	C(6)–C(7)	1.53(1)
C(1)–C(2)	1.50(1)	C(6)–C(8)	1.51(1)
C(2)–C(3)	1.34(1)	C(6)–C(9)	1.52(1)
C(3)–C(4)	1.44(1)	C(10)–C(11)	1.53(1)
C(4)–C(5)	1.31(1)	C(10)–C(12)	1.51(1)
C(2)–C(6)	1.53(1)	C(10)–C(13)	1.53(1)
C(4)–C(10)	1.52(1)		
C(1)–Zn–C(1)′	180.0(0)	C(2)–C(6)–C(8)	110.3(7)
Zn–C(1)–C(2)	108.4(6)	C(2)–C(6)–C(9)	110.7(8)
C(1)–C(2)–C(3)	121.7(7)	C(7)–C(6)–C(8)	109.9(8)
C(2)–C(3)–C(14)	130.4(7)	C(7)–C(6)–C(9)	106.6(8)
C(3)–C(4)–C(5)	123.6(8)	C(8)–C(6)–C(9)	108.4(8)
C(1)–C(2)–C(6)	114.8(8)	C(4)–C(10)–C(11)	114.3(7)
C(3)–C(2)–C(6)	123.6(7)	C(4)–C(10)–C(12)	108.7(7)
C(3)–C(4)–C(10)	116.0(8)	C(4)–C(10)–C(13)	111.4(7)
C(5)–C(4)–C(10)	120.4(8)	C(11)–C(10)–C(12)	106.9(8)
C(2)–C(6)–C(7)	110.8(7)	C(11)–C(10)–C(13)	106.5(7)
		C(12)–C(10)–C(13)	108.8(9)

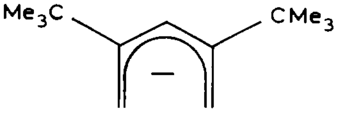
$J = 127.9$ Hz), 29.3 (t, 2C, $J = 126.6$ Hz). Selected IR bands (KBr pellet): 1633 (s) and 1621 (s) cm^{-1}.

Bis(2,4-di(t-butyl)pentadienyl)chromium, Cr[2,4-(t-$C_4H_9)_2C_5H_5]_2$. This compound could be prepared in 39% yield by a method analogous to that employed above for the titanium compound, simply by substituting 0.35 g of chromous chloride for the "$TiCl_2(THF)_x$" suspension described above. After the initial isolation of the green compound at −80 °C, the compound (mp 173–175 °C) could be purified by sublimation at 70–80 °C (no tetraene byproduct was observed). Anal. Calcd. for $C_{26}H_{46}Cr$: C, 76.05; H, 11.29. Found: C, 75.55; H, 11.79%. IR data (Nujol mull): 3100 (w), 3085 (w), 3050(sh), 1360 (s), 1273 (m), 1263 (sh), 1235 (s), 1203 (m), 1158 (s), 1033 (w), 1019 (m), 1009 (m), 933 (w), 918 (w), 905 (w), 860 (s), 827 (w), 700 (m) cm^{-1}.

X-ray diffraction study of Zn[2,4-(t-$C_4H_9)_2C_5H_5]_2$. Single crystals of this compound were obtained by slow cooling of its solutions in hydrocarbon solvents. Crystallographic data are summarized in Table 1. The space group was uniquely determined by its systematic absences. Data were collected out to $2\theta = 40°$ using ω–2θ scans, and corrected for absorption. All calculations were carried out using the TEXSAN-TEXRAY Structure Analysis Package (Molecular Structure Corp.). The structure was solved by direct methods, and the non-hydrogen atoms subsequently refined anisotropically. The hydrogen atoms were placed in calculated positions with isotropic thermal parameters 20% greater than the equivalent isotropic thermal parameters of their attached (0.95 Å) carbon atoms. A conventional weighting scheme was employed with an "ignorance" (p) factor of 0.03. Atomic coordinates are listed in Table 2, and pertinent bonding parameters are listed in Table 3. Additional bonding parameters, as well as the thermal and structure factors, may be obtained from the authors.

Results and discussion

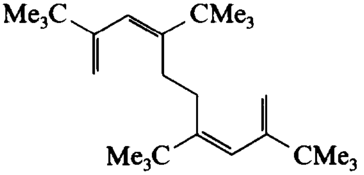
The potassium salt of the 2,4-di(t-butyl)pentadienyl anion (I) may be readily prepared by the metallation of 2,4-di(t-butyl)-1,3-pentadiene. Given that the analogous potassium 2,4-dimethylpentadienide is somewhat unusual in that it favors the U conformation (as a result of steric influences of the methyl groups) [6], it would have to be expected that the bulkier I should exert an even greater, perhaps overwhelming, preference for this conformation. In any event, this anion does react readily with dihalide complexes of zinc, chromium, and titanium to yield the appropriate open metallocenes, M[2,4-(t-C_4H_9)$_2$$C_5H_5$]$_2$ (eq. 1). Under some circumstances these products are accompanied by the ligand dimer, II, whose volatility is slightly greater than those of the above open metallocenes, allowing for effective separation [7*]. Notably, the titanium and chromium compounds are significantly less air sensitive than the corresponding M(2,4-C_7H_{11})$_2$ compounds or Zn[2,4-(t-C_4H_9)$_2$$C_5H_5$]$_2$, which may readily be attributed to the substantial steric constraints brought about by η^5 coordination of the bulky ligand I. This steric bulk also leads to higher melting points for these compounds relative to the low melting open metallocene analogs [8] (c.f., 173–175 °C for Cr[2,4-(t-C_4H_9)$_2$$C_5H_5$]$_2$), and in the case of zinc, to much higher thermal stability as Zn(2,4-C_7H_{11})$_2$ decomposes at room temperature [9].



I

$$\text{"MCl}_2\text{"} + 2\text{K}[2,4\text{-}(\text{t-C}_4\text{H}_9)_2\text{C}_5\text{H}_5] \rightarrow \text{M}[2,4\text{-}(\text{t-C}_4\text{H}_9)_2\text{C}_5\text{H}_5]_2 \qquad (1)$$

$$\text{M} = \text{Zn, Cr, Ti}$$



II

Analogous to their M(2,4-C_7H_{11})$_2$ analogs [8,10], the titanium and chromium compounds are respectively diamagnetic and paramagnetic (2 unpaired electrons). The conformational behaviors of both the titanium and the zinc compounds are surprisingly similar to those of the 2,4-dimethylpentadienyl analogs. For the titanium compound, one observes a seven-line pattern in the room temperature ^{1}H NMR spectrum, indicative of equivalent ligands in an unsymmetric conformation. From structural results on V(2,4-C_7H_{11})$_2$ [11] and Ti[1,5-(Me_3Si)$_2$$C_5H_5$]$_2$ [12], one would expect the conformation to be close to the ideally staggered form III, which

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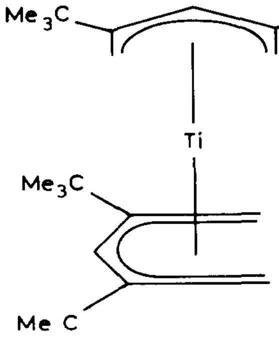
* Reference number with asterisk indicates a note in the list of references.

possesses a 90° twist from the *syn*-eclipsed configuration. While one might also



III

have expected to see a significantly higher barrier to ligand oscillation for the titanium compound relative to its 2,4-dimethylpentadienyl analog, in fact the barriers are almost identical ($\Delta G^{\neq} = 15.5(2)$ vs. 15.3(2) kcal/mole, respectively [13*]), although for Ti[1,5-$(Me_3Si)_2C_5H_5$]$_2$ even at 120 °C no evidence of signal coalescence or broadening was seen [2,12], indicating a much higher barrier. Interestingly, although the zinc compound should be expected to contain η^1-bound dienyl ligands, [14*] even at −100 °C not only were both ligands equivalent, but the two ends of each ligand were as well, apparently as a result of facile 1,5 metal shifts. Such behavior has also been observed for Zn(2,4-C_7H_{11})$_2$ and for related complexes of cyclic dienyl ligands (e.g., cyclohexadienyl, etc.), but not for $Zn(C_5H_7)_2$ or analogs with monomethylated pentadienyl ligands, which exist in W or S conformations for which a large spatial separation is present between the 1 and 5 positions [9].

A solid-state structural determination of the zinc compound has confirmed the expected η^1 bonding mode for the dienyl ligand (Fig. 1). The molecule lies on a crystallographic center of inversion, which relates one ligand to the other. To a good first approximation, the bonding parameters are consistent with a localized diene fragment. Thus, the Zn–C(1) distance of 1.969(8) Å is similar to related distances in other zinc alkyl compounds [15], although somewhat shorter than the distance of 2.031(12) Å in $Zn(C_5H_7)(Cl)$(tmeda) [9]. A long-short-long-short pattern is clearly evident for the C(1)–C(5) backbone. The dienyl ligands are indeed present in the U conformation, and one observes the usual contraction of internal C–C–C bond angles with alkylation [8a,16] in this case an average of 122.7(6)° being observed around C(2) and C(4), compared to 130.4 (7)° around C(3). However, for Mg(2,4-C_7H_{11})$_2$(tmeda) (tmeda = $Me_2NC_2H_4NMe_2$) one observes essentially no difference, 127.9(10)° vs. 127.1(13)° [17]. A complication does arise in that the external olefinic bond seems to have its π cloud oriented toward the zinc atom. This orientation comes about as a result of a twist along the backbone, which may be seen by the C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5) torsion angles of 8(1) and −61(1)°, respectively, which also leads to a significant distortion from planarity. Both C(4) and C(5) are closer to the zinc atom (3.06 and 2.85 Å, respectively) than the expected Van der Waals separation of ca. 3.1 Å [18]. Possibly this interaction could be responsible for the higher thermal stability of this compound relative to other bis(pentadienyl)zinc complexes, and the rapid exchange process

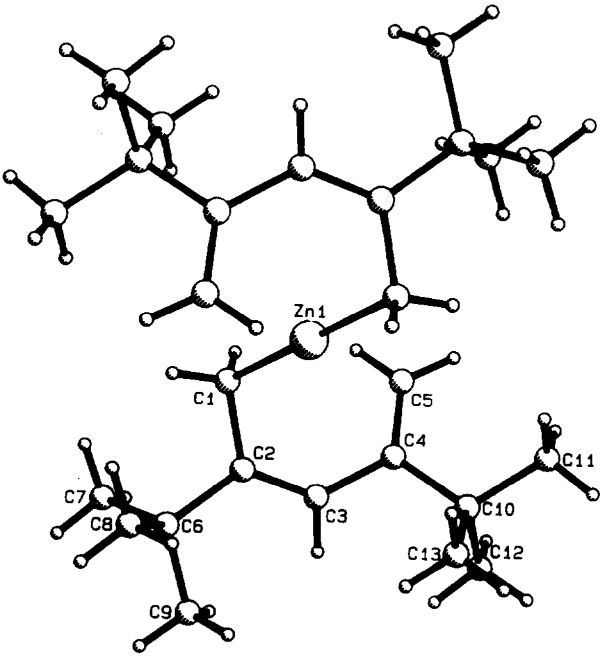


Fig. 1. Perspective view and numbering scheme for $Zn[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$.

that renders the two sides of the $2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5$ ligands equivalent. This can be substantiated in part by the observation that both $Zn(2,4\text{-}C_7H_{11})_2$ and $Zn[2,4\text{-}(t\text{-}C_4H_9)_2C_5H_5]_2$ are each isolated without coordinated THF, whereas $Zn(C_5H_7)_2$ and the monomethylated pentadienyl analogs (having W or S conformations) are isolated as bis(THF) adducts [9]. Interestingly, molecular orbital calculations on $Be(C_5H_7)(H)$ have indicated that the most stable (U) conformer should possess a similar interaction [19], reminiscent also of $Ta(C_5H_5)_2(\eta^3\text{-}2,4\text{-}C_7H_{11})$, for which Ta–C bond distances of 2.296(5) (alkyl), 2.302(4), and 2.245(4) Å were observed [20].

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