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CRYSTALLINE DIPENTADIENYLZINC. PREPARATION, CONFORMATIONAL ANALYSIS AND CHEMICAL REACTIVITY

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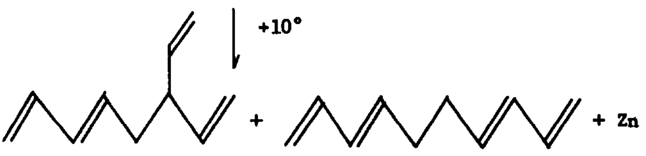
Preparations of acyclic dienylmetal compounds have received little attention except for dienylalkalimetal compounds[1~4], while the preparation, conformational analysis and reaction of a number of allylmetal compounds have been studied extensively[5]. We wish to describe herein a general procedure for the preparation, conformational analysis and some chemical reactions of dipentadienylzinc compounds, since several crystalline dienylalkalimetal compounds have became readily available[3].

Dipentadienylzinc-tetrahydrofuranate 1 (mp. -10°) was isolated as needles by reacting crystalline pentadienylpotassium with a half equimole of anhydrous zinc dichloride in tetrahydrofuran at -20°, evaporating the excess amount of tetrahydrofuran, extracting from the residue with n-pentane and then cooling the n-pentane solution to -78° to induce crystallization. All procedures were carried out in an argon atmosphere below 0°, as 1 was thermally unstable. Thermal decomposition of 1 began at 10° and the half life time at 30° was 10 min. Dipentadienylzinc-triethylamine complex 2 (mp. -5°), which was prepared by adding five moles equivalence of triethylamine to 1 in n-pentane solution and cooling the solution to -50°, also decomposed at room temperature to trans,trans-1,3,7,9-decatetraene[6], 3-vinyl-trans-1,5,7-octa-

$$2\ KC_5H_7{\cdot}THF + ZnCl_2 \xrightarrow{-20°} Zn(C_5H_7)_2{\cdot}THF + 2\ KCl$$



triene and metallic zinc. The half life time at 30° of 2 was 15 min. Thermally stable dipentadienylzinc compounds were isolated using a monodentate ligand having a very strong basicity or a bidentate ligand. The 1:1 complex of dipentadienylzinc-trimethylamine oxide 3 (mp. 115°) was stable at 80° in toluene as well as N,N,N',N'-tetramethylethylenediamine (TMEDA)-pentadienylzinc 4 (mp. 58°) and N,N,N',N'-tetramethylpropylenediamine (TMPDA)-pentadienylzinc 5 (mp. 50.5°). The molecular weights of 1, 2, 3, 4 and 5 determined cryoscopically in benzene correspond to those of monomeric 1:1 complexes. Each of the cmr spectrum of 1, 2 and 3 in d_6-benzene at 6° showed three peaks (Table 1), which suggest that these compounds assume U- or W-shaped conformation among the three possible planar conformations; U(cis-cis)-, W(trans-trans)- and sickle(cis-trans)-shaped conformations[7].

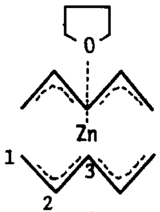
Table 1. Carbon-13 nmr Chemical Shift of Pentadienylzinc Compounds[a,b]

	C_1	C_2	C_3	C_4	C_5
$Zn(C_5H_7)_2 \cdot THF$ 1	65.3	139.2	115.3	-	-
$Zn(C_5H_7)_2 \cdot NEt_3$ 2	66.9	140.0	121.3	-	-
$Zn(C_5H_7)_2 \cdot ONMe_3$ 3	66.0	144.9	117.4	-	-
$Zn(C_5H_7)_2 \cdot TMEDA$ 4	20.5	141.0	118.2	147.1	105.0
$Zn(C_5H_7)_2 \cdot TMPDA$ 5	19.7	140.4	118.3	148.0	104.2

a. In ppm downfield from internal TMS in d_6-benzene (calibrated using the d_6-benzene peak, assumed to be 128.0 ppm). Data were collected at 25.2 MHz at 6° on a Varian XL-100-15 spectrometer equipped with a Digilab Model FTS-NMR-3 Fourier transform accessory.

b. Peak assignments were made in part from an off-resonance decoupled spectrum.

Pmr chemical shift of 1, 2 and 3 observed in d_6-benzene at 6° and the proton-proton coupling constant, J_{23}, of ca. 12 Hz correspond to trans conformation[8]. The coupling constant, J_{12}, of ca. 11.4 Hz corresponds well to an intermediate value between outer bond-cis, 7.5~9.0 Hz and outer bond-trans, 16 Hz[8]. Thus, the planar conformations of 1, 2 and 3 were determined to be W-shaped. Ir absorptions at 950(trans δCH) and 1620 cm^{-1}(νC=C) of 1, 2 and 3 in benzene are also consistent with the W-shaped conformation. Pmr spectra of 4 and 5 in d_6-benzene at 6° were sharply different from those of 1 and 2. The most striking feature of the spectra is that a doublet proton peak, which is assignable to a methylene proton of pentadienyl group bonded with zinc metal by σ-bond, was observed in higher field (ca. 1.43 ppm downfield from external TMS in d_6-benzene at 6°). Cmr spectra at 6° in d_6-benzene gave five peaks for 4 and 5. The structure of 4 or 5 was, therefore, concluded to be a terminally σ-bonded form, not a centrally delocalized carbanion form. Ir absorptions of both 4 and 5 at 970(trans δCH) and 1620 cm^{-1} (νC=C) support this conclusion. By elevating the temperature up to 80°, the compounds 1, 2 and 3 were decomposed completely but pmr spectra of 4 and 5 changed reversibly to that of W-shaped structure, which is consistent with a formula 4'. Model examination suggests that terminally bonded structure 4 is sterically most favorable and W-shaped delocalized structure 4' is possible only when the bidentate ligand coordinate loosely to zinc metal. On the other hand, pmr spectra of 1 and 2 also changed reversively to that of terminally σ-bonded structure(consistent with the structure of 4 and 5 at 6°) by cooling them to -60° in d$_8$-THF. Thus, the conformations of 1 and 2 below the temperature at -60° as well as 4 and 5 at room temperature found to be terminally σ-bonded structure[9]. Although the structure of 4 and 5 is different from that of 1, 2 and 3 at 6°, all these compounds gave a mixture of trans-, cis-1,3-pentadiene and 1,4-pentadiene in 50-70, 6-13 and 20-40% yield, respectively, by hydrolysis in benzene at 6°.



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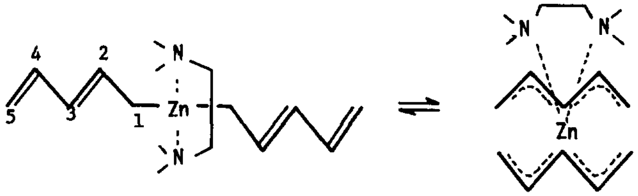

4 4'

This result was explained by an equilibrium existing between A and B in the reaction system. The formation of cis-1,3-pentadiene suggest that the barrier to rotation about the inner bond of B would be small.

A B

The reactions of pentadienylzinc compounds with acetaldehyde 6, acetone 7, methyl-isopropylketone 8 and di-isopropylketone 9 resulted in the formation of addition products, dienyl alcohols. The yield of the product reacted at C$_1$ of pentadienyl group increased with the increase in bulkiness of an alkyl group attached to carbonyl group. When the carbonyl compound having less bulky groups was reacted, equilibrium existing in the reaction system favored structure A to give only dienyl alcohol reacted at C$_3$ of pentadienyl group. These dienyl alcohols could not be obtained directly using pentadienylalkalimetal compounds, as aldol condensation occurred preferentially.

In conclusion, the reactions mentioned above will be useful as a general method for the preparation of a number of dienylmetal compounds and of organic dienyl derivatives.

Table 2. Percentage Yield of the Products Reacted at C_1 and C_3 Atoms of Pentadienylzinc with Carbonyl Compounds[a].

Carbonyl compd.	6		7		8		9	
Reaction site	C_1	C_3	C_1	C_3	C_1	C_3	C_1	C_3
1	0.0	100.0	0.0	100.0	50.2	49.8	92.0	8.0
3	0.0	100.0	0.0	100.0	96.0	4.0	98.0	2.0
4	0.0	100.0	0.0	100.0	97.5	2.5	98.5	1.5
5	0.0	100.0	0.0	100.0	97.6	2.4	99.0	1.0

a. Characterized by pmr, mass and ir after reacting both components in benzene at 6° for 1 hr, hydrolyzing at 6° and isolating each fraction by preparative glpc.

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