presented above removed any reasonable doubts as to the correctness of the structure proposed for compound **4**. It is pleasing to learn that the Woodward–Hoffmann selection rule[10] uniquely applies to the present system; in particular, the thermal conversion of **4** into **5** (reverse Diels–Alder reaction) but not into **3** in spite of the geometry of the C-2–C-10 bond of **4** disposed favorably to form the allylic radical (see **4′**).[11]

The significance of **4** is evident as it has been often cited in the recent literature of $(\text{CH})_{10}$ hydrocarbons,[4] and we do not elaborate here in this respect. However, we mention that formation of **4** from **1** and **2** *was* surprising indeed. Minor products **2** and **3** in these photolyses are strongly suggestive of the species[12] (of either ground state or excited state) which may be involved in the processes leading to the ultimate formation of **4**. Investigations directed toward this aspect and the fate of electronically excited **4** will be described in future publications.[13,14]

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[10] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[11] We have attempted to reduce **4** with dimide at -20 or $-40°$ to obtain tetracyclo$[4.4.0.0^{2,10}.0^{5,7}]$decane. However, apparently due to the low reactivity of the reducing reagent toward this type of compound at these temperatures, we isolated only bicyclo[4.2.2]decane and its partially unsaturated compounds even with 200-fold molar excess of potassium azodicarboxylate for 48 hr (*cf.* half-lives of **4**). In fact, reduction of bullvalene under similar conditions proceeded only to 50% completion.

[12] In ref 2b the authors reported that photolysis of **2** at a somewhat lower temperature than ours, followed by diimide reduction at $-70°$ and/or higher temperatures, provided $\sim$40% over-all yield of cyclodecane.

[13] We are grateful to the National Research Council of Canada for financial support and to Badische Anilin- und Soda-Fabrik AG for a generous gift of cyclooctatetraene.

[14] During the process of refereeing, E. Balad, D. Ginsburg, and M. B. Rubin reported that photoirradiation of 12-oxa[4.4.3]propella-2,4,7,9-tetraene afforded 12-oxapentacyclo$[4.4.0.0^{2,10}.0^{5,7}]$trideca-3,8-diene (*Tetrahedron Letters*, 2361 (1968)).

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Stereochemistry of Chlorobis(acetylacetonato)cyclopentadienylzirconium

Sir:

Nuclear magnetic resonance studies[1–4] of a considerable number of higher coordination number metal β-diketonate complexes have not yet provided stereochemical information for this important class of compounds in solution. In general, the lack of progress can be attributed to the lability of the complexes investigated. Among the zirconium acetylacetonate[5] complexes, for example, seven-coordinate $\text{Zr(acac)}_3\text{Cl}$ and eight-coordinate Zr(acac)_4, as well as six-coordinate $\text{Zr(acac)}_2\text{Cl}_2$, give single methyl proton resonance lines at temperatures even as low as $-130°$, because of rapid intramolecular configurational rearrangement processes which average the expected nonequivalent methyl group environments.[4] We wish to report here that the higher coordination number zirconium complex $(\pi\text{-C}_5\text{H}_5)\text{Zr(acac)}_2\text{Cl}$ is sufficiently stereochemically rigid at room temperature to observe nonequivalent environments for methyl and $-\text{CH}=$ protons on the chelate rings.

$(\pi\text{-C}_5\text{H}_5)\text{Zr(acac)}_2\text{Cl}$ was prepared following the method of Freidlina, Brainina, and Nesmeyanov.[6] The product was recrystallized twice from benzene and dried *in vacuo* at 80°: mp 189–190° (sealed capillary); lit.[6] 188–190°. *Anal.* Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4\text{ClZr}$: C, 46.20; H, 4.91. Found: C, 46.01; H, 5.00. Since the compound is readily hydrolyzed in solution, all solutions were prepared and subsequently handled under anhydrous conditions.

In nitrobenzene solution the compound is monomeric and a very weak electrolyte: mol wt 390 calcd *vs.* 407 found; $\Lambda < 0.014$ ohm^{-1} cm^2 mole^{-1} at a concentration of 7.3×10^{-3} *M*. A band due to a symmetric carbonyl stretching vibration is observed near 1595 cm^{-1} in CDCl_3 solution. No bands are found in the region 1626–1695 cm^{-1} where ketonic carbonyl modes have been reported for silicon(IV)[7] and platinum(II)[8–11] acetylacetonates containing uncoordinated carbonyl groups. These data indicate that the chlorine atom and all four carbonyl groups are coordinated to the zirconium atom in solution.

The proton nmr spectrum of $(\pi\text{-C}_5\text{H}_5)\text{Zr(acac)}_2\text{Cl}$ in benzene solution is presented in Figure 1. The resonance line at τ 3.50 is assigned to protons on the cyclopentadienyl ring. The remaining six lines are due to $-\text{CH}=$ and methyl protons on the acetylacetonate ligands. The two $-\text{CH}=$ lines at τ 4.75 and 4.82 have relative intensities 1:1.03 ± 0.03. Four methyl lines occur in the region τ 8.31 to 8.45. Relative to the line at τ 8.31, the two lines of equal intensity at τ 8.37 and 8.38 have a combined intensity of 2.03 ± 0.05, and the line at τ 8.45 has an intensity of 0.99 ± 0.03. The intensities were determined by planimetric integration of five spectra; errors are estimated at the 95% confidence level.

The nmr data cannot be interpreted in terms of an equilibrium mixture of compounds of different stoichiometries arising from disproportionation of the complex. Equal molar mixtures of $(\pi\text{-C}_5\text{H}_5)\text{Zr(acac)}_2\text{Cl}$ and $\text{Zr(acac)}_2\text{Cl}_2$, $\text{Zr(acac)}_3\text{Cl}$, Zr(acac)_4, H(acac), or $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ give spectra characteristic of the two compounds initially mixed. That is, the relative intensities of resonance lines found in the spectrum of a solution containing only $(\pi\text{-C}_5\text{H}_5)\text{Zr(acac)}_2\text{Cl}$ are not altered by varying the ligand composition. Therefore, it must be concluded that the observed methyl and $-\text{CH}=$ proton resonances result from nonequivalent environments for these groups in the $(\pi\text{-C}_5\text{H}_5)\text{Zr(acac)}_2\text{Cl}$ molecule. The existence of a single, sharp cyclopentadienyl resonance is attributed to rapid rotation of the ring about the metal–ring axis.

The simplest configuration which places each of the methyl and $-\text{CH}=$ groups in nonequivalent environments is based on an octahedron with the C_5H_5 ring at

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[1] A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966).

[2] T. J. Pinnavaia and R. C. Fay, *ibid.*, **5**, 233 (1966).

[3] F. A. Cotton, P. Legzdins, and S. J. Lippard, *J. Chem. Phys.*, **45**, 3461 (1966).

[4] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **7**, 502 (1968).

[5] $\text{CH}_3\text{COCHCOCH}_3^-$; abbreviation, acac.

[6] R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR, Chem. Sect.*, **138**, 628 (1961).

[7] R. West, *J. Amer. Chem. Soc.*, **80**, 3246 (1958).

[8] B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, R. J. Pauling, and G. B. Robertson, *Nature*, **195**, 1278 (1962).

[9] R. A. D. Wentworth and C. H. Brubaker, *Inorg. Chem.*, **3**, 1472 (1964).

[10] J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).

[11] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 440 (1967).

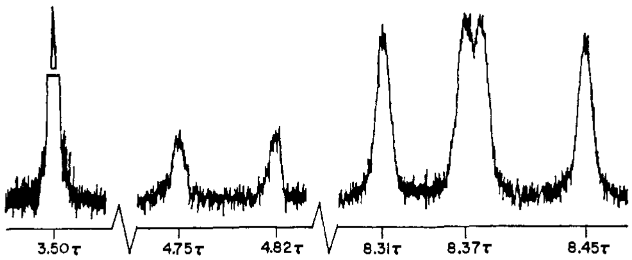
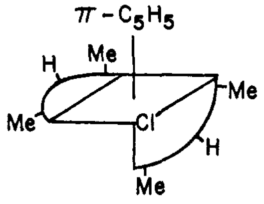
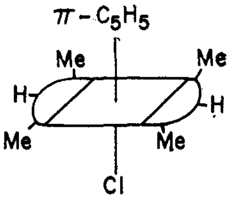


Figure 1. Proton nmr spectrum of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene solution at 36° (60 MHz); concentration is 7.5 g/100 ml of solvent.

one stereochemical position and the chlorine atom at a position *cis* to the ring (I). It may be noted that a



I



II

trans configuration such as II, which would have *apparent* C_{2v} symmetry in presence of rapid rotation of the C_5H_5 ring, cannot be present in an appreciable amount, as judged from the relative intensity data. Configurations somewhat similar to I may be derived from a D_{2d} dodecahedron and a D_{4d} square antiprism. In these higher polyhedra (Figure 2) it is assumed that the ring occupies a triangular face in forming three π bonds to zirconium. In the case of the dodecahedron, for example, the C_5H_5 ring may occupy an AAB face with the two acetylacetonate ligands spanning a g–g pair of edges and the chlorine atom at a B position. An analogous antiprismatic configuration may be readily visualized with the acetylacetonates spanning an s–s pair of edges. An X-ray diffraction structure determination on a single crystal by Stezowski and Eick[12] has shown that the stereochemistry more nearly approximates a dodecahedron than an antiprism or an "octahedron." In view of this result, one might have hoped to observe more than one stereoisomer in solution because at least five potentially detectable stereoisomers are possible based on a dodecahedron. Seven additional isomers are possible if the C_5H_5 ring is capable of bonding through an ABB triangular face. Four stereoisomers are possible based on an antiprism. However, no isomerization could be detected after the compound had been heated in benzene solution at 80° for 24 hr. At least four isomers are observed in solution for the benzoylacetonate[13] derivative, $(\pi\text{-}C_5H_5)Zr(bzac)_2Cl$, but, because the diketonate ligand is asymmetric, four geometric isomers can result from a single stereochemical configuration, such as the dodecahedral g–g, B stereoisomer described above.[14]

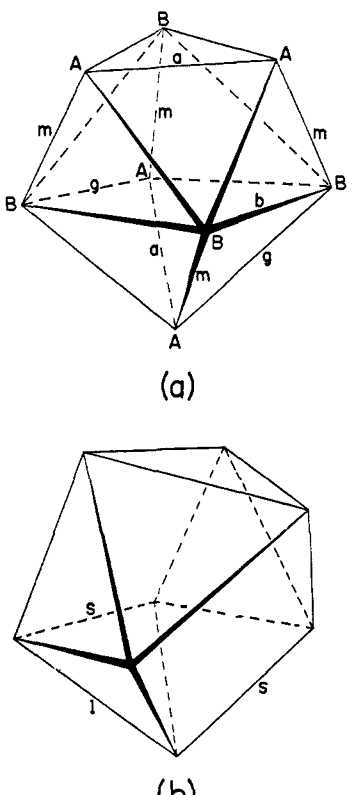


Figure 2. The D_{2d} dodecahedron (a) and D_{4d} square antiprism (b). Edge and vertex notation is from J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

The ability of the C_5H_5 ring to influence drastically the stereochemical rigidity, or nonrigidity, of the $Zr(acac)_2Cl$ moiety is rather remarkable. Variable-temperature nmr experiments are in progress to investigate this phenomenon.

Acknowledgment. We wish to acknowledge support by Michigan State University through All-University Research Funds, Project No. 5392.

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[12] J. J. Stezowski and H. A. Eick, Michigan State University, personal communication, 1968.

[13] $C_6H_5COCHCOCH_3^-$; abbreviation, bzac.

[14] E. D. Butler and T. J. Pinnavaia, unpublished results.

[15] National Defense Education Act Predoctoral Fellow, 1967–1968.

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Ammonium Ion Determination and Acid–Base Titrations in Liquid Ammonia Using a Glass Electrode

Sir:

The glass membranes of ordinary pH-sensitive glass electrodes show essentially infinite resistance and consequently no detectable sensitivity toward ammonium ion concentration when used in cells having liquid ammonia solutions.[1] However, we have observed that a commercial cationic glass electrode,[2] sensitive in varying degrees to Na^+, H_3O^+, K^+, NH_4^+, Ag^+, and Li^+, can be used to follow ammonium ion concentration in liquid ammonia solutions. In order to permit the use of the electrode in boiling liquid ammonia solutions contained in dewar vessels (−33°), we replaced the dilute aqueous HCl electrolyte in the inner part of the electrode with aqueous

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[1] A. H. A. Heyn and M. J. Bergin, *J. Am. Chem. Soc.*, 75, 5120 (1953).

[2] Beckman Instruments, Inc., Fullerton, Calif., Cationic Electrode No. 39137; see Beckman Bulletin 7017-a and Instructions 1154B.