of methyltitanium trichloride with symmetrical bidentate ligands in the exchange reaction (N < S < O)[1] may be explained as follows. Steric hindrance to twisting should be greatest in the complex with the bulkiest ligand, *viz.*, the complex $CH_3TiCl_3 \cdot (CH_3)_2NCH_2CH_2N(CH_3)_2$, so that this complex exhibits the highest coalescence temperature in the nmr study. If we now consider the complexes $CH_3TiCl_3 \cdot CH_3OCH_2CH_2OCH_3$ and $CH_3TiCl_3 \cdot CH_3SCH_2CH_2SCH_3$, it might be expected that, if steric factors alone were important, the latter complex should undergo exchange more readily since titanium–sulfur bonds would be longer than titanium–oxygen bonds. However, as already noted (*vide supra*), the dimethoxyethane complex is the more labile. This can be rationalized if there is significant interaction between the second lone pair of electrons on each sulfur atom and empty titanium d orbitals, interaction which would block the empty d orbitals to some extent and hinder the twisting process. The existence of such $p_\pi(S) \rightarrow d_\pi(Ti)$ bonding has been invoked previously for d^0 complexes to account for the fact that, according to thermochemical measurements, the Zr–S bonds in the complex $ZrCl_4 \cdot 2$(tetrahydrothiophene) are stronger than the Zr–O bonds in the complex $ZrCl_4 \cdot 2$(tetrahydrofuran).[12]

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Electron Paramagnetic Resonance Studies of the Electronic Structure of Dicyclooctatetraenylvanadium(IV) and Cyclooctatetraenyl(cyclopentadienyl)titanium(III)

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The epr spectra of $V(C_8H_8)_2$ and $Ti(C_8H_8)(C_5H_5)$ show both to be sandwich compounds with the unpaired electron in an a_{1g} orbital which is essentially metal d_{z^2}. The Ti compound shows a proton hyperfine structure which must be ascribed to σ bonding.

Introduction

Experimental studies of the electronic structure of organometallic compounds have been relatively common in the last few years. Most of the recent studies have involved the use of nmr or of epr, partly because the optical spectra of organometallic compounds are complicated and hard to interpret.

Much of the recent work has involved dicyclopentadienyl compounds of the iron series elements. Electron paramagnetic resonance studies of $V(C_5H_5)_2$,[1] $Fe(C_5H_5)_2^+$,[2] and the related $Fe(B_9C_2H_{11})_2^{2-}$ [3] have appeared, as have magnetic susceptibility studies of $Ni(C_5H_5)_2$[4] and $Fe(C_5H_5)_2^+$.[5] Photoelectron spectra of $Fe(C_5H_5)_2$, $Ni(C_5H_5)_2$, and $Co(C_5H_5)_2$ have been reported.[6] There has been, also, an extensive comparison of the nmr contact shifts of iron series dicyclopentadienyl compounds with the predictions of Wolfsberg–Helmholz theory, including both σ and π electrons.[7]

Simple theoretical arguments[8] suggest that the electronic structure of the iron series dicyclopentadienyl compounds involves extensive interaction between the $d_{\pm 1}$ orbitals of the metal and the e_1 orbitals of the cyclopentadienyl rings, yielding a low-lying pair of orbitals responsible for the greater part of the ring–metal binding and a high-lying pair of orbitals. Let us call these e_{1g} e_{1g}^*, respectively. Between the e_{1g} and e_{1g}^* pairs are found, relatively undisturbed, the d_0 and $d_{\pm 2}$ orbitals of the metal. They become a_{1g} and e_{2g} molecular orbitals.

This picture is in accord with the data on iron series dicyclopentadienyl compounds now available. The data on $Fe(C_5H_5)_2^+$ suggest that, in this compound at least, e_{2g} lies above a_{1g} and the similarity between the magnetic properties of $Fe(C_5H_5)_2^+$ and $Fe(B_9C_2H_{11})_2^{2-}$ suggests that e_{2g} is not much involved with the ligands. The photoelectron spectroscopic data show that a_{1g} is about 0.5 eV below e_{2g} in $Fe(C_5H_5)_2$.

The application of simple theoretical ideas to the cyclooctatetraenide compounds of the iron series suggests that the most important interaction for covalency would be that between the $d_{\pm 2}$ orbitals of the metal and the e_2 orbitals of the cyclooctatetraene dianion but that this should be slightly less than the corresponding interaction in the cyclopentadiene compounds because of geometrical factors. The d_0 and $d_{\pm 1}$ orbitals should be relatively undisturbed. According to Fischer's estimates of ring–metal overlaps and of orbital energies in the $Ti{-}C_8H_8$ system,[9] the d_0 overlap with the ring is

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[5] Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 3233 (1970).

[6] D. W. Turner, *et al.*, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970, pp 362–363.

[7] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 3432 (1969).

[8] G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

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small and, although the overlap of $d_{\pm1}$ with the e_1 orbitals of the ring is somewhat larger than the $d_{\pm2}$–e_2 overlap (0.312 *vs.* 0.282), the e_1 orbital is substantially more tightly bound than are the d orbitals (an estimated 13 V for e_1 *vs.* about 7 V for the d orbitals). On the other hand, the ring e_2 orbitals are estimated to be bound by about 9 V. It follows that the major interaction between the rings and the metal atom should involve the e_2 orbitals of the rings and the $d_{\pm2}$ orbitals of the metal.

Experimental Section

$V(C_8H_8)_2$ was prepared by the method of Breil and Wilke[10] and $Ti(C_8H_8)(C_5H_5)$ was prepared from $Ti(C_5H_5)_2Cl_2$ by the method of Van Oven and De Liefde Meijer.[11] Both compounds are very air sensitive and were handled on a vacuum line or on a manifold containing purified N_2. All solvents were dried carefully and distilled *in vacuo* or under purified N_2.

Epr measurements were made with a Varian V-4500-15 spectrometer. The magnetic field was calibrated with a proton resonance fluxmeter.

Results and Discussion

The epr spectrum of a fluid solution of $V(C_8H_8)_2$ in 2-methyltetrahydrofuran displays the expected eight lines. The isotropic coupling constant proves to be $\bar{A} = (-)79.5 \times 10^{-4}$ cm^{-1} and $\bar{g} = 1.983$. The spectrum of a fluid solution of $Ti(C_8H_8)(C_5H_5)$ in 2-methyltetrahydrofuran displays a spectroscopic splitting factor of 1.981. The average coupling constant for coupling to ^{47,49}Ti is $(-)20 \times 10^{-4}$ cm^{-1}.

The spectra of glassy solutions of both compounds in 2-methyltetrahydrofuran are relatively easy to analyze. The spectrum of the titanium compound is exceptionally straightforward, since most of the molecules are associated with an isotope of titanium without nuclear spin. One finds that $g_{\parallel} = 1.998$ and $g_{\perp} = 1.969$.

The spectrum of $V(C_8H_8)_2$ cannot be assigned quite so easily. A set of eight features, having $A_{\perp} = (-) 110 \times 10^{-4}$ cm^{-1} and $g_{\perp} = 1.974$, is assigned to the perpendicular orientation. One calculates, using these data and the solution spectrum, that $A_{\parallel} = (-)18 \times 10^{-4}$ cm^{-1} and $g_{\parallel} = 2.00$. The weaker parallel features are hidden under a perpendicular feature.

At low temperatures, in the range near −50°, just before the solvent glasses, the titanium compound displays a complex proton hyperfine structure which we were able to resolve only in part. One of our best spectra appears in Figure 1. As one sees, the spectrum is sufficiently distorted that it is hard to say just how many lines there are, and it is not possible to estimate intensities at all. There appear to be 17 lines, and the spacings are quite regular.

There is another point worthy of note about the spectrum from the Ti compound. As Figure 1 also shows, there is another paramagnetic species in the system, which displays a sharp resonance at $g = 2.00$. The resonance itself is devoid of structure, but is accompanied by a rather complicated set of satellites. We have verified, by examination of the spectrum as the solvent became glassy, that we should associate the parameters we have separated with the species which displays the proton hyperfine structure. The other species is responsible for a rather weak feature near $g = 2.00$ in the glass spectrum. The extra spectrum grows in rather slowly after the solution is prepared. We are unable to assign a structure to it.

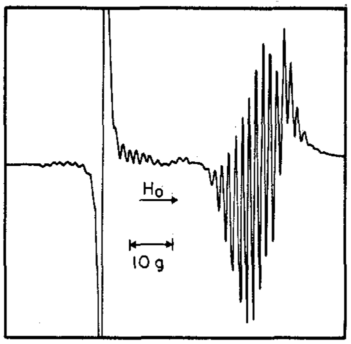

Figure 1.—Epr spectrum of a cooled fluid solution of $Ti(C_5H_5)(C_8H_8)$ in 2-methyltetrahydrofuran, showing proton hyperfine structure.

Our data have implications about both the geometry and the electronic structure of the compounds we have studied. The evidence suggests rather strongly that $V(C_8H_8)_2$ is a sandwich compound containing regular carbocyclic ligands, as $Ti(C_8H_8)(C_5H_5)$ is known to be.[12] We were unable to detect any deviation from axial symmetry in the magnetic parameters. This evidence is not, however, conclusive. It is possible that a geometry of low symmetry might not be reflected in the magnetic parameters of the complex. Also, it is likely that a structure involving a symmetrically distorted C_8H_8 grouping, a crown for instance, would have effective axial symmetry. Given the data, however, and the known structure of $Ti(C_8H_8)(C_5H_5)$, it is most likely that $V(C_8H_8)_2$ is a sandwich compound too.

Turning to the electronic structure, the facts that $g_{\parallel} = 2.00$ whereas $g_{\perp}$ deviates from 2.00 and that $A_{\parallel}(^{51}V) < A_{\perp}(^{51}V)$ show that the unpaired electron resides in an orbital which is largely d_{z^2} on the metal and, thus, has symmetry A_1. This result is consistent with our expectations about the structure of the compounds. In $V(C_8H_3)_2$ the e_2 orbitals, $d_{x^2-y^2}$ and d_{xy}, should interact with the rings to form a bonding pair of orbitals, filled with electrons from the ring, and a high-lying antibonding pair of orbitals. The d_{z^2} and the d_{xz}, d_{yz} pair are expected to be relatively uninvolved in bonding. One might expect d_{xz}, d_{yz} to be raised a bit as the antibonding components of molecular orbitals resulting from interaction with the rings. The d_{z^2} orbital should interact less because of unfavorable geometrical factors and because the corresponding orbitals on the ligands are less available for bonding, being bound more tightly. In $Ti(C_8H_8)(C_5H_5)$, both the orbital pairs $d_{x^2-y^2}$, d_{xy} and d_{yz}, d_{xz} should be involved in bonding leaving only d_{z^2} low in energy.

Although it is easy to rationalize the ground states of both compounds, the observed spectroscopic splitting factors do not agree well with our expectations regarding excited states. The deviation of $g_{\perp}$ from the free-electron value is due, in a simple picture, entirely to coupling between the ground state and the e_1 pair of states, d_{xz}, d_{yz}. Since these states are supposed to be close together in $V(C_8H_8)_2$, we would expect a large deviation of $g_{\perp}$ from the free-electron value in this compound. The compound $Ti(C_8H_8)(C_5H_5)$ should have $g_{\perp}$ much

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[11] H. O. Van Oven and H. J. De Liefde Meijer, *J. Organometal. Chem.*, **19**, 373 (1969).

[12] P. A. Kroon and R. B. Helmholdt, *ibid.*, **25**, 451 (1970).

nearer the free-electron value, since the e_1 orbitals presumably bond to the C_5H_5 ring.

Instead of our expectations, we see that both compounds have small deviations of $g_\perp$ from the free-electron value. The results place the e_1 pair of orbitals at 18,000 cm^{-1} in $V(C_8H_8)_2$ and at 15,150 cm^{-1} in $Ti(C_5H_5)(C_8H_8)$, assuming that the spin–orbit coupling constants are 125 and 126 cm^{-1} for Ti^{3+} and V^{4+}, respectively, a decrease of 20% from the free-ion values. We are, thus, forced to the conclusion that there is a large interaction between the C_8H_8 and the metal e_1 orbitals, which is surprising.

Returning to the characters of the electronic ground states of the molecules, we may estimate the distribution of the odd electron in $V(C_8H_8)_2$ from the anisotropy of the magnetic hyperfine interaction. In order to do this, we need a value of $P \equiv g_e\beta g_n\beta_n\langle r^{-3}\rangle$ for a vanadium d orbital. McGarvey[13] has tabulated P for various transition metal ions from Hartree–Fock calculations. He found P values of 85.7×10^{-4}, 128×10^{-4}, and 172×10^{-4} cm^{-1} for $^{51}V^0$, $^{51}V^{2+}$, $^{51}V^{4+}$, respectively. If we use the value for the 2+ ion, which is in the range of charges which provides a consistent interpretation of much of the data on transition metal magnetic resonance parameters,[14] we find that the occupancy of the vanadium d_{z^2} orbital by the unpaired electron is 0.85.

The isotropic ^{51}V coupling constant is rather small in $V(C_8H_8)_2$. Isotropic coupling constants are hard to interpret[13] but the result suggests that the orbital containing the unpaired electron has some 2% 4s character.

It is not possible to present a complete analysis of the proton hyperfine structure of $Ti(C_8H_8)(C_5H_5)$ because of the poor resolution. The minimum number of lines to be expected from 13 equivalent protons is 14 and the intensity ratio of the outmost two lines on either side of the spectrum should be 1:13. As one sees, there are too many lines and the intensity ratio of the outer lines is wrong. The most probable interpretation of the spectrum is that it is due to eight protons with a coupling constant equal to the observed spacing, 1.6 G, and five protons with a coupling constant twice as large, 3.2 G. The predicted hyperfine pattern consists of 19 lines and the outermost lines have intensities 1:8:33:96:220, etc. If we were unable, as is likely, to see the weak outer lines we would see 17 lines with intensity ratios 1:4+:12:27+, etc., which is roughly that observed.

It is useful to compare our results with those of Rettig and coworkers on $V(C_5H_5)(C_7H_7)$.[15] The magnetic parameters of $V(C_5H_5)(C_7H_7)$ are very similar to those of the compounds we have studied, except that the metal isotropic coupling constant is still smaller in magnitude. Since the g tensors of all three compounds are similar, $V(C_5H_5)(C_7H_7)$ must also have the e_1 pair of states placed about 2 eV above the ground state. This is in rather remarkable agreement with the 2.29 eV calculated by Rettig, *et al.*, using the Wolfsberg–Helmholz approximation.

The proton coupling constants of $V(C_5H_5)(C_7H_7)$ are +4.3 G, to the seven-membered ring, and +1.8 G, to the five-membered ring.[14] The proton coupling constant of $V(C_8H_8)_2$ must be much smaller than 4 G or it could have been observed in our experiments and, as we have seen, the proton coupling constants in $Ti(C_5H_5)(C_8H_8)$ are very probably 3.2 G to the five-membered ring and 1.6 G to the eight-membered ring. It is not clear to us why the seven-membered ring should have such a large proton hyperfine constant on the basis of simple arguments, but Rettig, *et al.*, calculated a hyperfine constant nearly as large as the one they observed in the aforementioned calculations. On the whole, the proton hyperfine constants in these compounds appear to be dominated by rather small interactions between the metal and the ligand σ system. This conclusion is supported by the known sign of the coupling constant, by calculations performed on $V(C_5H_5)(C_7H_7)$,[15] and by the magnitudes of the coupling constants in $Ti(C_5H_5)(C_8H_8)$. The coupling constants we have observed are too large to be attributed to spin delocalization through the π system, given the localization of the unpaired electron on the metal.

The most interesting conclusions from our study are, in our opinion, the regular geometry of $V(C_8H_8)_2$ and the fact that the ring–metal interaction in $V(C_8H_8)_2$ seems to be similar to that in $V(C_5H_5)(C_7H_7)$ and in $Ti(C_5H_5)(C_8H_8)$ despite the fact that a simple analysis of the electronic structure suggests major differences between $V(C_8H_8)_2$ and molecules containing a π-C_5H_5 grouping.

Acknowledgments.—The partial support of this work by NSF Grant GP-10063 is acknowledged gratefully.

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