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## Optically Detected Magnetic Resonance in the Photoexcited Triplet States of Ti(IV) and Zr(IV) Cyclopentadienyl Complexes

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The class of compounds (RCp)<sub>2</sub>MX<sub>2</sub>, where M is a group IV metal, Cp is cyclopentadienyl, R is an alkyl, and X is a halide, have been of continuing interest as precursors for olefin coordination polymerization catalysts.<sup>1</sup> The photochemical properties of these neutral compounds and the polymerization activity of the activated catalysts have been shown to be exquisitely sensitive to the nature of the alkyl substituent, R, on the cyclopentadienyl, Cp, ligand.<sup>1,2</sup> Progress in both theory<sup>3–5</sup> and experiments has led to a general understanding of how the halide and the Cp ring substituents affect the observed trends in redox potentials,<sup>6</sup> ionization energies,<sup>7</sup> and electronic spectra.<sup>8–10</sup> However, a quantitative understanding of the impact of the alkyl substituents on the electronic structure and particularly on the composition of the frontier molecular orbitals remains a subject of continuing research. In this communication, we demonstrate that the technique of optically detected magnetic resonance (ODMR) reveals subtle differences in the composition of the frontier molecular orbitals associated with the nature of the alkyl substituents on the Cp rings.

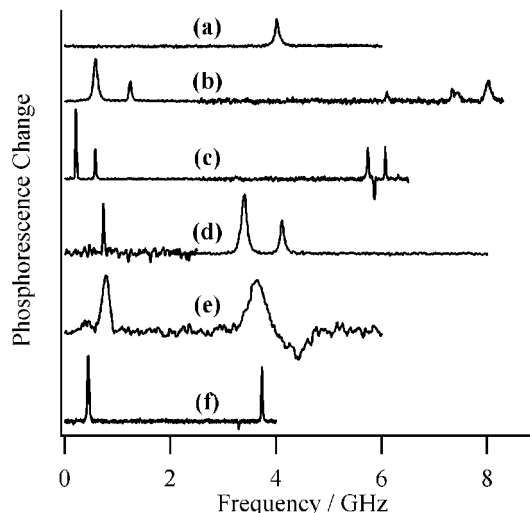
ODMR transitions are ESR transitions in the photoexcited triplet state that are indirectly detected from the change of intensity of the phosphorescence emission.<sup>10,11</sup> ODMR experiments were performed on a home-built instrument using an argon ion laser for optical excitation and either amplitude modulated CW or pulsed microwave irradiation. ODMR spectra of the titanocene and zirconocene samples in the form of polycrystalline powders or in frozen solution were recorded between  $T = 1.3$ – $20$  K. The ODMR spectra for several titanium(IV) and zirconium(IV) metallocenes are shown in Figure 1.

In the absence of an externally applied magnetic field, three ODMR transitions with frequencies  $2E$ ,  $D - E$ , and  $D + E$  are expected for a triplet state, where  $D$  and  $E$  are the zero-field splitting (ZFS) parameters defined by the spin Hamiltonian:<sup>12</sup>

$$H = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2) \quad (1)$$

The ODMR lines are uniquely assigned when all three transitions from a triplet state can be observed since the transition ( $D + E$ ) at higher frequency is simply determined by the sum of the two lower frequency transitions ( $2E$  and  $D - E$ ), where it has been assumed  $D, E > 0$ . In the case of axial symmetry,  $E = 0$ , only a single ODMR transition is observed.

The  $|D|$  and  $|E|$  values determined directly from these spectra are listed in Table 1. There are several features and trends of the data that we examine in detail: (1) the magnitudes of the  $|D|$  values, (2) the greater than expected number of ODMR lines for (Cp)<sub>2</sub>TiCl<sub>2</sub>



**Figure 1.** ODMR spectra of (a) CpZrCl<sub>3</sub>, (b) (Cp)<sub>2</sub>ZrCl<sub>2</sub>, (c) (Cp)<sub>2</sub>TiCl<sub>2</sub>, (d) (MeCp)<sub>2</sub>TiCl<sub>2</sub>, (e) (*n*-BuCp)<sub>2</sub>TiCl<sub>2</sub>, and (f) (Me<sub>5</sub>Cp)<sub>2</sub>TiCl<sub>2</sub> recorded at zero field. The relative intensities in the spectra of (b), (c), and (d) were adjusted as different microwave helix structures were used to record certain frequency ranges.

**Table 1.** Zero-Field Splittings, Phosphorescence Emission Maxima, and Calculated  $D$  Values and Spin Densities for Metallocenes

M <sup>a</sup>	$\lambda_{\text{max}}^{\text{exp}}$ nm	$D^{\text{exp}}$ GHz	$D^{\text{DFT}}$ GHz <sup>b</sup>	$E^{\text{exp}}$ GHz	spin Cl <sup>c</sup>	spin Ti/Zr <sup>c</sup>
(b)	450	6.71 7.72	1.16	0.61 0.29	0.20	0.78
(c)	640	5.96 6.02	1.33	0.10 0.29	0.20	0.95
(d)	655	3.76	1.25	0.35	0.14	0.97
(e)	670	3.90	1.22	0.35	0.16	0.98
(f)	700	3.52	1.14	0.22	0.10	1.01
(a)	470	4.02	1.19	0.0	0.20	0.85

<sup>a</sup> M: (a) (Cp)ZrCl<sub>3</sub>, (b) (Cp)<sub>2</sub>ZrCl<sub>2</sub>, (c) (Cp)<sub>2</sub>TiCl<sub>2</sub>, (d) (MeCp)<sub>2</sub>TiCl<sub>2</sub>, (e) (*n*-BuCp)<sub>2</sub>TiCl<sub>2</sub>, (f) (Me<sub>5</sub>Cp)<sub>2</sub>TiCl<sub>2</sub>. <sup>b</sup> Calculation details in ref 14. <sup>c</sup> Mulliken spin density from DMol3 (MSI, Inc).

and (Cp)<sub>2</sub>ZrCl<sub>2</sub>, (3) the single line for (Cp)ZrCl<sub>3</sub>, and (4) the relative line widths and intensities.

For the series (RCp)<sub>2</sub>TiCl<sub>2</sub>, R = H, Me, *n*-Bu, Me<sub>5</sub>, a large decrease ( $\sim 35\%$ ) in  $|D|$  is observed when a single alkyl replaces a H on the Cp ring. Further differences in  $|D|$  on the order of 10% are observed associated with the number and type of alkyl groups on the Cp rings. This contrasts with the progressive red-shift observed for the phosphorescence emission maxima for the same series of molecules, see Table 1. A large blue-shift in the phosphorescence of the zirconocenes is also not reflected in the ZFS values where the differences between the titanocenes and zirconocenes ZFS values is much smaller.

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The ZFS is comprised of two major contributions: the electron–electron dipolar interaction and the spin–orbit interaction. The electron dipolar contribution should be comparable for all molecules within the series  $(\text{RCp})_2\text{TiCl}_2$ , which all have a common core chemical structure and similar photoexcited triplet states. The spin–spin dipolar contribution of the ZFS  $D$  value was calculated using the Mulliken spin analysis obtained from the DFT electronic structure calculations.<sup>13</sup> The energy minimized structures calculated by DFT showed that one of the triplet molecular orbitals is predominantly localized on the metal, while the second triplet state molecular orbital is delocalized over the Cp and Cl ligands. The Mulliken spin density was used to weight the dipole–dipole contribution between the electron on the metal d-orbital and the second electron, which is delocalized over the individual nuclei of the ligands. The calculated  $D$  values are shown in Table 1. As expected based on the similarity of the chemical structures, the dipolar contribution to the  $|D|$  values are not substantially different among the metallocenes. However, the calculated dipolar contribution to the  $|D|$  values are only ~10–25% of the experimental  $|D|$  values. This implies a relatively large contribution of the spin–orbit coupling interaction to the observed  $|D|$  values.

The large contribution of the spin–orbit coupling to  $|D|$  reveals the origin of the large decrease in  $|D|$  for  $(\text{RCp})_2\text{TiCl}_2$  relative to that for  $(\text{Cp})_2\text{TiCl}_2$ . The spin–orbit coupling is determined by the Ti d-orbital and Cl p-orbital components of the triplet HOMO (the spin–orbit coupling coefficient for carbon is insignificant compared to the Ti and Cl atoms). The spin densities on the Ti and Cl atoms from the Mulliken analysis are shown in Table 1. The decrease in  $|D|$  for  $(\text{RCp})_2\text{TiCl}_2$  is a consequence of the smaller spin density on the Cl ligands relative to  $(\text{Cp})_2\text{TiCl}_2$ . The decrease of ~30% in the spin density on Cl determined by the Mulliken spin analysis is close to the ~35% decrease in the experimentally determined  $|D|$  value.

The combined ODMR and DFT results imply that the spin density of the triplet state of  $(\text{Cp})_2\text{TiCl}_2$  has more Cl p-orbital character than  $(\text{RCp})_2\text{TiCl}_2$ . A possible origin of this change in orbital character is the hyperconjugative effect arising from the orbital overlap between the alkyl carbon and Cp ring carbon to which it is attached. Such hyperconjugative effects have been described theoretically by Libit and Hoffman to account for the polarization effects on the electron density distribution in aromatics arising from methyl group substitutions on the rings.<sup>14</sup> Hyperconjugation has been invoked to explain X-ray photoelectron data on methyl group substitution for metal-coordinated cyclopentadienyl rings.<sup>7</sup>

The  $|D|$  values for the two zirconocenes are larger than for the titanocenes despite the fact that the spin density on the metal is lower and that the spin density on Cl is the same for  $(\text{Cp})_2\text{ZrCl}_2$  as for  $(\text{Cp})_2\text{TiCl}_2$ . This is a consequence of the larger spin–orbit coupling coefficient for Zr compared to Ti. The difference in the local symmetry of the CpZr molecular fragment accounts for the axial versus rhombic patterns observed for  $(\text{Cp})\text{ZrCl}_3$  vs  $(\text{Cp})_2\text{ZrCl}_2$ . The smaller  $|D|$  value for  $(\text{Cp})\text{ZrCl}_3$  implies greater covalency relative to  $(\text{Cp})_2\text{ZrCl}_2$ . The similarity of the phosphorescence and  $|D|$  values provides further support for the assignment of the optical transition and the triplet state to a  $\text{Cp} \rightarrow \text{M LMCT}$ .

We now turn to the surprising result that for  $(\text{Cp})_2\text{ZrCl}_2$  and  $(\text{Cp})_2\text{TiCl}_2$  six rather than the expected three ODMR transitions are observed. On the basis of the summation rules described above, these six lines are assigned to the three zero-field ODMR transitions originating from two separate triplets. The two triplet states can in principle arise from excited electronic triplet states of the same molecule, or they can each originate from separate distinct molecules. The presence of two triplet states was observed in

ODMR spectra recorded on powdered samples and frozen solutions of metallocenes in hydrocarbon solvents and for the metallocene dispersed in a butyl elastomer. These results indicate that the molecular environment such as crystal field or solvation effects cannot account for the presence of the two triplet states.

The lowest-energy configuration for bis-cyclopentadienylmetallocenes is obtained when the two Cp rings are in a staggered position ( $C_s$  symmetry). However, the difference in energy between the staggered and the eclipsed ( $C_{2v}$  symmetry) Cp ring positions is small. The barrier for the  $C_5$  axis rotation of the Cp ring for  $(\text{Cp})_2\text{TiCl}_2$  was estimated by temperature-dependent solid-state NMR to be less than 5 kcal/mol.<sup>15</sup> By inserting a monochromator in front of the photomultiplier detector in the ODMR experiments it was possible to determine that the two triplets differ in emission wavelength by approximately 30 nm (equivalent to an energy of ~4 kcal/mol). On the basis of these results, we hypothesize that the two triplet states observed for  $(\text{Cp})_2\text{TiCl}_2$  and  $(\text{Cp})_2\text{ZrCl}_2$  originate from two molecular conformations, differentiated with the Cp rings in either the eclipsed or staggered rotameric states.

In the case of  $(\text{RCp})_2\text{TiCl}_2$ , the alkyl groups on the Cp rings can avoid steric crowding in conformations where the alkyl is positioned on the open side of the bent metallocene. In the case of  $(n\text{-BuCp})_2\text{TiCl}_2$  and  $(\text{MeCp})_2\text{TiCl}_2$  more than one conformation of the staggered Cp ring positions is possible, contributing to an inhomogeneous broadening of the ODMR lines. In the case of  $(n\text{-BuCp})_2\text{TiCl}_2$ , the alkyl chain can also assume gauche or trans conformations, leading to additional inhomogeneous broadening of lines in the ODMR spectra. For  $(\text{Me}_5\text{Cp})_2\text{TiCl}_2$  all rotamer positions are equivalent resulting in narrow ODMR lines.

The differences in the composition of the frontier MOs revealed by ODMR should prove to be useful in further understanding how the polymerization activity of the activated molecules depends on the alkyl substituents of the Cp ligands.

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