On the Electronic Structure of Bis(η₅-cyclopentadienyl) Titanium

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Abstract
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Comments
On the Electronic Structure of Bis(η⁵-cyclopentadienyl) Titanium

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Prior to the first reported synthesis of the titanium analogue of ferrocene, bis(η⁵-cyclopentadienyl)Ti, there was theoretical speculation as to the electronic structure of what would become known as “titanocene”. In time, the original report of a successful synthesis was apparently shown to be incorrect, and a dimeric form of the substance was postulated as the correct structure. In the present work, high level ab initio and DFT calculations are performed on the titanocene monomer to help answer these structural questions, and to compare with early theoretical and experimental efforts. The need for a multi-configurational wave function is analyzed and found to be unnecessary. The present calculations predict that the ground state of titanocene monomer is a triplet with parallel and freely rotating cyclopentadienyl rings, which further suggests that experimentally synthesized “titanocene” is indeed some form of the dimer.

I. Introduction

A. Historical Background. The historical account given here is presented from a distinctly theoretical point of view. For an experimental perspective, see the recent review by Beckhaus. 1

Even before Fischer and Wilkinson reported the first synthesis of what they called d[π-cyclopentadienyl](titanium(II)) in 1956, 2 there was theoretical speculation as to the electronic structure of what would come to be known as “titanocene”. From 1953 to 1954, Dunitz and Orgel, 3,4 Jaffe, 5 and Moffitt, 6 in the light of molecular orbital theory and motivated by the recent discovery of ferrocene, 7 considered the electronic structure of all bis-cyclopentadienyl compounds in general. Moffitt assumed a D<sub>3d</sub> structure for the “beautifully symmetric” ferrocene, and broke the molecule into the iron atom and cyclopentadienyl (Cp) ring fragments to evaluate the bonding. For the rings, he used a simple p-orbital basis on each carbon atom to derive a linear combination of 10 MOs: \( a_{1g} + a_{2u} + e_{1g} + e_{2u} + e_{1u} + e_{2u} \). Moffitt then chose to describe the iron atom using its 4s \((a_{1g})\), 3d \((a_{1g}, e_{1g}, e_{2g})\), and 4p \((e_{1u}, a_{2u})\) orbitals. From there, qualitative arguments were used to estimate the orbital energies, and the resulting orbital interaction diagram was derived: in order of increasing energy, the frontier orbitals for titanocene were \((e_{1g})^2 (a_{2u})^2 (a_{1g})^3 \) \([a_{1g}(4s)]^0 (e_{1u})^4 (e_{2u})^4\), where the \(e_{1u}\) and \(e_{2u}\) orbitals are nearly degenerate. In his model, the stability of ferrocene was accounted for by significant overlap of the \(e_{1g}\) orbitals of the Cp rings and the corresponding \(d_{z^2}\) and \(d_{x^2-y^2}\) orbitals of the iron atom. By extrapolation, Moffitt suggested that titanocene, with its four valence electrons, should be a diamagnetic singlet, with the two nonbonding titanium electrons assigned to the \(a_{1g}(4s)\) orbital. However, Moffitt also suggested that if the Hund stabilization was significant, the paramagnetic triplet, with one electron in the metal’s \(e_{2g}\) orbital, would be more stable. Titanocene had yet to be synthesized experimentally at the time of Moffitt’s paper, so these predictions could not be tested.

A year later, Dunitz and Orgel 4 modified Moffitt’s qualitative approximation into a “semiquantitative” model, approximating overlap integrals between the metal atom and Cp ring orbitals. These calculations changed ferrocene’s frontier MO orbital energies (for titanocene occupation) from Moffitt’s order to \((a_{1g})^2 (a_{2u})^2 (e_{1g})^3 (e_{2u})^2 [a_{1g}(4s)]^0 (e_{1u})^4\) in order of increasing energy, the last three orbitals being “uncertain,” and approximately degenerate. This in turn changed the prediction for titanocene from a singlet to a triplet, since the two nonbonding metal electrons were assigned to the degenerate \(e_{2u}\) orbital.

Also in 1955, Fisher and Wilkinson 2 reported the first synthesis of titanocene. They were aware of the predictions of Moffitt, Dunitz, and Orgel, and since they found their substance to be diamagnetic, they used Moffitt’s scheme to support their observation that there were two forms of the compound: a green paramagnetic (triplet) form that converted spontaneously to a brown diamagnetic (singlet) form. On the basis of magnetic susceptibility experiments, they proposed that for unsolvated titanocene, the excited triplet state must be at a level at least \(kT\) (~0.75 kcal) above the singlet ground state.

In 1957, another theoretical paper appeared on metal aromatic structures by Liehr and Ballhausen. 8 They followed Moffitt’s basic treatment, and improved on Dunitz and Orgel’s calculations by using one-electron Hamiltonians and the variational principle, applied to each of the important molecular orbitals. They further estimated orbital energies using crystal field theory, allowing positive point charges on the Cp rings to interact with the metal’s \(e_{1g}\) orbital to simulate bonding interactions. Antibonding interactions were modeled with negative point charges on the Cp ring interacting with the same metal \(e_{1g}\) electrons, and nonbonding interactions were between negative point charges on the ring and electrons in the metal’s \(a_{1g}\) \((4s)\), \(a_{1g}\), and \(e_{2g}\) orbitals. Using this method, they found the order of increasing energy in MOs to be \((a_{1g})^2 (a_{2u})^2 (e_{1u})^4 (e_{1g})^3 [a_{1g}(4s)]^0\). This also suggested a singlet ground state for titanocene, but the authors used an adjustable parameter and the experimental results of Fischer and Wilkinson to generate this result after the fact.

Two years later, Matsen 9 used a “strong-field, ligand-field model” to predict a singlet ground state for titanocene, again in support of the known experimental evidence at the time.

In 1960, Robertson and McConnell, 10 in a magnetic resonance study, noted that based on Fischer and Wilkinson’s work,
titanocene should be diamagnetic, but they argued that this does not fit their ionic model well. The model represents the Cp ligands using circular line charges, which create a field potential. This potential splits the 3d orbitals, and an energy difference could be calculated. Based on experimental magnetic susceptibility data, the authors assumed that of the metal’s 3 d orbitals, $d_{xz}$ and $d_{yz}$ should be nearly degenerate, and lie much lower in energy than the $e_{1g}$. The authors noted that titanocene, with two electrons in these orbitals, does not fit this assumption, since it would then most likely be paramagnetic by Hund’s rule. They suggested that the observed magnetic properties may be a result of interaction with neighboring molecules in the crystal, which may “quench” the spin. They also suggested lowering the energy of one of the three d-orbitals, but ultimately did not adopt this since the other metalloccenes studied fit their model quite well. They considered titanocene an exception to their general conclusions.

An excellent review of the above theoretical approaches as they apply specifically to ferrocene is given by Scott and Becker. They also include the Yamazaki reference, which is the first theoretical treatment to use SCF theory, although that paper makes no specific reference to titanocene.

In 1964, Watt and Baye reported properties of FeCp$_2$, NiCp$_2$, and CrCp$_2$, and questioned Fischer and Wilkinson’s synthesis of TiCp$_2$: “[W]e have been unable to produce (C$_5$H$_5$)$_2$Ti by their procedure, by any modification thereof, or by other methods that might reasonably be expected to provide this compound.” In a later paper, these same authors along with Drummond noted two other reported syntheses of titanocene, but suggest that the characterizations of each were quite weak. They used IR data to support their claim that they had indeed produced titanocene, and reported that the substance is more stable thermally than had been reported by Fischer and Wilkinson. When their diamagnetic singlet green form is heated to 200°C, it turns black and appears to decompose, but then dissolves in benzene to form a green solution of titanocene which can be recrystallized. Their magnetic susceptibility experiments showed that all samples of titanocene were diamagnetic. They found the molecular weight (cryoscopically in benzene) to be 346, compared to 178.07 for (C$_5$H$_5$)$_2$Ti (178.07 g mol$^{-1}$). The authors noted that titanocene, with two hydride bound to the titanium atom. Brintzinger and Bartell subsequently elaborated on their earlier communication. They reported that “titanocene” is “...a titanium hydride complex and contains two of its four ring ligands in the form of C$_5$H$_4$ units.” They explained much of titanocene’s chemistry by analogy to a carbene. In another follow-up communication, Marvich and Brintzinger again claim to have isolated (C$_5$H$_5$)$_2$Ti, but only as the dimer. This appears to be the end of experimental speculation on “titanocene” in the literature.

In 1975, Lauher and Hoffmann published a theoretical study of bis(cyclopentadienyl)-ML$_n$ complexes. They constructed molecular orbitals for a bent bis($p^5$-cyclopentadienyl)Ti (TiCp$_2$) fragment, which serves as a starting point for a general overview of more complex organometallics. These authors considered the general MCP$_2$ fragment to be two parallel C$_5$H$_5$- ligands in D$_{sd}$ symmetry. In trying to understand how additional ligands attach to a MCP$_2$ fragment, the authors examined the frontier orbitals of a TiCp$_2$ fragment using extended Hückel calculations. To make maximum use of symmetry, they bend from the D$_{sd}$ geometry into a C$_{2v}$ structure. They found that the orbitals descended from the $e_{1g}$ orbitals are stabilized with bending, and those from $a_{1g}$ and $e_{2g}$ are destabilized. They concluded that the “typical” C$_5$-Ti-C$_5$ angle is 136°, and noted the similarity between their results and that of Brintzinger and Bercaw.

Finally, in 1978 Clack and Warren used INDO SCF calculations to come to the same conclusions as Hoffmann about the relative frontier orbital energies.

**B. The Present Approach.** It is clear that there has been much interest and speculation regarding the nature of the electronic structure of “titanocene.” (Here we will take “titanocene” to mean a single bis($p^5$-cyclopentadienyl)Ti fragment, abbreviated as TiCp$_2$.) There seems to be general agreement that attempts to prepare titanocene in the laboratory result in some form of the dimer, with or without hydride bridges, as discussed above. Still, the TiCp$_2$ fragment, while possibly not stable as the monomer, is still an important component of many useful catalysts, and a knowledge of its electronic structure will aid in the understanding of the chemistry of these species. Of course, it is also important to obtain an understanding of the molecular and electronic structure of TiCp$_2$ itself. We anticipate that future work will focus on the electronic structure of possible dimers.

Our approach will be to reexamine previous conclusions using high-level ab initio and density functional theory (DFT) theories to determine the structure and relative energies of the lowest energy singlet and triplet states of TiCp$_2$. First, the use of multi-configurational wave functions will be analyzed, to assess the need for such a wave function. Once it is established that single reference methods should be reliable, DFT, second-order perturbation theory (MP2) and coupled cluster [CCSD(T)] methods are employed to elucidate the low-energy form of TiCp$_2$.

**II. Methods.**

The all-electron 6-31G**$^{*}$ and PVTZ$^{26}$ basis sets were used for all atoms, including titanium. Geometries and numerical
Hessians were obtained at the Hartree–Fock, DFT, and MP2 levels of theory. For the MCSCF wave function, a (2,2) active space is used, where the two orbitals are the HOMO and LUMO based on the MP2 natural orbitals. Larger active spaces sets were also tested with similar results. MCSCF, ROHF, RHF, DFT (B3LYP), and closed-shell MP2 calculations were carried out using the GAMESS suite of programs, unrestricted MP2 (UMP2) calculations were performed using Gaussian 94, and Molpro was used for the CCSD(T) and UCCSD(T) calculations. The notation RHF/6-31G** refers to a geometry optimization at this level of theory, while RHF/PVTZ/RHF/6-31G** refers to a single-point RHF/PVTZ calculation at the RHF/6-31G** geometry. Numerical Hessians were evaluated throughout, using the double-difference method, and projected to eliminate rotational and translational contaminants. Because of numerical instabilities encountered, the default step size was reduced an order of magnitude to 0.001 bohr. Even so, many of the imaginary frequencies reported are due to numerical noise.

For C₂v and C₃ geometries, the C₅–Ti–C₅ angle is measured by defining the plane of each C₅ ring in terms of three points: the nuclei of the symmetry unique carbon and the two carbons furthest away from it in the same C₅ ring. The angle between the two vectors normal to these planes is defined as the Cp angle. When this angle is 180°, the molecular geometry will be referred to as “linear”.

III. Results and Discussion

A. Preliminary Considerations. Let us first consider the symmetry characteristics of the molecule in more detail. If the Cp rings are parallel to one another and staggered, TiC₅₂ has D₅h symmetry; if the rings are parallel but eclipsed, the symmetry is D₅d; decreasing the C₅–Ti–C₅ angle θ from 180° in D₅h symmetry gives C₂v, and similar bending from D₅d gives a C₃ geometry. Figure 1 shows the orientation of these four point groups relative to Cartesian coordinates. For the C₃ geometry, the xy plane is the mirror plane. Note that upon reducing symmetry from (D₅h/D₅d) to (C₂v/C₃), the molecule is rotated from (y, z, x) to (x, y, z) in order to maintain the z-axis as the principal axis. Consequently, orbital designations change also. For example, a dₓ orbital in C₃ is a dₓ in D₅d. For ease of reference, Table 1 summarizes this information.

B. Hartree–Fock Analysis. Preliminary calculations were carried out at the Hartree–Fock level. As shown in Table 2, the ROHF/6-31G** A (1B₁) (C₅v) and A' (1C₃) optimized geometries are nearly degenerate, and both lie 18.6 kcal/mol below the analogous A₂ (D₅h) structure, which itself is nearly degenerate with the A₂ (D₅d) structure. Similarly, the RHF A' (C₂v) geometry lies just 0.1 kcal/mol below the A' (C₃) structure, and 9.4 kcal/mol below the A₁ (D₅h) and A₁ (D₅d) structures, where the latter two are essentially degenerate. The A' (C₂v) state is 39.3 kcal/mol above the A' (C₃) state at this level of theory. All of the geometries at the HF level have the Cp rings within roughly 6 degrees of being parallel. Of course, D₅d and D₅h symmetries force the rings to be exactly parallel. Inefficient overlap of the cyclopentadienyl π orbitals is the most likely cause for the lack of bending of the Cp—Ti—C₅ angle in C₃ symmetry.

Numerical Hessians performed at this level show imaginary frequencies for the C₂v and C₃ geometries, while for higher symmetry (except triplet D₅d which has a small imaginary frequency) the geometries are positive definite. All attempts to step off these imaginary modes (as one does in an intrinsic reaction coordinate calculation, for example) and isolate a positive definite geometry failed. This may suggest that the numerical Hessians are very sensitive to step sizes due to the low-frequency ring modes.

For the triple-ζ basis set, one sees qualitatively similar behavior. It is especially revealing that the relative RHF/PVTZ/RHF/6-31G** energies are essentially identical to those for the full RHF/PVTZ optimization, as seen in Table 3. This suggests that the 6-31G** geometries are adequate at the Hartree–Fock level. Based on the results in Tables 2 and 3, we conclude that HF theory predicts TiC₅₂ has a triplet ground state with C₂v symmetry (B₁) that is ~40 kcal/mol below the lowest singlet (C₃v, 1A₁).

C. MCSCF/GVB Theory. Based on previous calculations for TiH₂ and TiH₃, one might expect TiC₅₂ calculations to require a multiconfigurational wave function. To assess the need for such a wave function, the singlet MP2 natural orbitals were used as a starting point for a TCSCF calculation with the MP2 HOMO (3dₓ) and LUMO (4pₐ) as the (2,2) active space. The resulting natural orbital occupation numbers (NOONs) in the active space show very little multiconfigurational character: 1.992 and 0.008 electrons in the HOMO and the LUMO, respectively. Using triplet TCSCF orbitals as a starting guess...
TABLE 2: Energies, \( E \) (kcal/mol), Are Relative to the Corresponding \( ^1A_1 \) (\( C_{2v} \)) State; \( \theta \) Is the Cp–Ti–Cp Angle; \( v \) (cm\(^{-1}\)) Are the Imaginary Frequencies\(^d\)

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<th>( ^1A' ) (( C_{1v} ))</th>
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<th>( ^1A'' ) (( C_{1v} ))</th>
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\(^a\) Intensity less than 0.001 D/amu \( \text{Å}^2 \). \(^b\) Zero intensity. \(^c\) The geometry is considered converged at a RMS gradient of less than 6.9 \( \times \) \( 10^{-5} \) hartree/bohr rather than the usual default of 3.0 \( \times \) \( 10^{-5} \). \(^d\) For DFT, the imaginary frequencies are calculated with the tight grid — see text for explanation. The 6-31G** basis is used throughout.

TABLE 3: Energies, \( E \) (kcal/mol), Are Relative to the Corresponding \( ^1A_1 \) (\( C_{2v} \)) State; \( \theta \) Is the Cp–Ti–Cp Angle; \( v \) (cm\(^{-1}\)) Are the Imaginary Frequencies

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for singlet TCSF results in the same occupation numbers. Even after TCSCF optimization starting from the bent MP2 structure, the NOONs changed very little: 1.995 and 0.005. For the triplet TCSCF, NOONs are 1.000 and 1.000. A second diagnostic are the NOONs resulting from a MP2 calculation itself. It has been shown that if these occupation numbers are significantly unphysical, i.e., much greater (less) than two (zero), the system is likely to require a multi-configurational wave function, since this behavior suggests the single-reference Hamiltonian has broken down. In the case of TiCp, the MP2 NOONs range from 2.0018 to 0.0075, where we have included all four geometries. These are not significant deviations from the physical expectations. We therefore conclude that a single-reference wave function is appropriate for TiCp.

**D. Density Functional Theory.** Density functional theory calculations summarized in Table 2 show a quantitative, but not qualitative shift relative to the Hartree–Fock results. Comparing double-\( \xi \) results, the lowest energy structure is still the \( ^3B_1 \) state, but it now lies only 15.0 kcal/mol below the lowest singlet \( C_{2v}, ^1A_1 \), and the \( ^3A_2 \) structures lie 9.0 kcal/mol above \( ^3B_1 \). The triplet geometries remain within nine degrees of linear, but the singlet \( C_{2v} \) and \( C_1 \) geometries bend by an additional 15.0° and 12.9°, to 158.9° and 167.06°, respectively. Both the singlet and triplet \( C_1 \) geometries display three imaginary frequencies using the default DFT grid size in GAMESS; however, these become similar to the Hartree–Fock values when a tighter grid is used. Similarly, all but one \( (D_{3d} ^3A_2) \) of the imaginary frequencies, with zero or very small intensities calculated using the default grid for the \( D_{3d} \) and \( D_{5h} \) geometries, disappear when the tighter grid is used—again similar to Hartree–Fock.

There are very small quantitative changes in going from a double-\( \xi \) to a triple-\( \xi \) basis set; ~2° in the geometries, ~1–5 kcal/mol in the relative energies, and ~10–15 wavenumbers in the imaginary frequencies. It appears that very little is gained by increasing the size of the basis set, although the splitting between the triplet geometries is reduced to 5.9 kcal/mol. Single-point energies at double-\( \xi \) geometries agree with full triple- \( \xi \) optimizations to within 0.3 kcal/mol.

While the singlet–triplet splitting is reduced to ~13 kcal/mol, compared with ~40 kcal/mol for HF, DFT still predicts a triplet ground state for TiCp.

**E. Second-Order Perturbation Theory.** The MP2/6-31G** results (Table 2) are very similar to those summarized above for DFT: The \( ^3B_1 \) (\( C_{2v} \)) ground state is predicted to be ~15 kcal/mol below the higher symmetry triplets and ~21 kcal/mol below the lowest energy \( ^1A_1 \) (\( C_{2v} \)) singlet state. One again finds small (~15i–50i cm\(^{-1}\)) imaginary frequencies, due to instabilities of the numerical Hessians. This picture is significantly altered when the larger triple- \( \xi \) basis set is used, as shown in Table 3. Now, all of the triplets are within ~1 kcal/mol of each other, with the higher symmetry \( D_{3d} \) and \( D_{5h} \) structures slightly lower in energy. The ground state is still predicted to be the
triplet, but now only by ~6 kcal/mol relative to the C2v, 1A1 singlet. The latter is still predicted to be the lowest energy singlet structure.

**F. Coupled Cluster Theory.** To further evaluate the relative energetics, CCSD(T) [UCCSD(T)] calculations were performed at the singlet [triplet] MP2/6-31G** [UMP2/6-31G**] geometries using the 6-31G** and PVTZ basis sets. The results are qualitatively similar to the perturbation theory results, as seen in Table 3. Note that because of program limitations, the restricted D3a(D5h) energy is evaluated using the Abelian C2v (C2v) point group. Based on MP2 and HF calculations, the Abelian energy is artificially 0–10 kcal/mol low due to split degeneracies; Table 3 reports uncorrected raw data from the restricted calculations. This is not an issue for the unrestricted triplet calculations. For the 6-31G** basis set, all the triplet geometries are more stable than the lowest singlet, and the splitting between triplet C2v/C1/D3a/D5h is 12.8 kcal/mol. As in the MP2 case, there is a qualitative shift when the PVTZ basis set is used; the triplet geometries are all still lower in energy, but in this case the lowest energy structure is the 3A2 (D5h).

This further suggests that the lowest energy geometry of the monomer is indeed linear about the Ti. As for MP2, there is also a significant basis set effect on the singlet–triplet splitting. The triplet is lower than the lowest energy singlet, 1A1 (C2v), by only ~8 kcal/mol at this level of theory.

**IV. Conclusions**

At all levels of theory, the triplet geometries are all lower than the lowest energy singlet, and as a general rule, the splitting between the high-symmetry and low-symmetry triplets becomes less as the level of theory is increased. In all of the above calculations where double- and triple-ζ optimizations are feasible, it is found that triple-ζ energies at double-ζ geometries reproduce the results of full triple-ζ optimizations to within 0.3 kcal/mol. At all applicable levels of theory, Hartree–Fock, B3LYP (with sufficiently tight grid) and MP2, the numerical Hessians show the high symmetry, linear geometries are positive definite or have imaginary frequencies with wavenumbers less than 20 cm⁻¹. An exception to this is the high-symmetry UMP2 results, where on the basis of further testing with different step sizes, we find that the four imaginary frequencies reported are due to numerical instabilities. On the basis of these data, we conclude that bis(η⁵-cyclopentadienyl)Ti is a linear paramagnetic triplet with freely rotating Cp rings. All attempts to synthesize this compound in the literature result in a diamagnetic singlet, which lends support to the suggestion that the true structure is some form of the dimer. It may be interesting to compare this conclusion with recent experimental results which give a nearly linear geometry for TiCp₂ with heavily substituted Cp rings.³⁹

We therefore use the triplet UMP2/6-31G** (D3a) geometry as a model to evaluate physical properties. The two high-spin electrons occupy an E₂g HOMO consisting of dₓ²−ᵧ² and dₓᵧ orbitals, as seen in Table 1. The Mulliken charge on the titanium atom is +0.66, leaving a charge of −0.33 on each Cp ring. The bond order between the titanium atom and each carbon is 0.287, which, along with the linear geometry, suggests true η⁵ bonding with the Cp rings.

It is particularly enlightening to compare these results with those of the early theorists summarized in the Introduction. Recall that before Watt and Baye’s failed synthesis of Fischer and Wilkinson’s “titancene”, this compound was assumed to have a molecular formula of (C₅H₅)₂Ti. This allows us to compare directly with the early results. Figure 2 shows the UHF orbital energies (in hartrees) for the 3A2 (D3a) state at the UMP2/

**References and Notes**

(10) Robertson, R. E.; McConnell, H. M. *J. Phys. Chem.* 1960, 64, 70.


