On the Electronic Structure of Bis(η^5-cyclopentadienyl) Titanium

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Prior to the first reported synthesis of the titanium analogue of ferrocene, bis(η^5-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 di(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] Jaffé,[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_{5d} 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: $a_{1g} + a_{2u} + e_{1g} + e_{2g} + e_{1u} + e_{2u}$. 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 $(e_{1g})^4\ (a_{2u})^2\ (a_{1g})^2\ [a_{1g}(4s)]^2\ (e_{1u})^4\ (e_{2g})^0$, where the e_{1u} and e_{2g} 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_{xz} and d_{yz} 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 $(a_{1g})^2\ (a_{2u})^2\ (e_{1g})^4\ (e_{2g})^2\ [a_{1g}(4s)]^0\ (e_{1u})^4$ 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_{2g} 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 electrons in 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}-(4*s*), a_{1g}, and e_{2g} orbitals. Using this method, they found the order of increasing energy in MOs to be $(a_{1g})^2\ (a_{2u})^2\ (e_{1u})^4\ (e_{1g})^4\ [a_{1g}(4s)]^2$. 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,

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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 3*d* orbitals, and an energy difference could be calculated. Based on experimental magnetic susceptibility data, the authors assumed that of the metal's *d* orbitals, a_{1g} and e_{2g} 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 metallocenes 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.[11] They also include the Yamazaki[12] 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[13] 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 $(C_5H_5)_2$-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,[14] 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°, 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 $(C_5H_5)_2Ti$ ($178.07 \times 2 = 356.14$).

Calderazzo, Salzmann, and Mosimann,[15] based on the above results, suggested a dimeric formula for titanocene, although they were not specific regarding the details of such a structure. In a later paper, Salzmann and Mosimann[16] suggested that the IR spectra of Watt, Baye, and Drummond's compound is too complex to be consistent with a simple ferrocene-like sandwich structure. They note the spectrum has characteristics of both σ and π ring-to-metal bonding, but were unsure as to the stability of this structure in solution.

In 1969, Brintzinger and Bartell[17] proposed that both Watt, Baye, and Drummond[14] and Salzmann and Mosimann[15] indeed had a compound $C_{10}H_{10}Ti$, but it in fact exists as a dimer and does not have the traditional sandwich structure of metallocenes. They used IR and NMR data to confirm Salzmann and Mosimann's suggestion that the Cp rings are σ bound as well as π bound to the titanium atom. Brintzinger and Bartell also reported extended Hückel calculations on the "hypothetical" molecule $(\pi\text{-}C_5H_5)_2Ti$. They used previous calculations on vanadocene[18,19] to suggest that the metal's nonbonding, unoccupied a_{1g} orbital (d_z^2) lies just above the filled ligand e_{1g} and e_{1u} orbitals. This would allow for a second-order Jahn−Teller geometrical distortion of E_{1g} or E_{1u} symmetry. The E_{1u} distortion would correspond to bending of the Cp rings away from axial symmetry. (They use D_{5d} notation, although they consider the molecule to be D_{5h}.) Their Hückel calculations suggest that a Cp−Ti−Cp angle of 140−150° should be most stable. They also considered the E_{1g} distortion that would convert the π sandwich molecule to a σ complex, but the authors performed no calculations on this distortion. It was also proposed that $(\pi\text{-}C_5H_5)_2Ti$ is unstable, and most likely decomposes by means of a hydride shift from one of the ring hydrogens to the Ti atom.

Brintzinger and Bercaw[20] 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_5H_4 units." They explained much of titanocene's chemistry by analogy to a carbene. In another follow-up communication, Marvich and Brintzinger[21] again claim to have isolated $(C_5H_5)_2Ti$, but only as the dimer. This appears to be the end of experimental speculation on "titanocene" in the literature. [22]

In 1975, Lauher and Hoffmann[23] published a theoretical study of bis(cyclopentadienyl)-ML_n complexes. They constructed molecular orbitals for a bent bis(η^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_5H_5- ligands in D_{5d} 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_{5h} 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" Cp−Ti−Cp angle is 136°, and noted the similarity between their results and that of Brintzinger and Bercaw.

Finally, in 1978 Clack and Warren[24] 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(η^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 multiconfigurational 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**[25] and PVTZ[26] basis sets were used for all atoms, including titanium.[27,28] Geometries and numerical

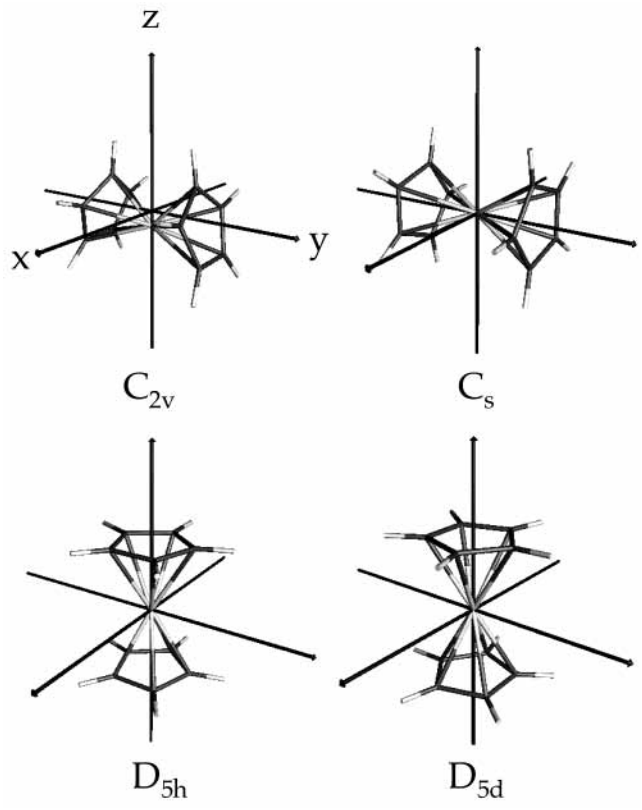

Figure 1. Relative geometries of the four possible point groups of $TiCp_2$.

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),[29] and closed-shell MP2 calculations were carried out using the GAMESS[30] suite of programs, unrestricted MP2 (UMP2) calculations were performed using Gaussian 94,[31] and Molpro[32,33] was used for the CCSD(T)[32] and UCCSD(T)[33] 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.[34] 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 C_{2v} and C_s geometries, the Cp−Ti−Cp angle is measured by defining the plane of each Cp ring in terms of three points: the nuclei of the symmetry unique carbon and the two carbons furthest away from it in the same Cp ring. The angle between the two vectors normal to these planes is defined as the Cp−Ti−Cp angle, θ. 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, $TiCp_2$ has D_{5d} symmetry; if the rings are parallel but eclipsed, the symmetry is D_{5h}; decreasing the Cp−Ti−Cp angle θ from 180° in D_{5h} symmetry gives C_{2v}, and similar bending from D_{5d} gives a C_s geometry. Figure 1shows the orientation of these four point groups relative to Cartesian coordinates. For the C_s geometry, the *xy* plane is the mirror plane. Note that upon reducing symmetry from (D_{5h}/D_{5d}) to (C_{2v}/C_s), 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 d_{xz} orbital in C_s is a d_{xy} in D_{5d}. For ease of reference, Table 1 summarizes this information.

TABLE 1: Relative Symmetries and Labels for $TiCp_2$ (See text for a note on the rotation of the Cartesian axes.)

D_{5d}	D_{5h}	C_{2v}	C_s	orbital designations for D_{5d}, D_{5h}	orbital designations for C_{2v}, C_s
A_{1g}	A_1'	A_1	A'	z^2	y^2
A_{2g}	A_2'	B_1	A''		
E_{1g}	E_1''	$A_2 + B_2$	$A' + A''$	*xz*, *yz*	*yz*, *xy*
E_{2g}	E_2'	$A_1 + B_1$	$A' + A''$	$x^2 - y^2$, *xy*	$x^2 - z^2$, *xz*
A_{1u}	A_1''	A_2	A''		
A_{2u}	A_2''	B_2	A'	*z*	*y*
E_{1u}	E_1'	$A_1 + B_1$	$A' + A''$	*x*, *y*	*z*, *x*
E_{2u}	E_2''	$A_2 + B_2$	$A' + A''$		

B. Hartree−Fock Analysis. Preliminary calculations were carried out at the Hartree−Fock level. As shown in Table 2, the ROHF/6-31G** $^3B_1$ (C_{2v}) and $^3A''$ (C_s) optimized geometries are nearly degenerate, and both lie 18.6 kcal/mol below the analogous $^3A_2$ (D_{5h}) structure, which itself is nearly degenerate with the $^3A_2$ (D_{5d}) structure. Similarly, the RHF $^1A_1$ geometry in C_{2v} symmetry lies just 0.1 kcal/mol below the $^1A'$ (C_s) structure, and 9.4 kcal/mol below the $^1A_1$ (D_{5h}) and $^1A_1$ (D_{5d}) structures, where the latter two are essentially degenerate. The $^1A_1$ (C_{2v}) state is 39.3 kcal/mol above the $^3B_1$ (C_{2v}) 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, D_{5h} and D_{5d} symmetries force the rings to be exactly parallel. Inefficient overlap of the cyclopentadienyl p_y orbitals is the most likely cause for the lack of bending of the Cp−Ti−Cp angle in C_s symmetry.

Numerical Hessians performed at this level show imaginary frequencies for the C_{2v} and C_s geometries, while for higher symmetry (except triplet D_{5d} 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 $TiCp_2$ has a triplet ground state with C_{2v} symmetry ($^3B_1$) that is ∼40 kcal/mol below the lowest singlet (C_{2v} $^1A_1$).

C. MCSCF/GVB Theory. Based on previous calculations for TiH_2,[35,36] and Ti_2H_6,[37] one might expect $TiCp_2$ 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 ($3d_{xz}$) and LUMO ($4p_z$) 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; θ Is the Cp−Ti−Cp Angle; ν (cm^{-1}) Are the Imaginary Frequencies[d]

		$^1A_1$ (C_{2v})	$^1A'$ (C_s)	$^1A_1$ (D_{5d})	$^1A_1$ (D_{5h})	$^3B_1$ (C_{2v})	$^3A''$ (C_s)	$^3A_2$ (D_{5d}) $(e_{2g})^2$	$^3A_2$ (D_{5h}) $(e_2')^2$
HF	*E*	0.0	0.1	9.4	9.4	−39.3	−39.3	−20.7	−20.7
	θ	173.91	180.00			178.21	180.00		
	ν							6[b]	
DFT	*E*	0.0	2.1[c]	19.4	19.4	−15.0	−14.2[c]	−6.0	−6.4
	θ	158.87	167.06			171.17	180.00		
	ν		27				18	21[b]	
MP2	*E*	0.0	1.7	13.8	13.7	−21.0	−21.0	−6.4	−6.7
	θ	148.43	180.00			176.90	179.59		
	ν	45	26, 13			59	19	412[b], 116, 116, 30[b]	2717[b], 116, 116, 30[b]

[a] Intensity less than 0.001 D/amu Å^2. [b] Zero intensity. [c] The geometry is considered converged at a RMS gradient of less than 6.9×10^{-5} hartree/bohr rather than the usual default of 3.0×10^{-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; θ Is the Cp−Ti−Cp Angle; ν (cm^{-1}) Are the Imaginary Frequencies

		$^1A_1$ (C_{2v})	$^1A'$ (C_s)	$^1A_1$ (D_{5d})	$^1A_1$ (D_{5h})	$^3B_1$ (C_{2v})	$^3A''$ (C_s)	$^3A_2$ (D_{5d}) $(e_{2g})^2$	$^3A_2$ (D_{5h}) $(e_2')^2$
HF/PVTZ// HF/6-31G**	*E*	0.0	0.0	15.1	15.1	−36.1	−36.1	−20.2	−20.2
HF/PVTZ	*E*	0.0	0.0	15.1	15.1	−36.1	−36.1	−20.2	−20.2
	θ	174.27	180.00			178.26	180.00		
	ν	26[b]		15[b]	14[b]			7[b]	
B3LYP/PVTZ// B3LYP/6-31G**	*E*	0.0	1.8	24.1	24.1	−13.3	−12.7	−7.2	−7.4
B3LYP/PVTZ	*E*	0.0	1.8	24.4	24.4	−13.1	−12.4[c]	−7.2	−7.4
	θ	160.98	169.90			171.37	180.00		
	ν	140	162, 36	136[a]	136[b]	121, 60[b]	146, 109[b], 69	128[a]	123[b]
(U)MP2/PVTZ// (U)MP2/6-31G**	*E*	0.0	2.0	19.9	19.7	−5.0	−4.4	−5.5	−6.3
(U)MP2/PVTZ	*E*	0.0	2.0	20.1	19.8	n/a	n/a	n/a	n/a
	θ	148.63	180.00			n/a	n/a		
CCSD(T)/6-31G**// (U)MP2/6-31G**	*E*	0.0	0.4	4.2	3.9	−19.3	−19.2	−6.5	−6.8
CCSD(T)/PVTZ// (U)MP2/6-31G**	*E*	0.0	0.5	6.8	6.5	−7.5	−6.9	−7.5	−8.3

[a] Intensity less than 0.001 D/amu Å^2. [b] Zero intensity. [c] The geometry is considered converged at a RMS gradient of less than 6.9×10^{-5} hartree/bohr rather than the usual default of 3.0×10^{-5}.

for singlet TCSCF 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[38] 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 $TiCp_2$, 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 $TiCp_2$.

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-ζ 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_s geometries bend by an additional 15.0° and 12.9°, to 158.9° and 167.06°, respectively. Both the singlet and triplet C_s 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_{5d} $^3A_2$) of the imaginary frequencies, with zero or very small intensities calculated using the default grid for the D_{5d} 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-ζ to a triple-ζ 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-ζ geometries agree with full triple-ζ 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 $TiCp_2$.

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-ζ 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_{5d} 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 C_{2v} $^1A_1$ 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,[33] the restricted D_{5d} (D_{5h}) energy is evaluated using the Abelian C_{2h} (C_{2v}) point group. Based on MP2 and HF calculations,[30] the Abelian energy is artificially 0−10 kcal/mol low due to split degeneracies; Table 3 reports uncorrected raw data from the restricted calcluations. 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 C_{2v},C_s/D_{5d},D_{5h} 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 $^3A_2$ (D_{5h}). 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, $^1A_1$ (C_{2v}), 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(η^5-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 $TiCp_2$ with heavily substituted Cp rings.[39]

We therefore use the triplet UMP2/6-31G** (D_{5d}) geometry as a model to evaluate physical properties. The two high-spin electrons occupy an E_{2g} HOMO consisting of $d_x{}^2 - y^2$ and d_{xy} 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 0.278, which, along with the linear geometry, suggests true η^5 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 "titanocene", this compound was assumed to have a molecular formula of $(C_5H_5)_2Ti$. This allows us to compare directly with the early results. Figure 2 shows the UHF orbital energies (in hartrees) for the $^3A_2$ (D_{5d}) state at the UMP2/PVTZ//UMP2/6-31G** level. Compared with these are the relative orbital energies given by Dunitz and Orgel in 1955 using *approximate* overlap integrals, and building from the group theoretical presentation given by Moffitt in 1954. It seems that their only error was an overestimation of the stability of the metal orbitals, in particular the metal's a_{1g} valence orbital. This profound and striking result is a testament to the power of group theory in the hands of clever chemists.

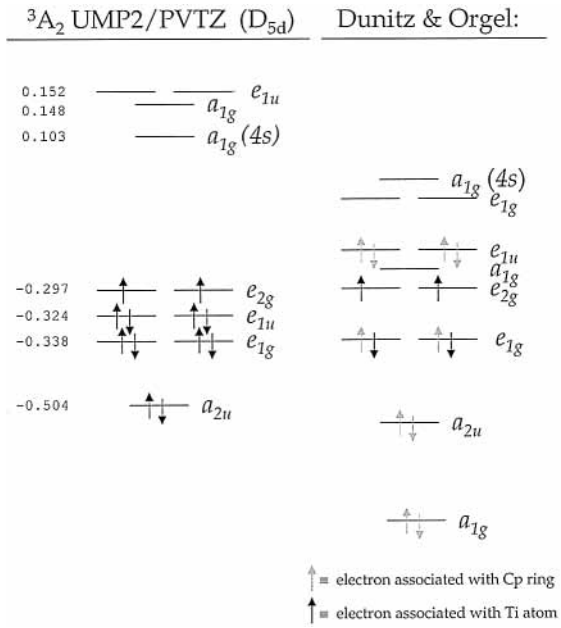

Figure 2. Orbital interaction diagrams for the present work and for that given by Dunitz and Orgel in 1955. Energies are given in hartrees, but the drawing is not strictly to scale.

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