has only very small pockets of negative density above and below the π plane, suggesting that the vinyl group of acrolein is not at all susceptible to electrophilic assault. Moreover, significant positive potential exists well out along the C=C axis suggesting increased susceptibility toward nucleophilic attack. Upon rotation of the carbonyl group, the region above the C=C group is now similar to butadiene, while that region below the C=C group (in the direction of the carbonyl rotation) looks like that of planar acrolein. Vinylamine resembles butadiene above and below the plane but has negative density out along the C=C axis. Again this suggests that electrophilic addition reactions can occur along this axis. When the NH_2 group is rotated out of plane, however, the vinyl group is quite similar to butadiene. We thus see that analytic electrostatic potential maps can recover the chemical reactivity data about a molecule that is often lost in other methods of analyzing charge density distribution.

6. Conclusions

An analysis of the properties of cis, trans, and 90° rotated butadienes showed that the properties of the bonds are not much affected by rotation. However, the π-electron population at the center of the C_2–C_3 bond in butadiene is considerably greater in the trans form than in the 90° rotated form. This is compensated by the opposing change in σ electron population leading to little net change. Thus, the description of the π-electron system which arises from the simple Hückel approach is essentially correct, but a description of the molecule requires that both σ and π electrons be considered.

The vinyl group of acrolein was found to be similar to that of butadiene. Some differences were found with vinylamine, but here the main difference is found with the electrostatic potential which correctly indicates its reactivity toward electrophiles.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation. R.E.R. acknowledges support via an NSF predoctoral fellowship.

Registry No. Butadiene, 106-99-0; acrolein, 107-02-8; 1-butene, 106-98-9; *trans-n*-butane, 106-97-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; vinylamine, 593-67-9.

Explanation of the Unexpected Differences in the Ground States of Dimethyl- and Dichlorobis(1,2-bis(dimethylphosphino)ethane)titanium

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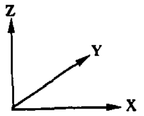
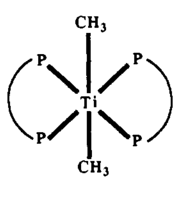
Abstract: Experimentally, $Ti(CH_3)_2(dmpe)_2$ has a *diamagnetic* singlet ground state while $TiCl_2(dmpe)_2$ has a *paramagnetic* triplet ground state. However, the stronger π donor, Cl, is expected to cause a larger splitting of the t_{2g}-like orbitals. Hence, if the ground states are different one would expect $TiCl_2(dmpe)_2$ to be diamagnetic and $Ti(CH_3)_2(dmpe)_2$ to be paramagnetic. In agreement with this simple reasoning, approximate molecular orbital calculations also predict a result contrary to experiment. Ab initio calculations with reasonable basis sets are required to produce qualitative agreement with the experimental results, while quantitative agreement requires significant correlation energy. Results reported here include single-determinant, generalized-valence-bond, complete-active-space, and direct configuration-interaction calculations in several basis sets on the title compounds and several model compounds. The explanation of the differences in states lies in the electronegativity difference between Cl and CH_3. The more electronegative Cl withdraws enough charge from the Ti to contract the d orbital sufficiently to cause the increased d–d electron repulsions in the Cl complex to outweigh the orbital splitting.

Introduction

A recent X-ray diffraction study on $Ti(CH_3)_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane][1] found it to be isostructural with $TiCl_2(dmpe)_2$.[2] Both compounds are pseudooctahedral with chelating phosphines in a rectangular-equatorial plane and Cl's or CH_3's in the axial positions. The coordination spheres for $Ti(CH_3)_2(dmpe)_2$ and $TiCl_2(dmpe)_2$ are shown in 1 and 2, respectively. Surprisingly, Girolami and co-workers found $Ti(CH_3)_2(dmpe)_2$[1] to be *diamagnetic*, a singlet ground state, while $TiCl_2(dmpe)_2$[2] was known to be *paramagnetic*, a triplet ground state.





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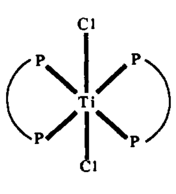

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In a pseudooctahedral system the metal 3d orbitals divide into a low-lying t_{2g}-like set and a high-lying e_g-like set. Since $Ti(CH_3)_2(dmpe)_2$ and $TiCl_2(dmpe)_2$ are d^2 metals, the electrons of interest will occupy the t_{2g}-like orbitals. The energy of the t_{2g}-like orbitals is dominated by the ligands π bonding; π acceptor ligands stabilize these orbitals while π donors destabilize them. Since the stronger π acceptors are in the equatorial plane, one of the low-lying t_{2g}-like orbitals is stabilized relative to the two remaining t_{2g}-like orbitals, which remain nearly degenerate. If the splitting of the t_{2g}-like orbitals, the energy difference between the low-lying nondegenerate orbital and the two nearly degenerate orbitals, is large (see 3) then the two metal 3d electrons will occupy the low-lying nondegenerate orbital, and the compound will be diamagnetic. Conversely, if the splitting is small, one metal 3d

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[†] Texas A&M University.

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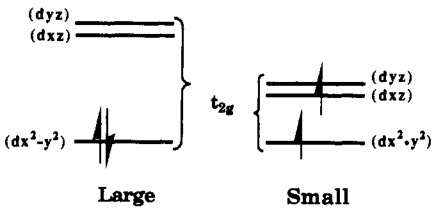

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electron occupies the low-lying nondegenerate orbital while the other electron occupies one of the nearly degenerate orbitals above, and the compound will be paramagnetic.

It is generally believed that CH_3 is a weaker π donor than Cl. Thus, CH_3 should destabilize the upper two t_{2g}-like orbitals less than Cl. Therefore, $Ti(CH_3)_2(dmpe)_2$ should have a small splitting within the t_{2g}-like orbitals and be *paramagnetic* while $TiCl_2(dmpe)_2$ should have a large splitting and be *diamagnetic*! Could our reasoning be wrong; could CH_3 be a better π donor than Cl? Alternatively, one might be tempted to explain the magnetic properties by appealing to the spectrochemical series where CH_3 is ordered as a stronger field ligand than Cl. Thus, one might argue that CH_3 causes a larger orbital splitting and therefore a diamagnetic ground state. However, the spectrochemical series refers to the splitting between the t_{2g} and e_g orbitals, not small splittings within the t_{2g}-like orbitals.

Approximate self-consistent-field (SCF) molecular orbital (MO) calculations support this qualitative argument. Fenske–Hall[3] calculations on $Ti(CH_3)_2(dmpe)_2$ and $TiCl_2(dmpe)_2$ give orbital splittings of 6.7 and 19.3 kcal mol^{-1}, respectively. Thus, it does not appear that the diamagnetism of $Ti(CH_3)_2(dmpe)_2$ could be due to the π interactions of the C–H bonds or the strong-field nature of CH_3, both of which are included in these calculations. In addition these calculations show that neither small differences in the phosphines nor some synergistic change in phosphine π acceptor ability can explain these results. Either both our intuition and approximate MO calculations are wrong or the origin of the diamagnetism is more complicated.

We will attempt to resolve this dilemma through the use of accurate ab initio calculations. Since this problem involves the singlet–triplet splitting of nearly degenerate, essentially nonbonding orbitals, we anticipate the need for extensive electron correlation and large basis sets to achieve even semiquantitative accuracy. Thus, we will have to replace the large dmpe ligands with simple model ligands. The computational problem can be schematically represented as **4** where we plot the accuracy of the model, the size

4

of the basis set, and the level of electron correlation as three Cartesian axes. We would like to do calculations far from the origin in all three directions, but for large molecules such as these, we will need to be satisfied with exploring each of these directions somewhat separately.

Theoretical Methods

Models. In this study three molecular models were used: $TiX_2(dmpe)_2$, $TiX_2(PH_3)_4$, and TiX_2Be_4 (X = CH_3 or Cl). The Ti–X, Ti–P, C–H, P–Ti–P, and T–C–H bond distances and angles were set to their reported experimental values.[1,2] For $TiX_2(PH_3)_4$ the P–H distance was set to the experimental value of 1.42 Å.[3] For $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$ the Ti–Be distances were adjusted to give a singlet–triplet splitting equal to the singlet–triplet splitting of $Ti(CH_3)_2(PH_3)_4$ and $TiCl_2(PH_3)_4$, respectively.

Basis Sets. The basis sets for Fenske–Hall[4] calculations were generated by the numerical Xα atomic orbital program of Herman and Skillman[5] used in conjunction with the Xα-to-Slater basis program of Bursten and Fenske.[6] Ground-state atomic configurations were used for all atoms except for the transition metals; these atoms assumed $d^{n+1}s^0$ cationic configurations. The valence s and p exponents for the transition-metal atoms were determined by minimizing the energy difference between the valence eigenvalues from molecular calculations and experimental ionization potentials of $M(CO)_6$ and $M'(PF_3)_4$ (M = Cr, Mo, W; M′ = Ni, Pd, Pt).[7]

For the ab initio calculations all basis sets except those for H[8] were derived from those of Huzinaga.[9] For Ti our small basis was the double-ζ basis (4321/321/31) used in previous transition-metal calculations.[10] A larger triple-ζ basis (53321/521/311) was derived from Huzinaga's fully contracted (5333/53/5) by splitting off the outer Gaussian. We augmented the triple-ζ basis set with f polarization functions[11] and diffuse s, p, and d functions with exponents $^1/_3$ that of the penultimate one. For the calculations with an effective core potential[12] (ECP) the Ti 1s, 2s, 2p, 3s, and 3p atomic orbitals were treated as a pseudopotential. The Ti 4s, 4p, and 3d atomic orbitals are described with a (21/11/41) basis. For P a double-ζ (3321/321) basis was used. For Cl a double-ζ (3321/321) and a larger double-ζ plus polarization (5321/521/1) set was used. For C a double-ζ (321/21) and a triple-ζ plus polarization (521/311/1) basis sets were used. For H a double-ζ (21) and a triple-ζ plus polarization (21/1) were used. In the calculation of the system with the full molecule the C and H atoms on the dmpe ligand were represented by fully contracted (33/3) and (3) basis sets, respectively. For Be an unsplit (33) basis set was employed.

Calculations. Approximate MO calculations were done by the method of Fenske and Hall.[4] Ab initio MO calculations were performed via the closed- and open-shell Hartree–Fock–Roothaan (HFR) methods.[13a,b] Four complete active space self-consistent-field (CASSCF)[14] calculations were performed on $Ti(CH_3)_2Be_4$: three without f functions on Ti and one with f functions on Ti. The CASSCF calculations had the following active spaces: (1) $2e^-$/3MOs (3 Ti t_{2g}-like orbitals), (2) $6e^-$/7MOs (2 Ti–C bonds, 5 Ti 3d MOs), (3) $8e^-$/8MOs (3 Ti 3p, 5 Ti 3d), (4) $6e^-$/7MOs (2 Ti–C, 3t_{2g}-like, 2 Ti–C*). The multireference configuration-interaction (MRCI) calculations contained all single and double excitations from all reference configurations in the CASSCF with coefficients greater than 0.01 with all virtual orbitals unless otherwise stated. The configuration interaction with all-single-and-double-excitations (CISD) calculations used the SCF results as starting solutions and only one reference configuration, except for the $14e^-$ singlet (basis III), which used 4 reference configurations. Two CISD calculations were performed, one with 2 electrons (2 Ti 3d) and the other with 14 electrons (6 Ti–L, 2 Ti 3d). (Not all of the calculations are reported here, see ref 18.)

All ab initio calculations were performed with the GAMESS[15] program package. The molecular orbital plots were generated with use of the interactive program MOPLOT.[16] Negative contours are shown by dashed

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(15) Guest, M. F., S.E.R.C. Daresbury Laboratory, Warrington, WA4 4AD U.K.

Table I. Restricted Hartree–Fock–Roothaan (RHF) Total Energy for the Low-Lying States of $TiX_2(PH_3)_4$ (X = CH_3 or Cl)

X	state	energy, au	splitting, kcal
CH_3	^1A	−2288.9664	0.0
	^3A	−2288.9822	9.9
	^3B	−2288.9891	14.2
Cl	^1A	−3125.2220	0.0
	$^3B_2$	−3125.2397	11.1
	$^3B_3$	−3125.2602	24.0
	$^3B_1$	−3125.2662	27.7

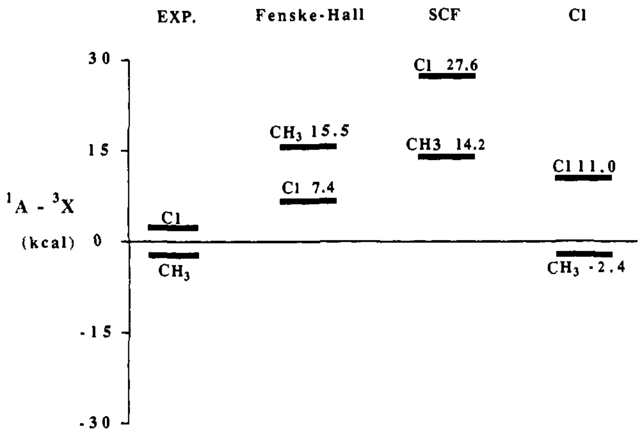

Figure 1. Comparison of the experimental singlet–triplet splitting of $TiX_2(dmpe)_2$ (X = CH_3 or Cl) with the theoretical single–triplet splitting from Fenske–Hall and SCF calculations on $TiX_2(PH_3)_4$ (X = CH_3 or Cl) and CI calculations on TiX_2Be_4 (X = CH_3 or Cl).

lines. The molecular orbitals are contoured geometrically with each contour differing by a factor of 2. The absolute value of the smallest contour is $\pm 2^{-7}$ (7.8125 × 10^3) (e $au^{-3})^{1/2}$. Calculations were carried out on the Department of Chemistry's VAX 11/780 and FPS 264 processor, Texas A&M University's IBM 3090-200E computer, Texas A&M University Supercomputer Center's Cray YMP2/116, and the Cornell National Supercomputing Facilities' FPS 264 processors and IBM 3090-600E mainframes.

Results and Discussion

Our initial calculations utilized $TiX_2(PH_3)_4$ (X = CH_3 or Cl) as a model and the small double-ζ basis set. The results are shown in Table I. For $Ti(CH_3)_2(PH_3)_4$ three triplet states, within the t_{2g}-like block, are possible, ^3A and two ^3B (C_2 point group). One of the ^3B states is the lowest in energy and gives a ^1A–^3B splitting of 14.2 kcal. For $TiCl_2(PH_3)_4$ the three triplet states are $^3B_1$, $^3B_2$, and $^3B_3$ (D_2 point group). The $^3B_1$ state is the lowest in energy and gives a $^1A_1$–$^3B_1$ splitting of 27.7 kcal. As expected for the single determinant SCF calculations the triplet states are lowest in energy.

These SCF results are visually compared to the experimental and Fenske–Hall results in Figure 1. Experimentally, the singlet–triplet splitting for $Ti(CH_3)_2(dmpe)_2$ is negative, i.e. $Ti(CH_3)_2(dmpe)_2$ has a singlet ground state, while the singlet–triplet splitting for $TiCl_2(dmpe)_2$ is positive, i.e. $Ti(Cl_2(dmpe)_2$ has a triplet ground state. The Fenske–Hall calculations give a larger singlet–triplet splitting for $Ti(CH_3)_2(PH_3)_4$ than for $TiCl_2(PH_3)_4$, a result in disagreement with experiment. Although the ab initio SCF calculations predict triplet ground states for both molecules, the magnitude of the splitting parallels the experimental results in contrast to the Fenske–Hall results, i.e. $Ti(CH_3)_2(PH_3)_4$ has a smaller splitting than $TiCl_2(PH_3)_4$. This level of agreement between SCF and experimental results is significant for two reasons. First, if enough correlation energy is added to the SCF calculations, both singlet–triplet splittings will decrease and the experimental results should be reproduced. Second, the SCF calculations on $Ti(CH_3)_2(PH_3)_4$ and $TiCl_2(PH_3)_4$ contain all the information needed to understand the experimental results at a qualitative level. We will continue with a discussion on the effect of basis sets, models, and electron correlation on the singlet–triplet splitting and conclude with an explanation for the observed ground states. Readers, who are not theoretically inclined, may want to skip the next two subsections (Models and Basis Sets, Electron Correlation) on their first reading.

Models and Basis Sets. As mentioned above there are three approximations (model, basis set, and electron correlation) to consider when solving this theoretical problem. Although we know that electron correlation will be essential to achieve quantitative agreement, we were concerned that a poor model or an inadequate basis set could thwart our attempt to achieve our goal. Most of the remaining calculations were on the CH_3 derivative since it is the one with the incorrect singlet–triplet splitting. Occasionally similar calculations were performed on the Cl analogue. Fenske–Hall calculations suggested that the PH_3 ligand was a better π acceptor than the dmpe ligand. Thus, our PH_3 model could result in too large an orbital splitting which could then effect the final correlated results. Therefore, ab initio SCF calculations were performed on the complete molecules, $Ti(X)_2(dmpe)_2$. The calculations lowered the singlet–triplet splitting by 1.1 and 0.6 kcal for CH_3 and Cl respectively (see Table II). Thus, the error due to replacing $(dmpe)_2$ by $(PH_3)_4$ is significant but small.

The model compound $Ti(CH_3)_2(PH_3)_4$ has 130 basis functions and 112 electrons, while $TiCl_2(PH_3)_4$ has 126 basis functions and 128 electrons. Thus, if we wish to significantly enlarge the basis set and/or add substantial electron correlation we must replace the PH_3 ligand with a simple model ligand. Interestingly, the Be atom has an ionization energy, 8.4 eV, very near the lone-pair ionization energy of PR_3 molecules (typically 8–9 eV). Since at the most fundamental level the PR_3 ligand is a σ donor having a lone pair with substantial s character, its replacement by a Be atom may yield reasonable results.

If Be is substituted for PH_3 the new model compounds, $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$, have 62 and 58 basis functions with 56 and 72 electrons, respectively. The new model compounds are small enough to allow large basis sets and substantial electron correlation to be applied and keep computational expenses reasonable. For $Ti(CH_3)_2Be_4$ a Ti–Be bond distance of 2.508 Å gives a singlet–triplet splitting of 14.6 kcal while for $TiCl_2Be_4$ a distance of 2.672 Å gives a singlet–triplet splitting of 27.6 kcal (see Table II). Although changing the Ti–Be distance modulates the singlet–triplet splitting the magnitude of the modulation is small. For example, in $Ti(CH_3)_2Be_4$ changing the Ti–Be distance from 2.508 to 2.538 Å changes the splitting from 14.6 to 15.6 kcal, a change of only 1.0 kcal.

With these smaller model systems we are now in a position to examine the effect of basis set on the singlet–triplet splitting. The results for $Ti(CH_3)_2Be_4$ in several basis sets are shown in Table III. Overall, the splitting is fairly stable with respect to changes in the basis set. In general, larger basis sets have smaller splittings; the largest difference among all basis sets is 1.9 kcal. Thus, together the error in the model and the basis set make an error of about 3 kcal at the SCF level of calculation.

Electron Correlation. As mentioned earlier, it was clear from the beginning that electron correlation of the two d electrons in the singlet state would need to be included for even a semiquantitative comparison. For comparison of singlet states, where the electron pair occupies a bonding orbital, and triplet states, where one electron is in the bonding orbital and the other is in the antibonding orbital, a simple GVB(PP)[17] calculation for the singlet state places it on essentially the same footing as the triplet state SCF calculations and often achieves at least a semiquantitative result. However, it became clear from a number of preliminary calculations[18] that this procedure or a modest extension

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(16) Interactive MOPLOT: a package for the interactive display and analysis of molecular wave functions incorporating MOPLOT (Lichtenberger, D.), PLOTDEN (Bader, R. F. W.; Kenworthy, D. J.; Beddall, P. M.; Runtz, G. R.; and Anderson, S. G.), SCHUSS (Bader, R. F. W.; Biegler-Koenig, F. W.), and EXTREME (Bader, R. F. W.; Biegler-Koenig, F. W.; Sherwood, P.; MacDougall, P. J.), 1989.

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Table II. Total Energy and Singlet–Triplet Splitting for Various Models of $TiX_2(dmpe)_2$ (X = CH_3 or Cl)

model	point group	singlet state	triplet state	energy, au		splitting, kcal
				singlet	triplet	
$Ti(CH_3)_2(dmpe)_2$	C_i	^1A_g	^3A_g	−2752.0893	−2752.1101	13.1
$Ti(CH_3)_2(PH_3)_4$	C_2	^1A	^3B	−2288.9664	−2288.9891	14.2
$Ti(CH_3)_2Be_4$	C_{2h}	^1A_g	^3B_g	−983.8935	−983.9168	14.6
$TiCl_2(dmpe)_2$	C_i	^1A_g	^3A_g	−3588.2751	−3588.3183	27.1
$TiCl_2(PH_3)_4$	D_2	^1A	$^3B_1$	−3125.2220	−3125.2662	27.7
$TiCl_2Be_4$	D_{2h}	^1A_g	$^3B_{1g}$	−1820.1295	−1820.1735	27.6

Table III. Total Energy and Singlet–Triplet Splitting of $Ti(CH_3)_2Be_4$ in Six Basis Sets

basis[a]	Ti basis	C basis	H basis	energy, au		splitting, kcal
				^1A_g	^3B_g	
I	(432/421/31)	(321/21)	(21)	−983.8935	−983.9168	14.6
II	(533211/5211/3111)	(521/311/1)	(211/1)	−985.1506	−985.1709	12.7
III	(432/421/31/1)	(321/21)	(21)	−983.9272	−983.9452	11.3
IV	(53321/521/311/1)	(321/21)	(21)	−984.6458	−984.6679	13.9
V	(533211/5211/3111/1)	(321/21)	(21)	−984.6834	−984.7015	11.4
VI	(ECP/211/111/411)	(321/21)	(21)	−139.8515	−139.8745	14.4

of it would not work in this situation, which is dominated by the dynamical correlation of the two nonbonding d electrons. In order to achieve a significant fraction of the difference in correlation energy between the singlet and triplet, larger CI's with larger basis sets are necessary. For example, basis sets I and II are insufficient, even if used in large CI calculations. Only basis sets with a more extensive d orbital space were successful, apparently because the radial correlation of the $3d^2$ configuration is so important.

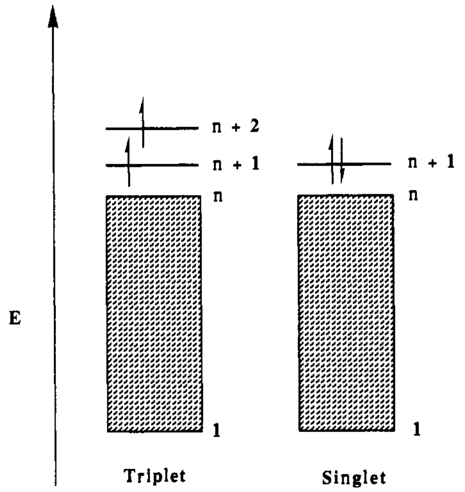
With basis set V the RHF SCF calculation on $Ti(CH_3)_2Be_4$ gave a singlet–triplet splitting of 11.4 kcal. Initially, we had hoped to perform a 6-electron 7-orbital CASSCF, which includes both Ti–C bonds in addition to the $3d^2$ pair, and then use the results as a starting solution for a MRCI calculation. However, the CASSCF calculations allowed Ti 3p character to mix with the active space orbitals of the singlet but not the triplet. This difference between the singlet and triplet would prevent a fair comparison of the subsequent MRCI calculations. Therefore, CISD calculations with 14 electrons (two from each Ti–L bond and the Ti 3d lone pair) were performed and gave a singlet–triplet splitting of −2.4 kcal. The CISD calculation had 23 641 and 87 446 configurations for the singlet and triplet states, respectively. A similar set of calculations on the higher symmetry $TiCl_2Be_4$ molecule yielded a final singlet–triplet splitting of 11.0 kcal with 8 205 and 29 176 configurations for the singlet and triplet states, respectively. These results are summarized in Figure 1.

An alternative way of keeping unwanted 3p character out of the active space would be to use a Ti basis set with effective core potentials in the CASSCF calculations. A 6/7 CASSCF calculation with a Ti ECP (basis VI) gave a singlet–triplet splitting of −1.3 kcal. For the singlet and triplet states 37 and 13 configurations, respectively, had coefficients greater than 0.1; all were used for the MRCI, which gave a singlet–triplet splitting of −1.5 kcal with 59 342 and 82 471 configurations for the singlet and triplet states, respectively. A similar set of calcualtions on $TiCl_2Be_4$ (basis VI) yielded a final singlet–triplet splitting of 15.2 kcal with 13 557 and 17 009 configurations for the singlet and triplet states of the MRCI, respectively. The results from these CISD (basis V) and SCF-CASSCF-MRCI (basis VI) calculations on $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$ are both consistent with experimental results, i.e. $Ti(CH_3)_2Be_4$ has a singlet ground state and $TiCl_2Be_4$ a triplet ground state. Of course, these calculations are still underestimating the stability of the singlet relative to the triplet.

Explanation for the Observed Ground States. One can see from the final results in Figure 1 that electron correlation simply serves to decrease the singlet–triplet splitting and achieve quantitative agreement with experiment. Qualitative agreement is achieved even at the SCF level where the splitting is smaller for the CH_3 derivative than for the Cl derivative, in contrast to minimal-basis approximate MO theory. Thus, an explanation of the unexpected ground states is possible through an analysis of the SCF results.

The first question to answer in our pursuit of an explanation is the degree to which the qualitatively correct SCF results depend on the details of the orbitals. In other words can we find a single set of orbitals which give the qualitatively correct results for the relative singlet–triplet splitting? Calculating the energy of the singlet states using the orbitals from the triplet states, we find that the singlet energies are higher by 5.6 and 5.2 kcal/mol for $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$, respectively. Since the energy differences between the true SCF singlet energy (E_S) and that calculated from the triplet orbitals ($E_{{}^\bullet S^\bullet}$) are equal and much smaller than the singlet–triplet splitting, we can use this single orbital set (for the triplet states) to determine why the triplet state for the Cl system is so much more stable than the singlet when compared to the CH_3 system.

Our general energy expressions for the singlet and triplet states are based on model **5**, where the system has n doubly occupied orbitals below the 2 electrons of interest. The total energy for the triplet state (E_T) can be written as equation 1. E_T is a sum of the energy contributions from MO's 1 to n, the kinetic energy



5

$$E_T = E_{1,n} + (T + Z)_{n+1} + (T + Z)_{n+2} + \sum_{i=1}^{n}(2J_{i,n+1} - K_{i,n+1}) + \sum_{i=1}^{n}(2J_{i,n+2} - K_{i,n+2}) + J_{n+1,n+2} - K_{n+1,n+2} \qquad (1)$$

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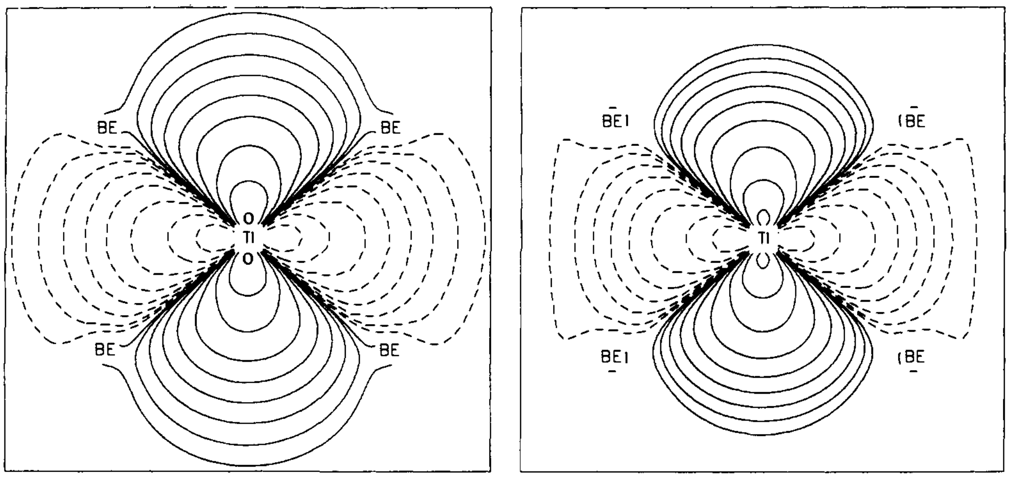
(18) Simpson, C. Q., II Ph.D. Dissertation, Texas A&M University, May 1991.

Table IV. Electron Correlation Results for $Ti(CH_3)_2Be_4$

basis[a]	calculation	energy, au ^1A_g	energy, au ^3B_g	splitting, kcal
V	RHF SCF	-984.6834	-984.7015	11.4
V	CISD 14e$^-$ (based RHF SCF)	-984.8288	-984.8249	-2.4
VI	RHF SCF	-139.8515	-139.8745	14.4
VI	CAS 6e$^-$/7 MO's (2 Ti-C, 3 t_{2g}-like, 2 Ti-C*)	-139.9038	-139.9018	-1.3
VI	MRCI (based on CAS 6/7)	-139.9306	-139.9282	-1.5

[a] Basis sets are given in Table III.



$Ti(CH_3)_2Be_4$ $TiCl_2Be_4$

Figure 2. MO plots of the low-lying singly occupied orbital for ^3B_g $Ti(CH_3)_2Be_4$ and $^3B_{1g}$ $TiCl_2Be_4$.

Table V. TiX_2Be_4 (X = CH_3 or Cl) Singlet–Triplet Splitting Terms (kcal)

	X = CH_3	X = Cl
ϵ_{n+1}	-521.3	-580.8
ϵ_{n+2}	-508.9	-572.5
$J_{n+1,n+1}$	344.4	366.6
$J_{n+1,n+2}$	325.8	340.9
$K_{n+1,n+2}$	13.9	15.3

and nuclear attraction terms for electrons in MO's $n + 1$ and $n + 2$, the coulomb and exchange interactions between electrons in MO's 1 to n and those in $n + 1$ and $n + 2$, and the coulomb and exchange interactions between electrons in MOs $n + 1$ and $n + 2$. Similarly, the total energy for the singlet state ($E_{\cdot S\cdot}$) can be written as eq 2. Equations 1 and 2 can be simplified by

$$E_{\cdot S\cdot} = E_{1,n} + (T + Z)_{n+1} + (T + Z)_{n+1} + \sum_{i=1}^{n}(2J_{i,n+1} - K_{i,n+1}) + \sum_{i=1}^{n}(2J_{i,n+1} - K_{i,n+1}) + J_{n+1,n+1} \quad (2)$$

substituting orbital energy expressions for the two singly occupied orbitals, eqs 3 and 4, to give eqs 5 and 6. Note that these orbital energy expressions are those appropriate for a single electron

$$\epsilon_{n+1} = (T + Z)_{n+1} + \sum_{i=1}^{n}(2J_{i,n+1} - K_{i,n+1}) \quad (3)$$

$$\epsilon_{n+2} = (T + Z)_{n+2} + \sum_{i=1}^{n}(2J_{i,n+2} - K_{i,n+2}) \quad (4)$$

$$E_T = E_{1,n} + \epsilon_{n+1} + \epsilon_{n+2} + J_{n+1,n+2} - K_{n+1,n+2} \quad (5)$$

$$E_{\cdot S\cdot} = E_{1,n} + 2\epsilon_{n+1} + J_{n+1,n+1} \quad (6)$$

outside the 2+ molecular ion and do not correspond to the usual orbital energy expression for either the singlet or triplet states (the usual orbital energy expressions include the coulomb and exchange interactions between electrons in MO's $n + 1$ and $n + 2$). The final singlet–triplet splitting, $E_{\cdot S\cdot} - E_T$, is given in eq 7. Equation

$$E_{\cdot S\cdot} - E_T = (\epsilon_{n+1} - \epsilon_{n+2}) + J_{n+1,n+1} - J_{n+1,n+2} + K_{n+1,n+2} \quad (7)$$

7 contains the orbital energy differences for orbitals $n + 1$ and $n + 2$ plus the coulomb and exchange terms. The first term represents the orbital energy difference based on the interaction of each electron with the 2+ molecular ion. The first J term in (7), $J_{n+1,n+1}$, represents the electron–electron (coulomb) repulsion when orbital $n + 1$ is doubly occupied and is a contribution from the singlet state. The second J term, $J_{n+1,n+2}$, represents the electron–electron (coulomb) repulsion when orbitals $n + 1$ and $n + 2$ are singly occupied, a contribution from the triplet state. The K term, $K_{n+1,n+2}$, represents the exchange interaction when orbitals $n + 1$ and $n + 2$ are singly occupied and is a contribution from the triplet state.

Each of the terms in eq 7, for $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$, are obtainable from our SCF calculations and are shown in Table V. The orbital energy differences for $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$ are quite similar with a difference of only 3 kcal. However, each of the J and K terms for $TiCl_2Be_4$ are substantially greater than those of $Ti(CH_3)_2Be_4$. The largest difference, 23 kcal, occurs in the $J_{n+1,n+1}$ term. The electron–electron repulsions in the singlet $TiCl_2Be_4$ are much greater than the electron–electron repulsions in the singlet $Ti(CH_3)_2Be_4$. Thus, $TiCl_2(dmpe)_2$ has a triplet ground state because the larger electron–electron repulsions of the singlet state overwhelm the splitting of the t_{2g}-like orbitals. Conversely, $Ti(CH_3)_2(dmpe)_2$ has a singlet ground state because the electron–electron repulsions of the singlet state are not as great and the splitting of the t_{2g}-like orbitals dominates. Therefore, the difference between $TiCl_2(dmpe)_2$ and $Ti(CH_3)_2(dmpe)_2$ lies in the electron–electron repulsions of the singlet state and not in the splitting of the t_{2g}-like orbitals.

Why does $TiCl_2(dmpe)_2$ have such large electron–electron repulsions? Figure 2 shows a plot[16] of the singly occupied, $n + 1$, orbital, i.e. the low-lying t_{2g}-like orbital, for $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$. Immediately, one notices that the orbital for $TiCl_2Be_4$ is smaller than the orbital of $Ti(CH_3)_2Be_4$, i.e. the low-lying orbital of $TiCl_2Be_4$ is more contracted; hence there are larger electron–electron repulsions.

The most obvious explanation for a more contracted d orbital is a higher effective nuclear charge on Ti. A higher effective nuclear charge on $TiCl_2Be_4$ than $Ti(CH_3)_2Be_4$ could arise from the electronegative difference between Cl and CH_3. Thus, the Cl ligand withdraws more electrons in forming more polar Ti–Cl bonds. In other words the closed-shell CH_3^- ligand is a better σ donor than the Cl^- ligand. Recently, Cioslowski and co-workers[19] compared three methods of population analysis on three inorganic molecules, using a variety of basis sets to determine which method gave the best (most stable) results. Their conclusion suggested that the Bader topological analysis of molecular charge densities[20-26] is the most stable and reliable. We used this method to determine the total charge within the Ti atomic basin. The integrated electron count was 21.13 and 21.04 electrons on $Ti(CH_3)_2Be_4$ and $TiCl_2Be_4$, respectively. Although not a large difference the additional 0.1 electron on the CH_3 derivative contributes to the expansion of the d orbital as shown in Figure 2.

Summary

Experimentally, $Ti(CH_3)_2(dmpe)_2$ has a singlet ground state while the similar $TiCl_2(dmpe)_2$ has a triplet ground state. Simple orbital splitting arguments suggest that if these molecules have different ground states $Ti(CH_3)_2(dmpe)_2$ should have a triplet ground state and $TiCl_2(dmpe)_2$ a singlet ground state. In order to predict this behavior in a semiquantitative fashion one must include a significant fraction of the d electron dynamical correlation. The most efficient approach to this appears to be a large CISD from an SCF solution in a reasonably large basis set which includes at least one f function. Physically, the origin of the difference between these compounds arises from a difference in the magnitude of the electron–electron repulsion which is reflected in the d orbital size. In ligand field terms this difference would be ascribed to the nephelauxetic effect. Thus, the Cl ligand in $TiCl_2(dmpe)_2$ withdraws more charge from Ti than the CH_3 ligand in $Ti(CH_3)_2(dmpe)_2$. The resulting higher effective nuclear charge causes the Ti orbitals on $TiCl_2(dmpe)_2$ to be more contracted. Therefore, the singlet state is disfavored in $TiCl_2(dmpe)_2$ but favored in $Ti(CH_3)_2(dmpe)_2$ which has weaker d electron repulsions.

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Stabilization Calculations on the π* Anion States of 1,4-Cyclohexadiene: Confirmation of the π_-* below π_+* Orbital Ordering

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Abstract: The stabilization method is used to calculate the energies of the π* anion states of 1,4-cyclohexadiene. These calculations show that the ground state anion is ^2A_u while the first excited state anion is $^2B_{2g}$. This order of the anion states is opposite that which would prevail were only through-space interactions present and is due to the domination of through-bond interactions. Stabilization calculations at Koopmans' theorem and single excitation CI levels of theory give splittings of 1.20 and 0.89 eV, respectively, as compared to the 0.92 eV splitting found experimentally.

I. Introduction

1,4-Cyclohexadiene (CHD) is a classic example of a species in which both through-bond (TB) and through-space (TS) interactions[1] are important. It is now well-established that TB interactions dominate over TS interactions in the occupied orbital space of CHD, causing the the b_{1u} (π_+) orbital to lie above the b_{3g} (π_-) orbital.[2,3] (The symmetry labeling of the orbitals is based on a molecular orientation with the carbon atoms lying in the *xz* plane and the methylene groups lying in the *xy* plane.) This inversion of the π orbitals relative to their "natural", i.e., TS, ordering is due to the strong hyperconjugative TB mixing of the

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