to be *lower* than that of Cyt by 1 kJ mol^{-1}, perhaps fortuitously in excellent agreement with the experiment. However, from the viewpoint of definitive predictions, the level of basis, the extent of correlation included, and the potential geometry changes with correlation to reflect the possible nonplanarity of cytosine may certainly introduce errors of the order of several kilojoules per mole for the calculated relative energies of tautomers of such nucleic acid bases.

Conclusions

Recently a few papers have appeared, devoted to the calculation of electron correlation contributions for large systems. An ab initio localized bond coupled-cluster and MBPT model introduced be Bartlett and co-workers[36] was applied in coupled-cluster calculations for nucleic acid bases.[37] However, the present results are the first to study the details of important electron correlation effects that contribute to the relative stabilities of nucleic acid bases. Comparison of the electron correlation contributions to the relative stabilities of nucleic acid bases and model compounds with the contributions from the zero-point vibrational energies shows that the electron correlation effects are greater or of the same order as the zero-point vibrational effects. In a related case of tautomeric equilibrium ($H_3PO \rightleftarrows H_2POH$), the electron correlation contribution has been estimated to be higher by three orders of magnitude than the contribution from the zero-point vibrational energies.[38]

The current results indicate that in the case of lactim–lactam tautomeric pairs of nucleic acid bases, the electron correlation contribution to the stability is greater for the lactim tautomer, while the energies calculated at the SCF level generally favor the lactam. The 6-31G** result for P(h) is an exception. Although the order of the relative electron correlation energies depends upon the systems considered, on the geometry of the tautomers, as well as on the method and basis set used for the calculation, this result seems to be fairly general. The same tendency of electron correlation to stabilize the lactim tautomer is observed also for other systems (formamide–formamidic acid, and the lactim–lactam tautomers of 2-oxopyridine). This result is also consistent with the tesults for the Cyt–Cyt(h) pair, with our recent studies on isocytosine tautomers,[39] as well as with an ab initio study by Rodwell, Bouma, and Radom[8] for the 1,3-sigmatropic shift: vinyl alcohol → acetaldehyde, Rodwell et al. also calculated relative electron correlation contributions for this pair[40] with a (DZ + polarization) basis set to be 6.1, 1.7, and 2.3 kJ mol^{-1}, respectively, in all cases in favor of the hydroxy tautomer. Also, in the case of the isomerization reaction of the methoxy radical, $CH_3O \rightleftarrows CH_2OH$, SDQ-MBPT(4) calculations[41] predict the electron correlation energy for the hydroxymethylene radical (CH_2OH) to be much greater (by 33.6 kJ mol^{-1}) than that for the methoxy radical (CH_3O).

In the case of amino–imino forms, the electron correlation contributions favor stability of the amino forms, as does the SCF. Hence, as would be predicted, the amino–lactim form Cyt(h) shows the largest effect of correlation $\Delta E^{\mathrm{corr}}_{\mathrm{Cyt,Cyt(h)}}$.

Acknowledgment. This work was supported by the National Institutes of Health under Research Grant GM-32988, and by the U.S. Army Research Office under Contract No. DAAG29-84-K-0025. J.S.K. wishes also to acknowledge travel support from the ministry of Science and Higher Education (Poland) within the Project CPBP 01.06. J.S.K. wishes also to thank Dr. Samuel J. Cole (QTP, Gainesville) for his help in explaining several computational aspects of the CC/MBPT computer codes.

Registry No. Ura, 66-22-8; Gua, 73-40-5; Cyt, 71-30-7; Ade, 73-24-5; F, 75-12-7; FA, 60100-09-6; Fl, 463-52-5; P(o), 142-08-5.

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Computational Evidence for an Unusual Transition State in the Fluxional Behavior of the Cyclopentadienyl Ligand in Chlorotris(cyclopentadienyl)titanium(IV)

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Abstract: The method of partial retention of diatomic differential overlap (PRDDO) was used to generate the potential surface for the η^1/η^5 rearrangement of the cyclopentadienyl ligand in chlorotris(cyclopentadienyl)titanium(IV). The calculations indicate that the ground-state structure consists of two η^5 and one η^1 Cp ligands. Prior NMR data are consistent with a rapid interconversion of these η^1 and η^5 bonding modes. At the ab inito level, the potential surface for this fluxional behavior is a symmetric curve with a maximum at 18.8 kcal/mol. The estimated transition-state structure exhibits "pseudo-η^3" coordination, with a retention of a relatively planar geometry for the Cp ring. There exists a strong σ interaction between one carbon and the titanium center with delocalization to the two adjacent carbons. A significant delocalization of the π orbitals in the Cp rings also exists, donating a total of ~0.20 e to the titanium per ring. This mechanism is unlike any other proposed for the η^1/η^5 rearrangement.

The cyclopentadienyl (Cp) ligand is one of the most common and important groups in organometallic chemistry. It exhibits a wide variety of coordination modes to metals and is known to be involved in fluxional processes which result in the apparent equivalence of all carbons on the NMR time scale. Typical fluxional behavior is observed in tetra(cyclopentadienyl)titanium, which isomerizes between the η^5 and η^1 bonding modes in solution.[1] Additional reactions involving rhenium and rhodium metal centers have also demonstrated the interconversion of the η^5 and η^1 coordination geometries.[2] The mechanism for the η^5/η^1 rearrangement is not known, but has been postulated to occur via three different transition states. In the case of rhenium and rhodium, the transition state has been suggested to involve a bent η^3 ring resembling the η^3 Cp ligand found in $Cp_2W(CO)_2$.[3] This structure presumably provides a smooth transition from the η^5 to η^1 geometries while maintaining the desirable 18-electron configuration. For the titanium species, an intermediate resembling the severely tilted η^5 Cp rings found in Cp_3MoNO has been proposed.[1] An additional intermediate proposed for the structural rearrangement in $TiCp_4$ contains three η^5 Cp ligands.[4] Planar η^3 coordination has been disregarded due to geometric arguments,[5] although this type of coordination has been observed in ground-state structures.[6] In this paper, we present a theoretical study of the potential energy surface for Cp interchange in the related system chlorotris(cyclopentadienyl)titanium(IV). We show that the fluxional behavior in this system is consistent with a new mechanism involving an estimated transition state which geometrically resembles planar η^3 coordination, although the electronic structure is closely related to that found in η^1 bonding.

Calculations

The method of partial retention of diatomic differential overlap (PRDDO)[7,8] was used to predict the ground-state structure of $TiCp_3Cl$ and construct the potential surface for the η^5 to η^1 interconversion in this complex. Geometry optimizations utilizing PRDDO were carried out on the Cray X-MP/24 computer made available through the University of Texas Center for High Performance Computing. The basis set on the metal for PRDDO calculations is described elsewhere.[9] Optimization of the ground-state structure assumed local D_{5h} symmetry of the η^5 ligand and local C_s symmetry of the η^1 ring. Essentially all degrees of freedom except the C–H distances were included, bearing in mind the assumed local symmetry of the ligands.

Geometries for points along the potential surface for the interconversion of the η^5 and η^1 structures were found by the linear synchronous transit/orthogonal optimization approach.[10] Mathematically, a path coordinate is defined as:

$$P = d_r/(d_r + d_p)$$

where the values of d_r and d_p are the distances of the current geometry from the starting (reactant) and ending (product) structures. Both d_r and d_p are defined similarly as:

$$d_r = \frac{1}{N} \sum_{w=x,y,z} \sum_{a=1}^{N} [(w_a(c) - w_a(r)^2]^{1/2}$$

Here the reactant and product geometries are at maximum coincidence.[10] The maximum energy structure along this pathway is then found by successive orthogonal (path coordinate constrained) optimizations of trial structures. All geometrical parameters were optimized except for the following: the C–H distances were fixed at 1.09 Å and the noninterchanging ring was assumed to be planar. No assumptions of local symmetry were made for the interchanging rings. Because an essentially continuous series of structures connecting the reactant and product are generated, the maximum energy structure is a good approximation to the transition state at the PRDDO level. A more detailed discussion of this approach and its utility in examining reaction surfaces can be found elsewhere.[11] This method provides estimates of transition-state structures without the calculation of force constants, which would be computationally prohibitive in a system of this size and complexity.

Table I. Metal Basis Set

orbital	exponent	expansion	orbital	exponent	expansion
1s	21.44020	3	3d	4.66100	2
2s	7.68816	3	3d	1.98300	2
2p	9.03231	3	4s	2.07500	1
3s	3.50700	2	4p	2.42900	1
3p	3.37300	2	4p	1.47700	1

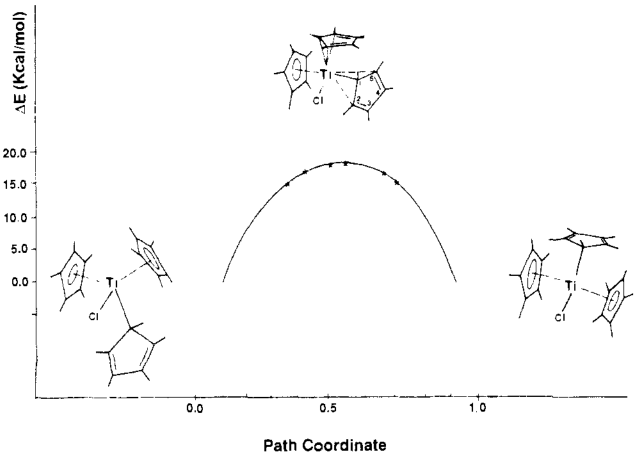

Figure 1. A plot of the potential energy surface for the η^5/η^1 rearrangement. The path coordinates of 0.0 and 1.0 correspond to chemically equivalent ground-state structures. The transition state occurs at a path coordinate of 0.5.

To determine the total energies along the pathway, all structures were then used in ab initio calculations,[12] employing a large basis set. The basis set consisted of the standard 3-21G[13] basis on the ligands except for the nonexchanging Cp and the Cl which were described by a 3G[14] basis. The metal basis consisted of a Gaussian expansion of a Slater orbital basis set optimized for the ground state of the neutral metal. Slater orbital exponents and Gaussian expansion lengths are given in Table I. This basis set is double in the 3d and 4p space and single ζ for the inner shells and the 4s region. A more detailed description of this basis set will appear elsewhere.[15] Each calculation required about 20 h of IBM 4381-P03 CPU time. Explicit calculation of the isomerization energies of $CpTiCl_3$ and Cp_2TiCl_2 using larger basis sets, specifically a double-ζ (4-31G[16]) representation on all ligands and a triple ζ 3d set on the Ti, yielded results within 3 to 4 kcal/mol of our final basis set.

To approximate the degree of steric strain in the relavent structures, empirical estimates of nonbonded ligand–ligand interactions were made at the PRDDO optimized geometries. These were estimated from the appropriate part of Allinger's force field approximation.[17] Coulombic interactions were included and were determined using the atomic charges generated by PRDDO and a dielectric constant of four.

Localized molecular orbitals were calculated with PRDDO and were determined by the Boys criterion.[18]

Results and Discussion

Results of geometry optimizations indicate that the ground state contains two η^5 and one η^1 Cp ligands, corresponding to a 16e configuration. For comparison, PRDDO correctly predicts the

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Table II. Comparison of Transition (A) and Ground-State (B) Structures

	A	B		A	B
		Distance, Å			
Ti–C_1	2.17	2.25	Ti–Cl	2.36	2.34
Ti–C_2	2.51	3.19	C_1–C_2	1.45	1.50
Ti–C_3	3.14	4.12	C_2–C_3	1.33	1.32
Ti–C_4	3.23	4.09	C_3–C_4	1.42	1.45
Ti–C_5	2.88	3.16	C_4–C_5	1.34	1.32
Ti–C_{21}	3.40	2.41	C_5–C_1	1.45	1.50
Ti–C_{22}	3.30	2.41	C_{22}–C_{23}	1.47	1.39
Ti–C_{23}	2.64	2.38	C_{21}–C_{25}	1.33	1.39
Ti–C_{24}	2.15	2.37	C_{21}–C_{24}	1.44	1.39
Ti–C_{25}	2.86	2.39	C_{22}–C_{24}	1.33	1.39
			C_{23}–C_{25}	1.46	1.39
		Angle, deg			
Cp–Ti–Cp^a		132.0	Cl–Ti–C_σ	116.8, 111.5	90.1
Cp–Ti–$C_\sigma{}^b$	106.2, 108.4^d	107.9, 103.8^c	Cl–Ti–Cp	110.0	106.8, 108.0
C_σ–Ti–C_σ	102.1		H–C_σ–Ti	118.9, 120.3	108.2

^{a} Cp represents the center of η^5 Cp ring. ^{b} C_σ represents σ carbon of η^1 or pseudo η^3 ring. ^{c} Both η^5 ligands are considered independently. ^{d} Interchanging Cps of transition state are considered independently (ring I, ring II).

Table III. Overlap Populations and Degrees of Bonding for C–C Bonds in Transition-State Structure

ring	overlap population	degree of bonding
I	0.867	1.047
	1.115	1.601
	0.912	1.163
	1.140	1.686
	0.855	1.061
II	0.888	1.130
	1.143	1.690
	0.842	1.026
	0.835	1.035
	1.155	1.736

known experimental structures of $CpTiCl_3$ (one η^5 ring), Cp_2TiCl_2 (both rings η^5), and Cp_4Ti (two rings η^1 and two rings η^5). The PRDDO ΔE's for these structures are as follows: $E(\eta^1CpTiCl_3 - \eta^5CpTiCl_3)$ = 54.1 kcal/mol, $E(\eta^1Cp\ \eta^5CpTiCl_2 - \eta^5Cp_2TiCl_2)$ = 29.6 kcal/mol, $E(\eta^5Cp_3\eta^1CpTi - \eta^5Cp_2\eta^1Cp_2Ti)$ = 23.1 kcal/mol, and $E(\eta^5Cp\eta^1Cp_3Ti - \eta^5Cp_2\eta^1Cp_2Ti)$ = 31.8 kcal/mol. The corresponding ab initio results are somewhat lower, but lead to the same qualitative conclusions.[19]

The potential surface for the η^1/η^5 rearrangement (Figure 1) indicates a maximum at 18.8 kcal/mol above the ground-state structure. Pmr data show a single peak for the complex which is consistent with ring interchange. The activation energy for this process is not known, but the analogous interchange in tetra(cyclopentadienyl)titanium has E_{act} = 16 kcal/mol[1]. At the estimated transition-state geometry the two exchanging Cp rings are structurally similar and resemble an unsymmetrical "pseudo η^3" mode of coordination (Table II) which is distinctly different from all previous proposed transition states. One carbon is strongly σ bonded to the titanium while the adjacent carbons bind unsymmetrically and weakly with the metal. The remaining two carbons are too distant to be involved in any metal bonding. The carbon–carbon distances in the interchanging ligands shed considerable light on the nature of the bonding in the estimated transition state. Referring to Figure 1 for the numbering system, the distances are (ring I): C_1–C_2 = 1.45 Å, C_2–C_3 = 1.33 Å, C_3–C_4 = 1.42 Å, C_4–C_5 = 1.34 Å, and C_5–C_1 = 1.45 Å. The analogous distances in the second ring (ring II) are 1.47, 1.33, 1.44, 1.33, and 1.46 Å. These distances compare very well with those of the optimized η^1 ligand in the ground-state structure (1.50, 1.32, 1.45, 1.32, and 1.50 Å, respectively) and suggest that the transition-state structure is best viewed as containing distorted η^1 ligands. Analysis of the overlap populations and degree of bonding between carbons (Table III) further support the η^1-like character of rings I and II in the transition-state structure. The localized molecular orbitals (LMO's) of the transition state also agree nicely with this viewpoint. The major component of the metal bonding to each interchanging Cp is found in a single LMO. This orbital is primarily of a two-center nature (Ti–C_1), but is slightly delocalized to the flanking π^* orbitals localized between C_2–C_3 and C_4–C_5 (Figure 2). The electron populations on Ti, C_1, C_2, and C_5 for this LMO are 0.660, 1.223, 0.027, and 0.054 e, respectively. The populations on the titanium and the analogous carbons for the equivalent LMO on ring II are 0.372, 1.022, 0.320, and 0.244 e. Additional information is gained from the ring LMO's (Figure 3), which exhibit well-defined C–C double bonds of the bent (τ) variety very similar to those seen for cyclopentadiene. Each of these four LMO's displays some delocalization to the titanium, totaling 0.24 e for ring I and 0.17 e for ring II. This delocalization helps to reduce the positive charge on the metal and thus stabilize the transition state.

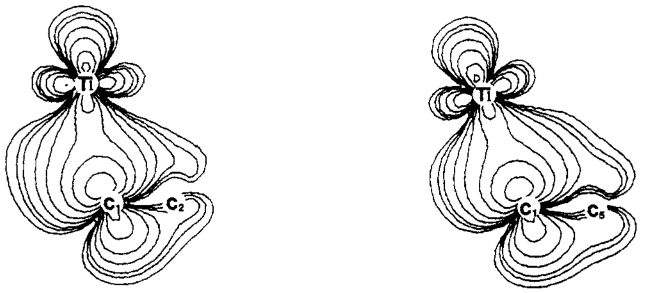

Figure 2. Contour plots of the Ti–C_1 LMO for the transition-state structure (contour values: 0.5, 0.4, 0.3, 0.2, 0.05, 0.02, 0.01, 0.005, 0.0035, 0.002 e/au^3). Contour plots of the similar LMO for ring II exhibit the same delocalization.

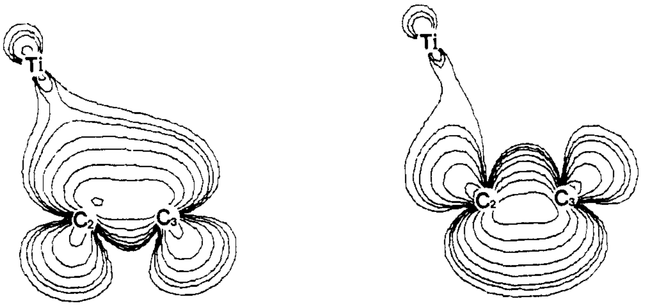

Figure 3. Contour plots of the C_2–C_3 π LMO for the transition-state structure (contour values are the same as Figure 2).

The chlorine–metal distances differ by no more than 0.02 Å between the transition-state and ground-state structures (Table II). PRDDO optimized titanium–chlorine distances appear to be unusually reliable. For example, PRDDO predicts a Ti–Cl distance of 2.168 Å[9] in $TiCl_4$ and 2.37 Å[19] in $TiCp_2Cl_2$ compared to the respective experimental values of 2.170[20] and 2.36Å.[21] Based on the optimized Ti–Cl distances and the population analysis, π donation from the chlorine appears to be very similar for both the transition- and ground-state structures. For the transition-state structure, the degrees of bonding and overlap populations associated with the Ti–Cl bond are 1.070 and 0.278, comparable to the values of 1.104 and 0.269 for the ground-state structure.

Analysis of the nonbonded interactions in the ground and transition states demonstrates that the transition state is less sterically strained than the ground-state structure by ~5 kcal/mol. Idealization of the calculated transition state would lead to an $\eta^5Cp(\eta^1Cp)_2TiCl$ geometry, which is estimated by ab initio cal-

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culations to be 29.2 kcal/mol higher in energy than the ground-state structure.[19,22] Thus, the distortion to the calculated unsymmetrical "pseudo η^3" coordination in the transition state stabilizes the structure by ~10 kcal/mol.

Comparison of our estimated transition state to those previously proposed for this and related systems reveals that our transition state is indeed novel. Our calculated Ti–C bond distances range from 2.15 to 3.40 Å for the interchanging ligands, compared to the metal–C distances ranging from 2.34 to 2.60 Å for the severely tilted η^5 ligands found in Cp$_3$MoNO. Because of the profound difference between the metal–C distances, the proposed transition state does not exhibit a tilted η^5 bonding configuration. In addition, optimization of the η^5Cp$_3$TiCl isomer generates a species with an energy 43.6 kcal/mol above the ground-state structure,[19] clearly arguing against the participation of such a conformation in the Cp exchange reaction. The interchanging Cp ligands are nearly planar, with the maximum twist angle between four adjacent carbons (i.e., C_1–C_2–C_3–C_4 and C_1–C_5–C_4–C_3) being ~6.5°. For comparison, the nonplanar η^3 coordination found in Cp$_2$W(CO)$_2$ is bent 20° out of plane.[3] The hydrogens remain in the plane of the Cp ring with the exception of the hydrogens on the σ carbons, which form a 119° angle with respect to the titanium.

Conclusion

In summary, the coordination of the interchanging ligands in the estimated transition state is significantly different from those proposed previously. Structurally, it resembles planar but unsymmetrical η^3 bonding. Electronically, the coordination is best described as stabilized η^1, with the stabilization due to delocalization of the Ti–C bond to adjacent π^* orbitals on the Cp's, and slight delocalization of the Cp π bonds into the metal valence shell.

Registry No. CpTiCl$_3$, 1270-98-0; Cp$_2$TiCl$_2$, 1271-19-8; Cp$_4$Ti, 63726-15-8.

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(22) Optimization of this structure omitted one mode to prevent the collapse of the η^1 geometry to an η^5 mode of bonding.

The Circular Dichroism of the Carbonyl n–π^* Transition: An Independent Systems/Perturbation Approach

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Abstract: An independent systems/perturbation approach is used to determine analytic expressions for the circular dichroism (CD) of the n–π^* transition in carbonyl compounds. It is shown that all available experimental data can be understood in terms of the predictions made by this theory. In general, for uncharged, nonpolar systems, the CD varies according to the octant sector rule of Moffitt et al.;[1] however, exceptions to this rule do arise for certain geometries and for situations in which the substituents on the compounds exclude the solvent in an unsymmetrical manner. Different geometry dependences are derived for polar and charged species and are found to explain the existing data.

1. Introduction

The circular dichroism (CD) of n–π^* transitions in carbonyl compounds has been the subject of speculation and analysis for many years. The octant rule of Moffit et al.[1] has proved to be a unifying feature for much of this work by providing a reference against which experiment has been compared. In its original form Moffit's octant rule (which we shall call the dynamic coupling octant (dco) rule for reasons that will become apparent) stated that the CD of the n–π^* carbonyl transition reflects positions of other parts of the molecule relative to the carbonyl group, according to the product $-xyz$, where (x, y, z) is a position vector in the right-handed coordinate system defined with the z axis along the C=O bond, the y axis in the carbonyl plane, and the origin centered on the nodal surface of the orbitals involved in the n–π^* transition (cf. Figure 1). The xz and yz reflection planes are thus defined by the approximate C_{2v} symmetry of the carbonyl part of the system, and the third plane by the orbitals involved in the transition. A perturbation theory analysis of the CD induced into the n–π^* transition of an achiral carbonyl chromophore by a chiral environment enabled Höhn and Weigang[2] to give a theoretical justification of the dco rule. This was the first use of what we shall call the independent systems/perturbation (ISP) approach (see, e.g., ref 3 and 4 for further details). An alternative formalism, which is somewhat less suited to the symmetry analysis approach of ref 7, is provided by the work of Buckingham and Stiles.[5]

Although the dco rule has proved to be highly successful, there are sufficiently numerous exceptions (e.g., ref 6–8) for closer examination to have been warranted. A number of empirical modifications to the dco rule have been made in attempts to extend its range of applicability. These have included the postulate that the third plane should be a curved surface, either convex[6] or concave[7] with respect to the carbonyl, or that it is the length of the primary zigzag[9] (see below) that determines the CD, or simply an anti-dco rule for some situations. Such empirical rationalizations, while they may be helpful for a given series of compounds, do not provide a global approach to carbonyl CD. Consideration of all terms in the ISP expansion of the CD provides a means of extending the analysis of Höhn and Weigang[2] to all potentially significant mechanisms for systems where the n–π^* transition can be considered to be essentially localized in an achiral carbonyl chromophore (see below). There is now available in the literature a wide range of systematically collated experimental data. In addition, the methodology for the symmetry analysis of ISP mechanisms has been developed for magnetic dipole allowed (mda)

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