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A Molecular Orbital Study of Conformational Preferences of the Cyclopentadienyl Ligand in Titanium(IV) and Titanium(III) Complexes

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A theoretical study of the conformational preferences of the cyclopentadienyl (Cp) ligand in titanium(IV) and titanium(III) systems is presented. The method of partial retention of diatomic differential overlap is used to optimize the geometries of Cl_3CpTi, Cl_2Cp_2Ti, $ClCp_3Ti$, Cp_4Ti, and Cp_3Ti. We estimate the relative stability of structures exhibiting alternative coordination modes of the cyclopentadienyl ligand (η^1, η^2, and η^5) at the ab initio level with an expanded basis set, in some cases including MP2 correlation corrections. From this study, we have determined that the ground-state conformations of (cyclopentadienyl)titanium(IV) and -titanium(III) complexes are predominantly influenced by electronic factors. A detailed bonding analysis of the unusual η^2 coordination in tris(cyclopentadienyl)titanium(III) indicates that the η^2 conformation is stabilized by π-donating substituents on the nonbonding carbons. We present a simple localized bonding description of the η^2-bound ligand and offer suggestions for further stabilizing this unusual coordination.

Introduction

The cyclopentadienyl (Cp) ligand is ubiquitous in organometallic chemistry. It is of particular structural interest because it has the capacity for exhibiting several modes of bonding. By far the most common and best understood are the η^5- and η^1 bonding modes. Less common modes of bonding occur, including the bent η^3 coordination found in rhenium[1] and rhodium[2] complexes and the "pseudo" planar η^3 coordination found computationally for the estimated transition state in the fluxional process in chlorotris(cyclopentadienyl)titanium(IV).[3] Perhaps the most intriguing and least noted bonding found for this ligand is the unusual η^2 coordination found in tris(cyclopentadienyl)titanium(III).[4] Whereas it is accepted that the η^1 Cp donates two electrons and the η^5 ligand contributes a total of six electrons to a metal, the number of electrons contributed by intermediate modes of bonding such as η^2 is less obvious. The coordination mode of the Cp ligand in organometallic complexes appears to be influenced by the total number of bonding electrons and to some extent by steric interactions. In most cases, an ideal 18e configuration is achieved through combinations of the various bonding modes, but early-transition-metal complexes, such as dicarbonylbis(indenyl)vanadium,[5] and many of the complexes considered here are 16e structures. Complexes which include more than one Cp ligand are subject to steric crowding and often exhibit different modes of bonding within the same complex. For instance, tris(cyclopentadienyl)nitromolybdenum contains one η^1 and two severely tilted η^5 Cp ligands.[6] Tetrakis(cyclopentadienyl)titanium(IV), one of the complexes included in this work, contains two η^5- and two η^1-coordinated Cp ligands, resulting in a 16e configuration.[7] The conformational preferences of the Cp ligand appear to result from a subtle balancing of steric and electronic factors.

Table I. Structures and Coordination Geometries Considered

structures	a	b	c	d
Cl_3CpTi (I)	η^5	η^1		
Cl_2Cp_2Ti (II)	$2\eta^5$	$\eta^5\eta^1$		
$ClCp_3Ti$ (III)	$3\eta^5$	$2\eta^5\eta^1$	$\eta^5 2\eta^1$	
Cp_4Ti (IV)	$4\eta^5$	$3\eta^5\eta^1$	$2\eta^5 2\eta^1$	$\eta^5 3\eta^1$
Cp_3Ti (V)[a]	$3\eta^5$	$2\eta^5\eta^2$	$2\eta^5\eta^1$	

[a] The possibility of an η^3 structure was explored, constraining the geometry such that the η^3 ligand would not slip to η^5, η^1, or η^2 coordination. This resulted in a structure 29 kcal/mol higher in energy at the PRDDO level.

In addition to the rich structural chemistry of the cyclopentadienyl ligand in titanium(IV) and titanium(III) complexes, these systems are important in a number of synthetic applications. In particular, titanium–cyclopentadienyl systems are important Ziegler–Natta catalysts.[8] Compounds such as dichlorobis(cyclopentadienyl)titanium and its derivatives have also been cited for their importance in cancer research, where the geometries and nature of the Cp ligand greatly influence the potency of these compounds.[9] Thus, exploring the bonding capabilities of the Cp ligand in these systems may provide information about the involvement of the Cp ligand in synthetically and biologically interesting processes. In light of the importance of these systems, there exists a clear need for a theoretical study of cyclopentadienyl complexes of early transition metals using modern theoretical techniques.

Previous theoretical work directed at the bonding characteristics of the cyclopentadienyl ligand in early-transition-metal complexes has included qualitative studies employing SCF-Xα scattered wave calculations[10] and the extended Hückel method.[11] In larger systems including more than two Cp rings, the resultant loss of symmetry makes such methods, which are grossly dependent on symmetry, less useful. In spite of the importance of the Cp ligand in organometallic chemistry, very little reliable

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Table II. Results of Geometry Optimization for Titanium(IV) Complexes: Experimental versus Calculated

complex	geometric parameter	PRDDO	EXP
Cl_3CpTi η^5	Cp[e]–Ti	2.06	2.01[a]
	C–Ti	2.37	2.31
	Cl–Ti	2.22, 2.22	2.20, 2.25
	Cl–Ti–Cl	102.4, 102.3	104.1, 102.2
	Cl–Ti–Cp	115.8	114.3, 117.2
Cl_2Cp_2Ti $2\eta^5$	Cp–Ti	2.07	2.06[b]
	C–Ti	2.40	2.37
	Cl–Ti	2.37	2.36
	Cp–Ti–Cp	139.8	130.9
	Cl–Ti–Cl	91.8	94.5
	Cp–Ti–Cl	105.2	106.4
$ClCp_3Ti$ $2\eta^5\eta^1$	Cp–Ti	2.07	
	Cl–Ti	2.34	not available
	C_π[f]–Ti	2.40	
	C_σ[g]–Ti	2.25	
	Cp–Ti–Cp	132.0	
	Cp–Ti–C_σ	107.9, 103.8	
	H–C_σ–Ti	108.2	
	Cl–Ti–C_σ	106.8, 108.0	
	Cl–Ti–Cp	90.1	
Cp_4Ti $2\eta^5 2\eta^1$	Cp–Ti	2.11	2.08[c]
	C_π–Ti	2.43	2.38
	C_σ–Ti	2.23	2.33
	Cp–Ti–Cp	129.6	129.9
	C_σ–Ti–C_σ	91.5	86.3
	Cp–Ti–C_σ	106.2, 108.4	106.2
Cl_4Ti	Ti–Cl	2.168	2.170[d]

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Table III. PRDDO Geometries for Titanium(IV) Isomers

complex	geometric parameter	value in Å or deg	complex	geometric parameter	value in Å or deg
Ib	C_σ[a]–Ti	2.09	IVa	Cp–Ti	
	Cl–Ti	2.21, 2.19		C_π–Ti	not available
	Cl–Ti–Cl	104.6			
	Cl–Ti–C_σ	118.6, 109.4		Cp–Ti–Cp	
	H–C_σ–Ti	120.3	IVb	Cp–Ti	2.24
IIb	Cl–Ti	2.23		C_π–Ti	2.53
	Cp[b]–Ti	2.06		C_σ–Ti	2.26
	C_π[c]–Ti	2.37		Cp–Ti–C_σ	99.8
	C_σ–Ti	2.12		Cp–Ti–Cp	117.0
	Cp–Ti–C_σ	107.4		H_σ–C_σ–Ti	103.6
	Cp–Ti–Cl	115.2	IVc	Ti–Cp	2.09
	C_σ–Ti–Cl	107.2		C_π–Ti	2.40
	H_σ–C_σ–Ti	121.3		C_σ–Ti	2.12
IIIa	Cp–Ti	2.24		Cp–Ti–C_σ	111.5, 112.9, 114.5
	C_π–Ti	2.53			
	Cp–Ti–Cp	118.8			
	Cp–Ti–Cl	95.4		C_σ–Ti–C_σ	110.3, 101.8, 105.3
	Cl–Ti	2.59			
IIIc	Cp–Ti	2.07			
	C_σ–Ti	2.11		H_σ–Ti–C_σ	118.2, 104.4, 119.7
	Cp–Ti–C_σ	114.6			
	H_σ–C_σ–Ti	109.2			
	C_π–Ti	2.38	η^5 Cp	C–C	1.40
	Cl–Ti	2.24		C–C–C	108.4
	Cp–Ti–Cl	120.8		C–C–H	126.0
	C_σ–Ti–Cl	101.8	η^1 Cp	C–C	1.50, 1.32, 1.45
	C_σ–Ti–C_σ	100.8			
				C–C–C	101.0, 110.4, 109.1
				C–CH	116.4, 123.3, 127.6

[a] Carbon which is σ-bound to the titanium. [b] Centroid of an η^5 Cp ligand. [c] Carbon of an η^5-bound Cp ligand.

theoretical work has appeared on the various modes of Cp coordination. This is obviously a consequence of the large size and electronic complexity of real organometallic complexes exhibiting these various modes of Cp coordination.

In this work we present a theoretical study of the conformational preferences of the Cp ligand in Cl_3CpTi, Cl_2Cp_2Ti, $ClCp_3Ti$, Cp_4Ti, and Cp_3Ti. We examine in detail the unusual η^2 coordination found in tris(cyclopentadienyl)titanium(III). We estimate the relative stability of each structure exhibiting alternative coordination modes of the Cp ligand, and we provide a simple localized bonding description of an η^2 bound Cp ligand which may be useful in designing new complexes with this coordination geometry.

Calculations

The structures and the various coordination geometries of interest in this work are presented in Table I. The method of partial retention of diatomic differential overlap (PRDDO)[12,13] was used to optimize the geometries for all structures considered. Geometry optimizations were primarily 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.[14] The energetics of most structures were then reevaluated at the ab initio level. We note here that, while PRDDO optimized geometries are often closer to experiment than similar ab initio geometries, a meaningful comparison of the two methods is difficult, since the basis sets employed are always different. PRDDO employs a minimum basis set with $ns = np$ exponent constraints and a fixed contracted double-ζ representation for the 3d orbitals. We know of no comparable ab initio calculations, but we would expect ab initio calculations with our basis sets to yield similar results.

Geometries of the η^1 and η^5 Cp ligand were optimized by assuming local C_s and D_{5h} symmetry, respectively. The internal ring modes (C–C distances and C–C–C angles) were optimized thoroughly for structures Ia and Ib. With some exceptions, these geometries were then assumed to be optimum in the remaining titanium(IV) structures, II through IV. The specific geometrical parameters optimized in structures II through IV are summarized in Tables II and III. In the titanium(III) system, the η^5 Cp geometry taken from Ia was assumed to be optimum for the Cp_2Ti fragment, while the remaining unique η^1, η^2, and η^5 Cp geometries were completely optimized with the following exceptions: the C–H distances were fixed at 1.10 Å and the mode that would allow interconversion of the η^1 or η^2 Cp ligand to the η^5 conformation was omitted. C_s symmetry was maintained in structures I, II, and V throughout the optimizations. Structures III and IV were of C_1 symmetry, but during the optimizations similar coordination geometries, all η^1 ligands for example, were assumed to be geometrically equivalent with respect to the metal–ligand bond distance. Geometries were optimized by using the restricted and unrestricted Hartree–Fock approximations (RHF and UHF) within PRDDO for the titanium(IV) and titanium(III) complexes, respectively.

Ab initio calculations (using the program GAMESS[15]) were then used to determine the relative energy differences between the isomeric forms of structures I through III and structure V. Because the basis set in the ab initio calculation is substantially larger than that employed in the PRDDO calculations, we believe that the energetics are more accurately represented at the ab initio level. The size and complexity of structures IVa–d limited the theory to the PRDDO level. Because of the large size of some of these complexes, ab initio calculations could not be performed

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Table IV. Basis Sets Used in ab Initio Calculations

complex	ligand basis	metal basis
Cl_3CpTi (I)	C, Cl 6-31G[a] H STO-3G[b]	single ζ: 4s, core double ζ: 32p, 4p, 3d
Cl_2Cp_2Ti (II)	C, Cl 6-31G H STO-3G	same as above
$ClCp_3Ti$ (III)	C[d] 3-21G[c] C, H, Cl STO-3G	single ζ: 4s, 3p, core double ζ: 4p, 3d
Cp_3Ti (V)	C[d] 3-21G H, C STO-3G	same as above
Cp_3Ti^+ (V)	C[d] 3-21G H, C STO-3G	same as above

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with the same basis set throughout. In structures I and II, the carbons and chlorines were described by a double-ζ basis set. In the most complex system studied at the ab initio level, structures IIIa–c, only the two Cp ligands that changed in coordination geometry were described by a double-ζ basis.[16] The metal basis for all ab initio calculations consisted of a Gaussian expansion of a Slater orbital basis set optimized for the ground state of the neutral metal atom.[17] A summary of the basis sets used is presented in Table IV.[18] Restricted open-shell Hartree–Fock calculations (ROHF) were performed on Vb and Vc of the titanium(III) system. In addition, RHF calculations are included for the cations of structures Va–c.

The effect of electron correlation on the relative energies for some of the isomeric forms was determined by including MP2 perturbation theory.[19] These calculations were done by using GRADSCF at the RHF level.[20]

To approximate the degree of steric strain in the relevant structures, empirical estimates of the nonbonding ligand–ligand interactions were made at the PRDDO optimized geometries. These were estimated from the appropriate part of Allinger's force field approximations.[21] Coulombic interactions were included and were determined by using the atomic charges generated by PRDDO and a dielectric constant of 4.

Localized molecular orbitals were determined by using the Boys criterion[22] from the PRDDO wave function for the closed-shell species $\eta^2Cp\eta^5Cp_2Ti^+$. Similar localizations were done on the doubly occupied orbitals of the neutral species at the ROHF level. Although the results of the LMO calculations for the neutral complex will not be explicitly presented here, they parallel in all respects the results found for the cation. The LMO's for the cation did provide useful information about the unusual η^2 coordination of the Cp ligand in tris(cyclopentadienyl)titanium(III). LMO calculations also provide a simple way to partition charge between the metal and the ligands, particularly in the absence of symmetry. This is accomplished by performing a Mulliken population analysis in the LMO basis. For example, η^5 bonding between a metal and a Cp ligand inevitably results in three bonding three-center LMO's. The charge in these three LMO's can then be partitioned between the metal and the Cp group, giving a qualitative idea of the number of electrons donated from the ligand to the metal. Direct comparisons to other forms of bonding (e.g. η^1), where the number of electrons donated is different in a formal sense, can also be made.

In addition to Mulliken population analyses, the degrees of bonding[23] were calculated for all PRDDO wave functions.

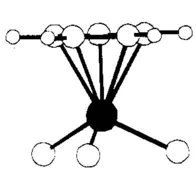
Table V. Calculated Relative ΔE's (kcal/mol)

method	complex	a	b	c	d
PRDDO	Cl_3CpTi	0.0	53.1		
ab initio		0.0	29.8		
PRDDO	Cl_2Cp_2Ti	0.0	29.6		
ab initio		0.0	16.4		
PRDDO	$ClCp_3Ti$	46.0	0.0	42.2	
ab initio		43.6	0.0	29.2	
PRDDO	Cp_4Ti	not available	23.1	0.0	33.8
PRDDO UHF	Cp_3Ti	18.2	0.0	7.2	
ab initio ROHF		not available	0.0	−1.2	
PRDDO	Cp_3Ti^+	27.3	0.0	9.2	
ab initio		44.2	0.0	2.3	
ab initio/MP2		34.8	0.0	24.1	

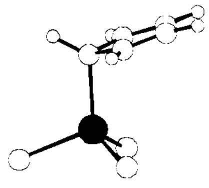
Results and Discussion

Titanium(IV) Complexes. Results of the PRDDO optimizations for the titanium(IV) ground-state structures are presented in Table II. Reasonable agreement is found between the experimental and PRDDO optimized geometries. The average errors associated with Ti–C and Ti–Cl distances were 0.05 and 0.01 Å, respectively, and the average error in the ligand–metal–ligand angles was only 3°. For all structures considered, PRDDO accurately predicted the ground-state and generated reasonable geometries for the remaining isomeric forms. These structures are summarized in Table III. In all instances, the geometries appear to be distorted tetrahedrons. Both ab initio and PRDDO results for the relative energy differences among the isomeric forms are summarized in Table V.

The η^5 coordination in structure Ia is overwhelmingly favored over the η^1 conformation Ib. The η^5 coordination mode should contribute more electron density through delocalization of the Cp π system onto the electron-deficient metal center, and evidence of this is seen in the Mulliken charges on the titanium, 0.972 (Ia) and 1.066 (Ib), and in the population analysis. The population analysis on the titanium in the LMO basis indicates the η^5-bound ligand contributes 1.21e through the three-centered Cp–Ti LMO's versus 0.87e donated to the metal from the σ interaction in structure Ib. Two LMO's describe each metal–chlorine bonding interaction, suggesting significant π donation from the chlorine lone pairs. This is a characteristic of the Ti–Cl bonding in both structures. Multiple bondlike character in the LMO's, often indicative of π donation, is further evidenced by the relative Ti–Cl degrees of bonding, 1.330 (Ia) and 1.375 (Ib). More donation is predicted in structure Ib to compensate for the reduced electron density between the metal and η^1 Cp ligand. When compared to the remaining titanium(IV) complexes considered in this work (Table VI), the Mulliken charges on the chlorines are noticeably more positive in structures Ia and Ib, and the metal–Cl bond distances, although quite similar for Ia and Ib, are at least 0.05 Å shorter than the Cl–Ti bond distance in, for example, structure II. Because the titanium is electron-deficient, the 12e configuration is understandably more stable than the 8e structure.



Ia



Ib

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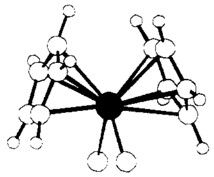
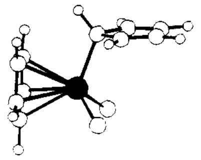
Table VI. Mulliken Charges, Degrees of Bonding, and Overlap Populations for Structures I–IV

complex	Mulliken charge		av degree of bonding			av overlap pop.		
	Ti	Cl	C_{η^5}–Ti	C_{η^1}–Ti	Cl–Ti	C_{η^5}–Ti	C_{η^1}–Ti	Cl–Ti
Ia	0.972	−0.349	0.395		1.339	0.025		0.277
Ib	1.066	−0.335, −0.337		1.019	1.375		0.373	0.288, 0.277
IIa	0.896	−0.438	0.388		1.069	0.022		0.258
IIb	0.946	−0.402	0.384	0.984	1.251		0.406	0.270
IIIa	0.897	−0.506	0.339		0.847	0.037		0.232
IIIb	0.873	−0.449	0.329	0.926	1.103	0.017	0.444	0.269
IIIc	0.941	−0.416	0.364	0.976	1.287	0.017	0.455	0.297
IVb	0.940		0.273	0.928		0.035	0.434	
IVc	0.830		0.350	0.935		0.022	0.474	
IVd	1.001		0.351	0.940		0.023	0.452	

Dichlorobis(cyclopentadienyl)titanium(IV) is one of the most synthetically important complexes considered in this work as well as one of the most documented for its structural characteristics. The stability (16.4 kcal/mol) of structure IIa (a 16e structure) over structure IIb (a 12e structure) can be easily explained by electronic effects just as in structures Ia and Ib.



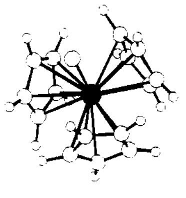
IIa



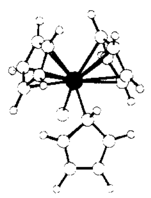
IIb

Comparison of the Mulliken charges on the titanium indicates that the two η^5 ligands collectively reduce the positive charge on the titanium when compared to the $\eta^1\eta^5$ conformation, 0.8956 (IIa) versus 0.9530 (IIb). From the population analysis, each η^5-bound ligand contributes a total of 1.12e to the metal through the three-centered LMO's in structure IIa, while the η^5 and η^1 bound ligands contribute 1.10e and 0.81e, respectively, in structure IIb. π donation from the chlorine ligands is distinguishably different between the two structures. Only one LMO describes each Ti–Cl bonding interaction in IIa, whereas two LMO's are found for each Ti–Cl bond in IIb. The Cl–Ti bond is not only 0.11 Å shorter in structure IIb, but there is an increase in the degree of bonding (1.251 for IIb versus 1.070 for IIa) and overlap population (0.270 for IIb versus 0.258 for IIa) between the Ti and Cl. π-Donating substituents such as the Cl contribute to the stability of structure IIb. Evidence of this is seen when chlorine is substituted with hydrogen, and the resulting ΔE at the PRDDO level increases by 35 kcal/mol favoring the $2\eta^5$ conformation. The ΔE between the 12e and 8e configuration for complex I is 29.8 kcal/mol, while the 16e configuration characteristic of the ground-state structure in complex II is favored to a lesser extent (16.4 kcal/mol) over the 12e configuration. This is probably due to the increased number of electrons available for bonding in II when compared to I.

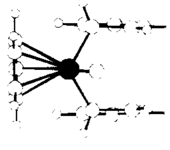
The predicted ground-state structure for chlorotris(cyclopentadienyl)titanium contains two η^5 and one η^1 Cp rings.[3] This 16e structure (IIIb) is favored by 43.6 kcal/mol over the 20e structure (IIIa) and 29.2 kcal/mol over the 12e structure (IIIc). It is not surprising that the 20e structure is unstable, since it obviously exceeds the ideal 18-electron count for transition-metal complexes. From the LMO population analysis, we find that the η^5 ligands donate approximately 0.96e in structure IIIa, 1.02e in structure IIIb, and 1.00e in structure IIIc. The η^1 ligands contribute 0.81e in structure IIIb and 0.77e in structure IIIc. The Mulliken charge on the titanium is most positive for structure IIIc (0.941), which is expected due to the reduced electron density contributed through the metal–Cp bonding. The charge on the titanium in structure IIIa is 0.897 versus 0.873 in the ground-state structure (IIIb). One might predict that the metal charge would be less in structure IIIa, but the C_{η^5}–Ti bond distances are considerably longer in IIIa than in IIIb (2.53 versus 2.40 Å) resulting in a decrease in the effective overlap of the Cp π system with the metal. Significant π donation from chlorine is seen in structure IIIc only. There are two LMO's associated with the Cl–Ti bond in IIIc, whereas in IIIa and IIIb only one LMO describes the metal–chlorine bond. The Cl–Ti bond distances and the relative degrees of bonding (Table VI) are indicative of the trends associated with an increase in the number of electrons available for bonding upon going from IIIc to IIIa (i.e., an increase in the Cl–Ti bond distance, reduced π donation from the lone pairs, and reduced multiple bondlike character).



IIIa



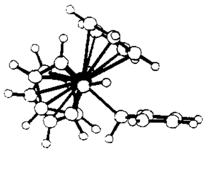
IIIb



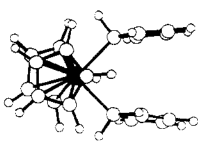
IIIc

With three cyclopentadienyl ligands in complex III, one would predict that steric hindrance might contribute to destabilization of an isomeric form such as IIIa. Results of the nonbonded interaction calculations suggest that the $2\eta^1\eta^5$ structure is sterically less hindered than either structure IIIa or the proposed ground-state structure IIIb. The nonbonded energies (which includes a coulombic term) relative to the ground-state structure associated with structure IIIa and IIIc are 37.2 and −32.9 kcal/mol, respectively. Thus, sterics play an important role in destabilizing IIIa, but electronic factors are overwhelmingly important in determining the relative stability of IIIb and IIIc.

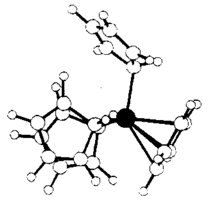
Initial calculations for structure IVa showed that the ΔE was over 100 kcal/mol above the ground-state structure (IVc), while the PRDDO values for the ΔE's of structures IVb and IVd relative to the ground state were 23.1 and 31.8 kcal/mol, respectively. Ab initio calculations were not



IVb



IVc



IVd

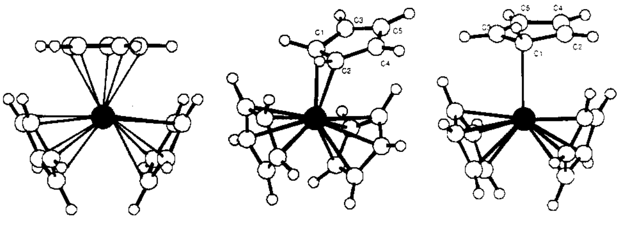
Table VII. PRDDO Geometries for Structure V (deg and Å)

geometric parameter	exp	PRDDO	geometric parameter	exp	PRDDO
			$2\eta^5\eta^2Cp_3Ti$		
Cp_1–Ti–Cp_2	133.2	132.9	C_1–C_2	1.43	1.43
Cp_1–Ti–Cp^a	108.9	111.6	C_1–C_3	1.40	1.43
Cp_2–Ti–Cp	116.8	115.5	C_3–C_5	1.38	1.40
H_1–C_1–Ti	93.9	104.7	C_5–C_4	1.39	1.40
H_2–C_2–Ti	93.3	104.7	C_4–C_2	1.40	1.43
C_5–$(C_1C_2)^b$–Ti	106.2	118.7	Cp_1–Ti	2.06	2.10
H_5–C_5–(C_1C_2)	175.7	180.0	Cp_2–Ti	2.04	2.10
C_1–Ti	2.45	2.36	C_{η^5}–C_{η^5}	1.37	1.40
C_2–Ti	2.48	2.36	C_{η^5}–Ti	2.36	2.41
C_3–Ti	3.35	3.34	Cp–Ti	2.36	2.25
C_4–Ti	3.31	3.34	C_1–C_2–C_4	107.9	107.4
C_5–Ti	3.78	3.81	C_3–C_1–C_2	106.4	107.4
			$2\eta^5\eta^1Cp_3Ti$		
Cp_1–Ti		2.08	C_{η^1}–C_{η^1}		1.53, 1.32, 1.46
Cp_2–Ti		2.08	Cp_1–Ti–Cp_2		134.8
C_1–Ti		2.27	Cp–Ti–Cp_1		112.7
H_1–C_1–Ti		106.8	C_{η^5}–C_{η^5}		1.40
C_{η^5}–Ti		2.40			
			$3\eta^5Cp_3Ti$		
Cp_1–Ti–Cp_2		123.3			
Cp–Ti–Cp_1		118.1			
C–Ti		2.26			
C–C		1.40			

[a] Cp = centroid of Cp ligand which varies in coordination mode for the three structures. [b] (C_1C_2) = midpoint of η^2 carbons.

done on this class of compounds due to the enormous computational demands. On the basis of previous calculations, we would predict the ab initio ΔE's to be somewhat lower. As noted for the series of structures in group III, the positive charge on the titanium does not progressively increase with the decrease in the number of electrons available for bonding; rather, a minimum positive charge on the metal is found for the ground-state structure. The Mulliken charges of the metal in the 20e, 16e, and 12e species are 0.940, 0.830, and 1.001 respectively. As in the previous complexes considered, the averaged LMO population analysis for structures IVb–d shows that the η^5 ligand contributes more electron density to the metal (0.90e) through three three-centered LMO's compared to the contribution of the η^1 ligand (0.77e) through a single two-centered LMO. As in the Cl_2Cp_2Ti and the $ClCp_3Ti$ systems, the 16e configuration is favored. In a complex this large, we would expect that steric factors would have more influence on the mode of bonding. The nonbonded energies relative to the ground-state structure are 24.3 and −23.5 kcal/mol for structure IVb and IVd, respectively. As in the case of III, steric interactions are an important factor in destabilizing the structure with three η^5 Cp ligands, but electronic factors clearly determine the ground-state structures. In structures II, III, and IV, the ground-state configuration is a 16e species; and in all structures considered, the ground-state structures have smaller positive charges on the metal when compared to the other isomers.

Tris(cyclopentadienyl)titanium(III). Results of the PRDDO geometry optimization are presented in Table VII. Again, good agreement is found between experimental and PRDDO geometries, in particular for the η^5Cp_2Ti fragment. For the η^2-bound ligand, a somewhat shorter C_{η^2}–Ti bond distance is predicted (2.36 Å), compared to the reported value of ~2.46 Å. These shorter distances result in a stronger σ interaction and an opening of the C_5–(C_1C_2 midpoint)–Ti angle. The H–C_{η^2}–Ti angle for the optimized geometry reflects the sp^3 hybridization of the η^2 carbons. Forcing the C_{η^2}–Ti bond distance and the C_5–(C_2C_1midpoint)–Ti angle to mimic the experimental geometry results in an increase in the total energy of only 1.5 kcal/mol. Thus, the use of PRDDO optimized geometries should not significantly affect the calculated energetics at higher levels of theory. Prior to the crystallographic work of Lucas, Green, Forder, and Prout,[4] both structures Va and Vc were proposed as ground-state configurations.[24] PRDDO clearly predicts the η^2 coordination, structure Vb, as the ground-state structure (Table V).



Va Vb Vc

To more accurately gauge the relative energies of Vb and Vc, we performed ab initio calculations using the restricted open-shell Hartree–Fock approximation. Structure Va was omitted from the ab initio ROHF calculations because it is a 19e complex and is predicted to be 18 kcal/mol higher in energy at the PRDDO level. In addition, Va is least favored from a steric viewpoint (nonbonding energies relative to the ground-state structure for Va and Vc are 37.7 and −1.8 kcal/mol, respectively). Ab initio calculations (Table V) suggest that structures Vb and Vc are nearly degenerate. This near degeneracy could be an artifact caused by basis set deficiencies and/or the lack of inclusion of correlation corrections. For the series of calculations presented here, the largest basis set on the Cp ligand was limited to double-ζ. The most apparent deficiency in this basis set is the lack of polarization functions on the carbons. The Cp_3Ti system, however, is much too large (141 basis functions with a double-ζ description of the unique Cp ligand only) to include polarization functions. Instead, we added polarization functions to the carbons in a model system Cl_3CpTi, where the Cp ligand was bound in either

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[24] Siegert, F. W.; DeLiefde Meijer, H. J. *J. Organomet. Chem.* **1968**, *15*, 131. Siegert, F. W.; deLiefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *20*, 141.

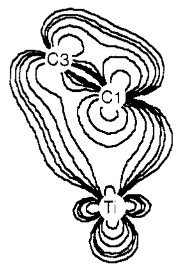
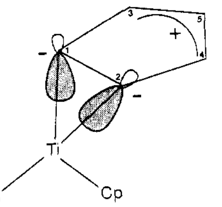


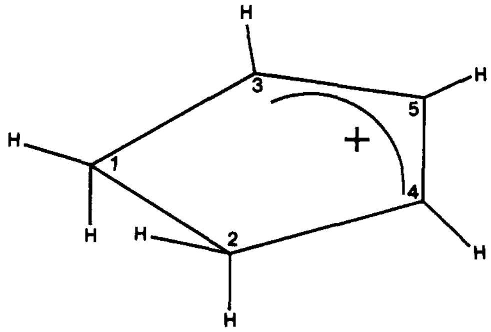
Figure 1. Contour plots of the Ti–C_1 LMO in the Ti–C_1–C_2 plane (contour values 0.5, 0.4, 0.3, 0.2, 0.05, 0.02, 0.01, 0.005, 0.0035, 0.002 e/au^3).

an η^1 or η^2 fashion and these ΔE's were compared to double-ζ results. The ΔE's calculated with both basis sets were within 0.2 kcal/mol. These results suggest that a polarized double-ζ basis set on the ligands would probably not affect our calculated ΔE's significantly. Effects of electron correlation can be estimated by MP2 perturbation theory. Unfortunately, MP2 methodology was not available for our open-shell systems. If, however, the Cp_3Ti^+ system could model the results for Cp_3Ti, correlation effects could be estimated.

Magnetic properties of the complex indicate there is only one unpaired electron in the system.[25] Population analysis at both the PRDDO and ab initio levels indicates that this unpaired electron is located on the metal and is highly localized. Because this odd electron is not involved in bonding, the Cp_3Ti^+ RHF wave function should mimic the wave function of the open-shell system. Indeed, this is the case as demonstrated by the ΔE's presented in Table V for the cations of structures Va, Vb, and Vc. From closed-shell ab initio calculations, we were then able to estimate the effects of electron correlation. The ΔE between structures Vb and Vc increased to 24.1 kcal/mol while the ΔE between structures Vb and Va decreased to 34.8 kcal/mol. The increase in the degree of stabilization of structures Va and Vb is coincidental to the increase in delocalization of the localized molecular orbitals on the metal and the Cp ligand. For example in Va there are nine three-centered LMO's compared to eight found in Vb and only six found in Vc. Thus, correlation effects tend to favor the experimentally observed η^2 geometry.

A bonding analysis of the η^2 Cp ligand provides useful information about this unusual metal–ligand coordination geometry. LMO calculations at the ROHF level parallel in all respects the results found for the cation. This is not unexpected since the single unpaired electron is highly localized on the titanium. The η^2 carbons (C_1 and C_2) form σ bonds with the titanium with delocalization of the C_{η^2}–Ti bond out to the adjacent carbons. A plot of the electron density associated with this LMO appears in Figure 1. The LMO population on the metal is 0.60e, while the population on C_1 (similarly C_2) is 1.14e and the population on C_3 (similarly C_4) is 0.21e. Analysis of the localized molecular orbitals for the η^2 Cp ring show a three-centered C_3–C_5–C_4 bond, bearing resemblance to an allyl cation. The population on carbons three through five corresponding to this LMO are 0.44e, 0.44e, and 1.10e, respectively. To a first approximation, the η^2 Cp ligand structurally and electronically resembles $C_5H_7^+$.





To confirm this, we optimized the structure of $C_5H_7^+$ at the PRDDO level. The C_3–C_5 and C_4–C_5 bond distances were 1.404 Å and the C_1–C_2 bond was 1.454 Å while the C_3–C_1 and C_2–C_4 bonds were 1.462 Å compared to the equivalent C–C bond distance of 1.402, 1.434, and 1.427 Å found in structure Vb. The C_1–C_2, C_2–C_4, and C_1–C_3 bond distances were slightly shorter than the equivalent C–C distances found in $C_5H_7^+$, probably due to the more delocalized nature of the metal–carbon bonding in the titanium complex. The carbon–titanium bonding in the η^2 ligand involves a total of 4 electrons. Because the bonding characteristics are similar in the neutral species and the odd electron does not contribute to the Cp–Ti interaction, we consider tris(cyclopentadienyl)titanium(III) to be a 17e complex.

The localized valence structure described above suggests an obvious approach to stabilize η^2 coordination. Substitution of hydrogen with π-donating ligands on one or more of the noncoordinating carbons should stabilize the η^2 conformation by contributing electron density to a relatively positive center and stabilizing the allyl cation valence structure found in the LMO's. π-Donating ligands (F, OH, and OCH_3) were chosen and substituted for hydrogen at positions C_3 and C_4 in order to stabilize η^2 bonding by donation of electron density to these relatively positive carbons. PRDDO predicts the substituted η^2 species to be significantly more stable.[26] We would like to confirm these findings at the ab initio ROHF level, but these systems are too large and lack symmetry; therefore they exceed our computational limits. We did however construct a model system where the two η^5 Cp ligands were substituted by chlorines. Substitution of Cp ligands with Cl is a common practice.[27] Recent work in this group would suggest that this substitution in the Ziegler–Natta polymerization system is quite practical.[28] At the ROHF level the η^1 conformation of $CpCl_2Ti$ is degenerate with the η^2 structure. Addition of the OH substituents to yield $C_5H_3(OH)_2Cl_2Ti$ resulted in a stabilization of the η^2 conformation by 9.5 kcal/mol.[27] These results indicate that substitution of hydrogens at C_3 and C_4 with π-donating ligands (e.g. OH and OCH_3) have a net stabilizing effect on the η^2 configuration. With this information, the experimentalist might be able to design new complexes ex-

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(25) Canty, A. J.; Coutts, R. S. P.; Wailes, P. C. *Aust. J. Chem.* **1968**, *21*, 807.

(26) The energy differences between $2\eta^5$ $(Cp_2)\eta^1(C_5H_3X_2)Ti^+$ and the ground-state $2\eta^5(Cp_2)\eta^2(C_5H_3X_2)Ti^+$ structure at the PRDDO level for X = F, OH, and OCH_3 are 14.8, 20.4, and 21.0 kcal/mol, respectively.

(27) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *J. Am. Chem. Soc.* **1983**, *105*, 2280.

(28) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.*, in press.

(29) The basis set on the carbons was 4-31G, while an STO-3G basis was employed on the hydrogens and chlorines. The basis set on the metal remained unchanged.

hibiting this unusual coordination geometry.

Conclusion

The ground-state conformations of (cyclopentadienyl)titanium(IV) and -titanium(III) complexes are predominantly influenced by electronic factors. The ground-state structures in the titanium(IV) series are characterized by a lesser positive charge on the titanium, and where enough electrons exist through ligand–metal bonding, these structures are 16e species. This study has provided valuable insight into alternative coordination modes of the Cp ligand. A detailed study of the η^2-coordination geometry allows us to predict a means of stabilizing this unusual bonding mode. Substitution of hydrogen with π-donating groups such as F, OH, or OCH_3 at positions C_3 and C_4 of the Cp ligand could enhance the η^2-bonding capability by stabilizing the allyl cation-like character of carbons three through five. A challenge can now be made to the experimentalist to synthesize new η^2-coordinating compounds.

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Registry No. Cl_3CpTi, 1270-98-0; Cl_2Cp_2Ti, 1271-19-8; $ClCp_3Ti$, 11079-20-2; Cp_4Ti, 11079-32-6; Cp_3Ti, 52700-41-1.

Activation of 1-Alkynes at 16-Electron Rhodium Fragments. Some Examples of Thermodynamically Favored Rearrangements $[M(\pi\text{-}HC{\equiv}CR)] \rightarrow [M(H)(C{\equiv}CR)]$

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The 16-electron fragments $[(NP_3)Rh]^+$ and $[(PP_3)Rh]^+$ react with 1-alkynes in THF at room temperature yielding Rh(III) cis hydride acetylide complexes of formula $[(L)Rh(H)(C{\equiv}CR)]BPh_4$ [L = NP_3, $N(CH_2CH_2PPh_2)_3$; L = PP_3, $P(CH_2CH_2PPh_2)_3$; R = H, n-C_3H_7, Ph, $SiMe_3$, CH_2OH, CHO, CO_2H, CO_2Et]. The crystal structure of the ethynyl derivative $[(NP_3)Rh(H)(C{\equiv}CH)]BPh_4{\cdot}1.5THF$ was determined by X-ray crystallography. The metal atom in the complex cation is octahedrally coordinated by the four donor atoms of NP_3, a σ-bonded ethynyl group, and a hydride ligand. Crystal data: monoclinic, space group $P2_1/n$, a = 15.769 (3) Å, b = 32.458 (6) Å, c = 13.277 (6) Å; β = 105.21 (2)°, U = 6557 (1) Å^3; Z = 4. The structure was solved by Patterson and Fourier techniques and refined to an R factor of 0.079 (R_w = 0.086) by using 3735 reflections with $I > 3\sigma(I)$. Decreasing the temperature to −40 °C does not change the nature of the products except for the reactions with $HC{\equiv}CCO_2Et$. In this case, the π-alkyne adducts $[(L)Rh(\pi\text{-}HC{\equiv}CCO_2Et)]BPh_4$ (L = NP_3, PP_3) are formed which are thermodynamically unstable in ambient temperature solutions to irreversibly give the corresponding hydride acetylide derivatives. The $[Rh(\pi\text{-}HC{\equiv}CCO_2Et)] \rightarrow [Rh(H)(C{\equiv}CCO_2Et)]$ rearrangement is preceded at lower temperature by a fluxional process on the ^{31}P NMR time scale which involves the π-alkyne species. At low temperature, also propiolic acid, $HC{\equiv}CCO_2H$, forms with the $[(NP_3)Rh]^+$ fragment a π-alkyne complex which converts, in ambient temperature solutions, into hydride acetylide and hydride carboxylate derivatives via two independent, almost equally favored pathways. Most of the hydride acetylide complexes of rhodium(III) react with excess $NaBH_4$ in THF/ethanol yielding Rh(I) σ-acetylides of formula $[(L)Rh(C{\equiv}CR)]$ (R = n-C_3H_7, Ph, $SiMe_3$, CH_2OH, CO_2Et, CHO). No interconversion between the NP_3 hydride acetylide complexes and the parent vinylidenes $[(NP_3)Rh\{C{=}C(H)(R)\}]BPh_4$ was observed.

Introduction

The stoichiometric reactions between terminal alkynes and unsaturated metal fragments give different products depending on the alkyne and metal components. In cases of ethyne or of alkynes bearing inert substituents like aryl or alkyl groups, three species can be isolated: π-alkyne, hydride acetylide, or vinylidene complexes.[1] While it is generally agreed that the initial interaction between the metal system and the alkyne molecule is of the π-type and that only at a later stage, the π-intermediate eventually converts into hydride acetylide or vinylidene derivatives,[1c–i] there are still doubts about the whys and mechanism of the metal–π-alkyne degradation. In particular, it is not completely established whether the hydride acetylide system is a precursor to the vinylidene functionality as it

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[†] ISSECC, CNR.

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