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Geometry and Electronic Structure of Titanacycloalkenes

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A number of titanacycloalkenes, $H_2TiC_2H_2$, $HTiC_3H_3$, $H_2TiC_4H_4$, and $HTiC_5H_5$, have been studied using ab initio techniques. Vibrational frequencies were computed at the RHF, MP2, BLYP, and B3LYP levels. Both a LANL2DZ pseudopotential and an all-electron TZV basis set was used for each method. The electronic structure of the systems of interest is characterized in terms of natural resonance theory (NRT) and the atoms in molecules (AIM) analysis. All rings are planar except for titanabenzene, $HTiC_5H_5$. $H_2TiC_2H_2$ has C_{2v} symmetry and has single Ti−C bonds. $HTiC_3H_3$, unlike the isovalent cyclobutadiene and silacyclobutadiene, has C_{2v} symmetry and shows significant electron delocalization. In $H_2TiC_4H_4$ the TiC_4 ring is planar with equivalent single Ti−C bonds and has C_{2v} symmetry. $HTiC_5H_5$ has a boat-shaped geometry where the angle between the CTiC plane and the plane formed by the neighboring four carbon atoms is nearly 90°. AIM analysis isolates a weak critical point between Ti and the para-C atom, and NRT analysis confirms the weak bonding interaction.

Introduction

Titanium finds its way into many organometallic compounds and thus offers a very practical transition metal to study. Like carbon, titanium has four valence electrons and the most common oxidation state is Ti(IV).[1] Similarities in the valence electron configuration provides similar characteristics in terms of bonding. For example, both $TiCl_4$ and CCl_4 have tetrahedral geometries. However, unlike carbon, titanium utilizes d orbitals in its bonding to other atoms. Furthermore, C and Ti differ in atomic orbital size, polarizability, and electronegativity. As a result, the carbon atom is not always prone to form double and triple bonds with Ti as it would with another C atom.

Understanding the carbon−titanium interaction is important in many industrial processes and compounds. Catalytic processes being one of the most common, e.g., the Ziegler−Natta alkene polymerization.[1] In terms of cluster chemistry, carbon−titanium bonding has focused primarily on metallocarbohedrenes (metcars), such as those of Castleman and co-workers.[2] Recently, however, experimental studies of small carbon titanium clusters,[3] TiC_x (x = 2−5), show these molecules to have a preference for forming rings similar to those of YC_x[4] and LaC_x.[5] The theoretically based investigation of TiC_x[6] clusters indicate that the x = 3 and 4 structures are planar ring structures with singlet ground states. In that study bonding between Ti and C was determined to be primarily ionic. Little work has been done on aromatic hydrocarbons with titanium carbon substitution. Exploring the nature of the Ti−C bond in unsaturated hydrocarbons would be of interest in expanding the understanding of both catalytic processes and met-cars chemistry.

We present here an ab initio study of a single Ti substitution for a C atom within a series of unsaturated cycloalkenes. Recently, $H_2TiC_2H_2$ was isolated by Lee, Manceron, and Papái[7] by co-deposition of ground-state Ti atoms and ethene molecules in excess argon at low temperature followed by selective electronic excitation of the Ti atoms. Their study concluded that the ground state of the molecule was a singlet. Furthermore, the theoretical studies of TiC_3 and TiC_4 indicate the ground state of these small molecules to be a singlet and to have a fan or ring structure.[6] In the systems presented here, the open valences of Ti and C are filled with hydrogen and, therefore, the four molecules characterized in this study are presumed to have singlet ground states with cyclic geometries. In the case of $HTiC_3H_3$, a system isovalent to cyclobutadiene and silacyclobutadiene, the triplet state is expected to be low-lying and the singlet−triplet splitting is determined. We attempt to characterize the bonding in these novel transition metal compounds, as well as to present the geometry and vibrational frequencies. We have not determined every possible isomer but presume our structures to be low-lying if not the true ground states.

Calculation Details

Restricted Hartree−Fock (RHF) geometries were first obtained with the Los Alamos effective core potential plus double-ζ (LANL2DZ) of Hay and Wadt[8] on Ti and an all-electron Dunning[9] 9s5p (D95) basis with additional p and d functions[10] on C and an additional p function[10] on H. The combination of these functions will be referred to as the ECP. Correlation corrections to the RHF wave functions were included at the level of second-order Möller−Plesset perturbation (MP2). Energy calculations, analytic geometry optimizations, and analytic frequency calculations were also performed using density functional methods (DFT) with the correlation functional of Lee, Yang, and Parr[11] in combination with Becke's 1988 exchange functional[12] (BLYP) and Becke's three-parameter hybrid functional[13] (B3LYP). In the instance of the triplet state of $HTiC_3H_3$, all calculations were performed with restricted open-shell Hartree−Fock (ROHF), restricted open-shell Möller−Plesset perturbation (ROMP2), restricted open-shell BLYP (ROBLYP), and restricted open-shell B3LYP (ROB3LYP). All electron basis calculations were performed following the LANL2DZ calculations with a TZV basis on Ti as given in ref 15c of Glezakou and Gordon[14] and a TZV[15] basis on C and H. The Ti TZV basis is a Watcher's[16] basis (14s9p5d) extended to triple-ζ quality. Diffuse s, p, and d polarization functions were included as given in Glezakou and Gordon.[14] All calculations were performed with the Gaussian94 package.[17] Geometries

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TABLE 1: Calculated Geometries for the Ground-State Structure of $H_2TiC_2H_2$

	RHF/TZV	MP2/ECP	MP2/TZV	BLYP/TZV[a]	B3LYP/ECP	B3LYP/TZV
r_{Ti-C} (Å)	1.99	1.95	1.99	2.00	1.97	1.99
r_{Ti-H} (Å)	1.76	1.68	1.75	1.75	1.70	1.74
r_{C-C} (Å)	1.29	1.36	1.33	1.33	1.33	1.32
r_{H-C} (Å)	1.07	1.09	1.08	1.09	1.09	1.08
α(HCC)	139.08	130.55	135.66	134.79	135.74	136.07
α(HTiH)	121.10	127.69	127.95	123.92	124.75	124.17
α(CTiC)	37.84	40.69	39.04	38.82	39.35	38.63
α(TiCC)	71.08	69.65	70.48	70.59	70.33	70.68

[a] TZV+2f basis function.

TABLE 2: Vibrational Frequencies with Various Methods with the TZV Basis (cm^{-1})

RHF	MP2	B3LYP	BLYP[a]	LMP[b]	exptl	mode
314	206	145	22	248	277	HTiH wag
341	257	344	339	285	TiH_2 twist	
385	325	350	340	429	399	HTiH def
573	547	558	546	571	TiC str	
622	621	584	565	620	598	TiC str + CCH def wag
653	640	663	622	653	668	HCCH tilt
777	714	709	698	720	688	TiH_2 def + CCH def
842	828	797	775	751	765	CCH def
968	909	910	885	895	HCCH tors	
1131	1036	1038	1006	1015	1000	CCH def + TiC def
1623	1514	1536	1473	1448	1465	CCstr + CCH def
1663	1670	1651	1608	1639	1585	TiH str
1748	1712	1689	1637	1647	1611	TiH str
3360	3235	3166	3069	3041	CH str	
3398	3265	3197	3099	3077	CH str	

[a] TZV+2f basis. [b] LMP are the computed vibrational frequencies with C_s molecular symmetry and the BLYP functional from ref 7.

were optimized without symmetry, and frequencies were computed with the highest level symmetry available. Natural resonance theory (NRT) resonance structures and bond orders were acquired from NBO 4.0.[18] Calculations were carried out on PC computers running Linux with some of the larger calculations being performed on an IBM RS/6000 workstation.

Results

The RHF and MP2 wave functions of titanacyclopropene, $H_2TiC_2H_2$, have an energy-optimized molecular symmetry of C_{2v} with the CTiC atoms lying in a plane along with the C−H bonds as shown in Figure 1A. The two H−Ti bonds lie above and below the CTiC plane with the HTiH plane perpendicular to the C−C bond. The B3LYP functional also gives C_{2v} molecular symmetry, however, only with the TZV basis. Both BLYP and B3LYP functionals give the molecular symmetry of C_s with the ECP basis; the BLYP functional gives C_s symmetry with the TZV basis. In these lower symmetry geometries the HTiH plane forms an angle with the C−C bond of 129.8°, 123.2°, and 162.2° for the B3LYP/ECP, the BLYP/ECP, and the BLYP/TZV, respectively. Upon inclusion of f basis functions[19] to the TZV basis, the BLYP functional optimized the molecular geometry to C_{2v} symmetry. The energy to optimize from the C_s BLYP/TZV geometry to the energy-optimized BLYP/TZV+2f C_{2v} geometry is 1.1 kcal/mol, reflecting the shallow nature of the HTiH wagging potential. ECP and all-electron TZV bond lengths and bond angles for the various techniques are summarized in Table 1. The Ti−C bond length varies by less than 0.01 Å for each method, whereas the C−C bond length varies by 0.05 Å. This implies a greater sensitivity of the C−C bond to methodology than for the Ti−C bonds. The ECP bond lengths are very similar to the all-electron TZV basis with the largest difference in the Ti−C bond length being 0.04 Å greater for MP2/ECP than the MP2/TZV, the largest difference in the C−C bond length being 0.03 Å less for MP2/ECP than the MP2/TZV, and less than 0.01 Å on the C−H bond lengths for all methods. Greater discrepancies were found for the Ti−H bond lengths with the greatest increase of 0.07 Å from the MP2/ECP to the MP2/TZV.

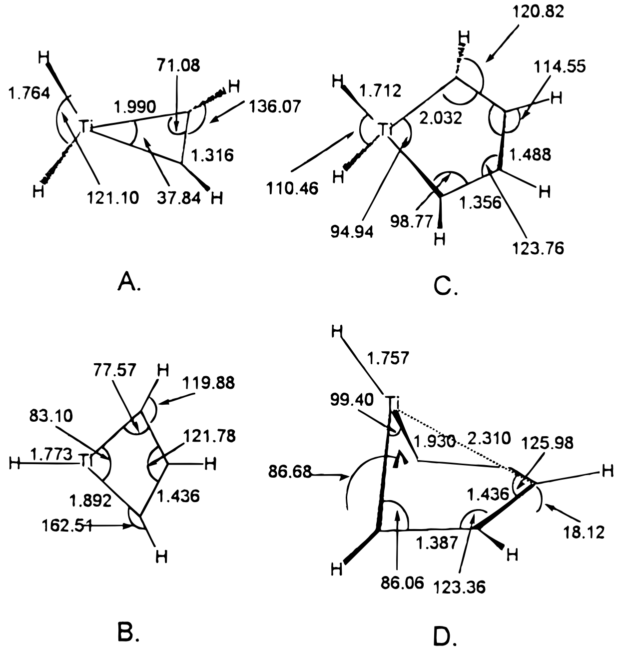

Figure 1. Ground-state B3LYP/TZV geometries of the titanacycloalkenes.

As mentioned in the Introduction, this molecule has been observed in a recent matrix isolation experiment.[7] The authors reported vibrational frequencies and results of DFT calculations. Table 2 provides the vibrational frequencies of our work along with the BLYP and experimental results of the reference work. Our theoretical vibrational frequencies compare well with both the experimental frequencies and those calculated in the

TABLE 3: B3LYP/TZV NRT Bond Order

molecule	bond	covalent	ionic	total
$H_2TiC_2H_2$	Ti−C	0.52	0.45	0.97
	Ti−H	0.59	0.36	0.95
	C−C	1.89	0.08	1.97
	C−H	0.75	0.22	0.97
$H_2TiC_4H_4$	Ti−C	0.49	0.56	1.05
	Ti−H	0.69	0.29	0.98
	C−C	1.79	0.11	1.90
		0.97	0.06	1.03
	C−H	0.78	0.21	0.99
		0.76	0.21	0.97
$HTiC_3H_3$	Ti−C	0.64	0.76	1.40
	Ti−H	0.51	0.46	0.96
	C−C	1.26	0.17	1.43
	C−H	0.80	0.19	0.99
		0.75	0.21	0.96
$HTiC_5H_5$	Ti−C	0.68	0.59	1.27
		0.12	0.14	0.26
	Ti−H	0.63	0.33	0.96
	C−C	1.41	0.18	1.59
		1.14	0.09	1.23
	C−H	0.78	0.21	0.99
		0.74	0.23	0.97
		0.75	0.23	0.98

reference work with the exception of the HTiH wag. In the work of Lee et al., the BLYP and BP86 methods optimize the molecular geometry to C_s symmetry. They reasoned that a shallow HTiH wagging potential and the low HTiH experimental vibrational frequency indicated that the molecule was better modeled by BP86 and BLYP functionals in C_s symmetry. However, with additional f basis functions, the nonhybrid method of BLYP gives an even lower HTiH wagging vibrational frequency than does B3LYP in the C_{2v} symmetry. The experimental value for the HTiH wag was assigned as 277 cm^{-1}. RHF/TZV and MP2/TZV results give this same frequency at 314 and 206 cm^{-1}, respectively, whereas B3LYP/TZV and BLYP/TZV+2f give lower values of 145 and 22 cm^{-1}. The overall average of the differences between all of the computed and the experimental frequencies is 76 cm^{-1} for RHF/TZV, 56 cm^{-1} for MP2/TZV, 51 cm^{-1} for B3LYP/TZV, and 47 cm^{-1} for BLYP/TZV+2f. The average differences are reduced for the B3LYP and BLYP by 9 and 23 cm^{-1} if the HTiH wagging frequency is neglected.

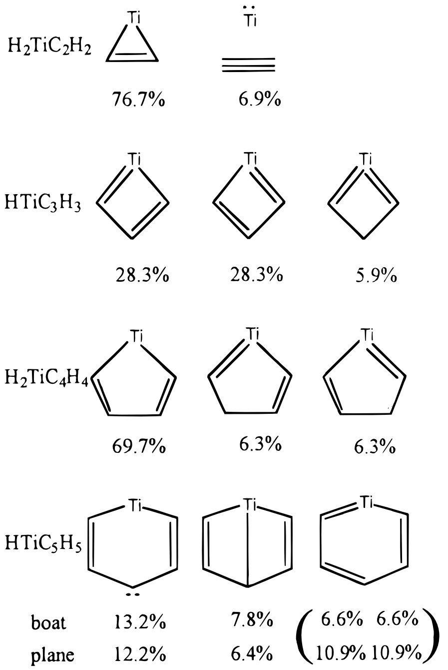

Figure 2. NRT resonance structures and percentage contributions.

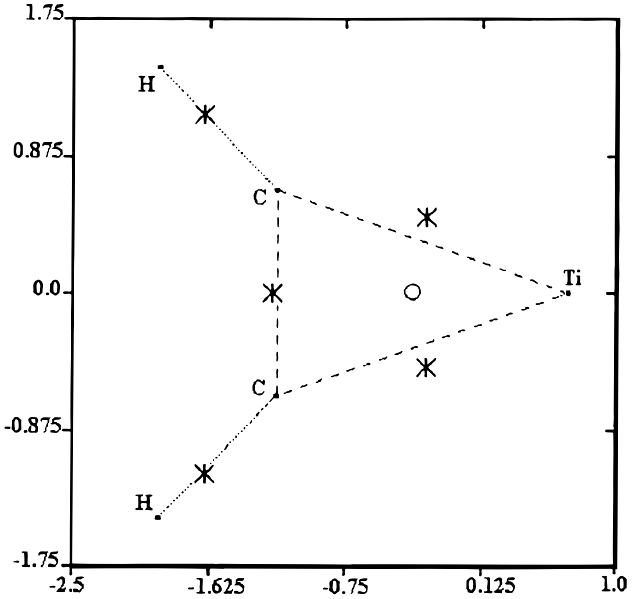

Figure 3. Critical points of $H_2TiC_2H_2$ marked by an "*" and the ring point marked by an open circle.

Several methods are available for evaluating wave functions. This paper reports the results of two methods, natural resonance theory (NRT)[20] and atoms in molecules (AIM).[21] NRT provides a method of interpreting the one-particle density matrix in terms of chemical resonance structures and their percentage contribution to the molecular density; bond orders and significant resonance structures are provided in Table 3 and Figure 2. NRT indicates that the Ti−C bonds and the Ti−H bonds are quite ionic. This is not surprising considering the electronegativity of Ti is considerably less than either carbon or hydrogen. The B3LYP Mulliken charges are +0.70*e*, −0.36*e*, and −0.19*e* on Ti, C, and the Ti-bound H, respectively. The total C−C and Ti−C bond orders are 1.97 and 0.97, respectively. The primary resonance structure shows a contribution of 76.7% and corresponds to a double C−C bond and single Ti−C, Ti−H, and C−H bonds. A "nonbonded" structure contributes 6.9%; all other NRT resonance structures have contributions below 2% and are neglected. Bond strain has been reported in similar systems such as the silatitanacyclobutanes.[14] Bader's AIM analysis is used to locate critical points and to evaluate bond strain in the ring. The critical points are locations where the gradient of the density is zero and therefore allow the identification of bond paths and rings. Figure 3 shows critical points and the ring point for the B3LYP/TZV density of $H_2TiC_2H_2$. Considerable bond strain occurs between the Ti−C bonds, whereas critical points lie directly on the lines between the other bonded atoms.

To the authors' knowledge, no experimental or theoretical data is available for the remaining three molecules. In considering the systems presented here, two molecules have one H bound to the Ti center and two have two H atoms bound to Ti. It is advantageous to compare the systems according to the number of H atoms bound to the Ti atoms because of obvious similarities in metal−C bonding. Therefore, the next system of discussion is $H_2TiC_4H_4$. Geometry optimization at all levels of theory lead to a molecule of C_{2v} symmetry with all Ti and C atoms in a plane along with the C−H bonds. B3LYP/TZV bond lengths and angles can be found in Table 4 and Figure 1C. Results for the other methods and basis are given in Table SI in Supporting Information. The B3LYP/TZV Ti−C bond length of 2.03 Å is

TABLE 4: B3LYP/TZV Bond Lengths and Angles for $H_nTiC_mH_m$

	$H_2TiC_2H_2$	$H_2TiC_4H_4$	$HTiC_3H_3$	$HTiC_5H_5$
r_{Ti-C} (Å)	1.99	2.03	1.89	1.93
r_{Ti-H} (Å)	1.74	1.71	1.77	1.76
r_{C-C} (Å)	1.32	1.36	1.44	1.39
		1.49		1.44
r_{H-C} (Å)	1.08	1.08	1.08	1.08
		1.09	1.09	1.09
				1.08
α(CTiC)	39.35	94.94	83.10	99.40
α(TiCC)	70.33	98.77	77.57	86.06
α(CCC)		123.76	121.78	123.36
				125.98

0.04 Å longer than the corresponding bond in $H_2TiC_2H_2$. The C−C bonds adjacent to the Ti−C bonds are 1.36 Å, and the single C−C bond opposite the Ti atom is 1.49 Å. The bond lengths indicate that there is double bond character in the C−C bonds adjacent to the Ti−C bonds, and this is confirmed by NRT results. This C−C double bond is 0.04 Å longer than the C−C bond of $H_2TiC_2H_2$ corresponding to a slightly more delocalized double bond. The H−Ti bonds are 1.71 Å, or 0.03 Å shorter than in $H_2TiC_2H_2$. Mulliken population charges indicate the Ti charge is +0.75*e* or 0.03*e* more positive than the Mulliken charge on the Ti atom in $H_2TiC_2H_2$ whereas the (H−Ti) H atom charge of −0.16*e* is less negative, 0.02*e*, than the corresponding H in $H_2TiC_2H_2$. Mulliken charges on the C-ring atoms are −0.43*e* for the carbons adjacent to the metal center and −0.14*e* on the remaining C. The average charge on the carbon atoms is −0.28*e*, which is 0.07*e* less than the Mulliken charges on the C atoms in $H_2TiC_2H_2$.

NRT bond orders and significant resonance structures are provided in Table 3 and Figure 2. The primary resonance structure shows a contribution of 69.7% and corresponds to single Ti−C bonds, a single bond between the two carbons at the end opposite the Ti, and double bonds between the remaining C atoms. The remaining resonance structures each have a 6.3% contribution and correspond to interchanging double and single bonds between the Ti and C atoms. The B3LYP/TZV NRT gives a bond order near 1.0 for each Ti−C bond and near 1.0 for each Ti−H bond. As with $H_2TiC_2H_2$, the Ti−C bond has a large ionic character. The Ti−H bond is, however, less ionic than the Ti−H bond in $H_2TiC_2H_2$. The C−C bond adjacent to the Ti−C bond has a bond order of 1.9, which is only slightly less than the C−C bond of $H_2TiC_2H_2$. As with $H_2TiC_2H_2$, bond strain occurs between the Ti−C bonds; however, bond strain is less with the five-member ring.

The next system of interest is titanacyclobutadiene, $HTiC_3H_3$. Before discussion of the results of $HTiC_3H_3$, there are two isovalent molecules that require consideration: cyclobutadiene and silacyclobutadiene. At the moment, we will consider only the lowest-lying electronic state of these molecules, which in each case is a singlet. Theory predicts[22] and experiment indicates[23] that the ground-state structure of cyclobutadiene is rectangular with D_{2h} symmetry. The unequal bond lengths suggest two localized double bonds and are considered to be caused by the molecule's antiaromatic π system.[24] Experimental[25] and theoretical[26] work on silacyclobutadiene show the molecule to be planar with C_s symmetry, and all four ring bonds having different lengths. Both Si−C bond lengths and C−C bond lengths are different, indicating localized double bonds.

Unlike cyclobutadiene and silacyclobutadiene, the geometry of titanacyclobutadiene shows two equivalent Ti−C bonds and two equivalent C−C bonds; B3LYP/TZV bond lengths and angles can be found in Table 4. Results for the remaining methods are in given in Table SII in Supporting Information. All methods optimize to C_{2v} symmetry with the given basis sets except for the BLYP.[27] The RHF/TZV Ti−C bond lengths are 1.91 Å and are 0.03 and 0.02 Å long compared to MP2/TZV and B3LYP/TZV, respectively, whereas the RHF/TZV C−C bond lengths are 1.43 Å and are 0.01 Å short relative to both MP2/TZV and B3LYP/TZV. This is consistent with the previous titanacycloalkenes where the RHF metal−carbon bond lengths are longer than the "correlated" techniques and the C−C bond lengths are shorter than the "correlated" methods. Vibrational frequencies and relative intensities for the B3LYP/TZV can be found in Table 5.

The RHF/TZV HOMO−LUMO gap is small and suggests the possibility of a low-lying triplet state. This is consistent with cyclobutadiene and silacyclobutadiene, which have singlet−triplet splittings of 6 [22] and 5 kcal/mol,[26,28] respectively. At the ROHF level of theory, calculations on $HTiC_3H_3$ reveal the triplet state to be lower in energy by 24.5 kcal/mol. Calculations with ROB3LYP/TZV, ROBLYP/TZV, and ROMP2/TZV, however, place the singlet state as the ground state by 14.4, 22.0, and 27.6 kcal/mol, respectively. These methods yield a greater singlet−triplet splitting than found in silacyclobutadiene[28] and correspondingly indicate greater aromatic character. We present an explanation for possible aromaticity within this 4π electron ring in the section on bonding below. Geometries for the triplet state with the TZV basis and the various methods are provided in Table SIII in Supporting Information. For all of the theoretical methods except RHF, the triplet state exhibits only a slight asymmetry. For example, the Ti−C bond lengths and the C−C bond lengths differ by less than 0.001 Å. By contrast, the RHF/TZV Ti−C bond lengths differ by 0.01 Å and the C−C by 0.09 Å.

NRT bond orders and significant resonance structures for the singlet state are provided in Table 3 and Figure 2. The B3LYP/TZV NRT gives a bond order of 1.40 for both of the Ti−C bonds and 1.43 for both of the C−C bonds. The near-equivalence in the pair of Ti−C and the pair of C−C bond orders is consistent with the equal bond lengths and suggests significant delocalization within the ring. Relative to the previous systems studied, the larger Ti−C bond orders in $HTiC_3H_3$ compared to $H_2TiC_2H_2$ and $H_2TiC_4H_4$ are expected on the basis of simple valence electron count. That is, H−Ti has three electrons to contribute in bonding to the carbon framework (two σ and one π bond), whereas H_2Ti has only two electrons to contribute (two σ bonds). The Ti−H bond in $HTiC_3H_3$ is also more ionic than the previous systems. As expected, the Ti−H bond order is near 1.0 and highly ionic, 48%, whereas the corresponding Ti−H bonds in $H_2TiC_2H_2$ and $H_2TiC_4H_4$ were 38% and 29% ionic, respectively. The other C−H bond orders are also near 1.0 and are primarily covalent. NRT shows two primary structures of equal weights of 28.3% contribution and correspond to alternating double bonds. The third resonance structure contributes 5.9%; it is a result of the d orbitals on Ti and would not likely be present in cyclobutadiene or silacyclobutadiene. As with $H_2TiC_2H_2$ and $H_2TiC_4H_4$, bond strain occurs between the Ti−C bonds.

The final molecule studied is $HTiC_5H_5$ or titanabenzene. Geometry optimization of titanabenzene at all levels of method and basis indicates the structure to have a boat-shaped or Dewar geometry, with the Ti atom and the para-C atom sitting above a plane of four carbon atoms as shown in Figure 1D. The symmetry of the molecule is C_s, with a single plane of symmetry passing through the Ti−H bond and the para-C−H bond. The energy difference between the optimal planar conformation and

TABLE 5: B3LYP/TZV Vibrational Frequencies and Relative Intensities

$H_2TiC_2H_2$			$H_2TiC_4H_4$			$HTiC_3H_3$			$HTiC_5H_5$		
ν (cm^{-1})	sym	IR intens (km/mol)	ν (cm^{-1})	sym	IR intens (km/mol)	ν (cm^{-1})	sym	IR intens (km/mol)	ν (cm^{-1})	sym	IR intens (km/mol)
145	B_2	290	140	B_1	1	29	B_1	135	237	A'	17
344	A_2	0	194	A_1	18	414	B_1	61	259	A'	1
350	B_1	0	289	B_1	33	445	B_2	12	339	A''	19
558	A_1	3	294	A_2	0	539	A_1	42	429	A''	24
584	B_2	103	416	B_2	7	622	B_2	33	455	A''	36
663	B_1	72	517	A_2	0	676	B_1	208	471	A'	75
709	A_1	101	547	A_1	47	751	A_2	0	500	A'	0
797	A_1	29	566	B_2	53	777	A_1	0	664	A'	44
910	A_2	0	595	B_1	106	906	B_2	157	687	A''	43
1038	B_2	81	657	A_1	110	932	B_1	0	701	A'	41
1536	A_1	45	764	B_2	118	1034	A_1	17	702	A''	7
1651	B_1	627	797	A_2	0	1105	B_2	74	786	A'	109
1689	A_1	377	887	A_1	5	1205	A_1	7	835	A'	3
3166	B_2	1	996	B_1	0	1307	B_2	1	920	A''	0
3197	A_1	0	1015	A_2	0	1609	A_1	803	940	A'	15
			1095	A_1	12	3120	A_1	6	963	A'	2
			1114	B_2	2	3207	B_2	0	990	A''	2
			1307	B_2	25	3211	A_1	0	1094	A'	11
			1345	A_1	11				1154	A''	9
			1483	A_1	25				1248	A''	49
			1575	B_2	0				1262	A'	30
			1689	B_1	480				1382	A''	11
			1720	A_1	442				1454	A''	0
			3079	B_2	8				1472	A'	10
			3096	A_1	48				1635	A'	740
			3168	B_2	5				3100	A'	16
			3168	A_1	0				3101	A''	14
									3177	A'	1
									3177	A''	1
									3188	A'	6

the boat-shaped molecule is 22.7 kcal/mol with B3LYP/TZV functional and basis. In summary of the B3LYP/TZV results of Table 4, the Ti−C bond length of 1.93 Å is 0.04 Å longer than the corresponding bond in $HTiC_3H_3$. The CC bonds adjacent to the Ti−C bonds are 1.39 Å, and the single C−C bonds opposite the Ti atom are 1.44 Å. These bond lengths differ by less than 0.05 Å, indicating that there is some double bond character in both of the C−C bonds, and this is confirmed by AIM and NRT results. The B3LYP/TZV C−C bond length in $HTiC_3H_3$ is the same length, 1.44 Å, as the para/meta C−C bond, confirming the somewhat delocalized nature of the C−C bonds in $HTiC_5H_5$. Mulliken charges indicate the Ti atom charge is $+0.75e$, the ortho-C atom charge is $-0.38e$, the meta-C atom charge is $-0.18e$, and the para-C atom charge is $-0.27e$. The distance from the Ti atom to para-C atom is 2.31 Å and is 0.01 Å greater than the distance from the meta-C atom. Yet the larger charge on the para-C atom and the boat-shaped geometry of the molecule indicate charge transfer taking place between the para-C atom and the Ti atom. Structural data for all methods are given in Table SIV in Supporting Information. All methods compare well, with the greatest differences being between the MP2/ECP and the B3LYP/ECP. Here, the MP2/ECP method predicts longer bond lengths than any other method, whereas the B3LYP/ECP compares more favorably with the TZV results of the other methods. The MP2/TZV method was not done because of resource limitations; however, on the basis of results from previous systems, it should compare well with B3LYP.

NRT bond orders and significant resonance structures are provided in Table 3 and Figure 2. The B3LYP/TZV NRT gives a Ti−C bond order of 1.27 and C−C bond orders of 1.59 for the bonds adjacent to the Ti−C bond and 1.23 for the C−C bonds opposite the Ti−C bond. There is a weak bond of order 0.26 between the Ti atom and the para-C atom in the boat-shaped structure. The NRT results shown in Figure 2 make clear that the molecule exhibits a complex electronic structure. For example, the highest weight resonance structure contributes only 13.2%. The three other structures shown in Figure 2 average only 7% each. There are a large number of structures, not shown, that contribute less than 5% each. Two resonance structures with weight of 6.6% are benzene-like with alternating double bonds. The primary resonance structure, however, shows a contribution of 13.2% and corresponds to a lone pair on the para-C atom and double C−C bonds adjacent to the Ti−C bonds. The next most significant resonance structure, 7.8% contribution, replaces the lone pair of the first resonance structure with a bond between the Ti atom and the para-C atom. These resonance structures indicate an interaction that is both consistent with the Mulliken charges and the boat structure of the molecule. Though less than the smaller systems discussed in this work, AIM critical points show bond strain between the Ti−C bonds. AIM also indicates the existence of a critical point midway between the Ti atom and the para-C atom, again supporting a weak "bonding" interaction between the Ti atom and the para-C atom. The interaction of the Ti atom with the para-C atom can be explained by considering an available d orbital on the Ti center. The mechanism for this long bond interaction can be explained in terms of orbital diagrams and is discussed below.

Overall Bonding

The initial interaction between a bare transition metal and ethene is often described by ethene donation of π-electron density to an empty σ-orbital of the metal atom. This weakens the π-bond of ethene and lowers the π^*-orbital energy. Electrons are then accepted from a back-donating d-orbital of the metal atom.[29] The above model is used when describing a bare transition metal approaching an unsaturated hydrocarbon. In the evaluation of the bonding in the systems of this study, however, we must consider the H atoms bound to the Ti metal center. It would be better to consider a TiH_2 approaching ethyne, as in

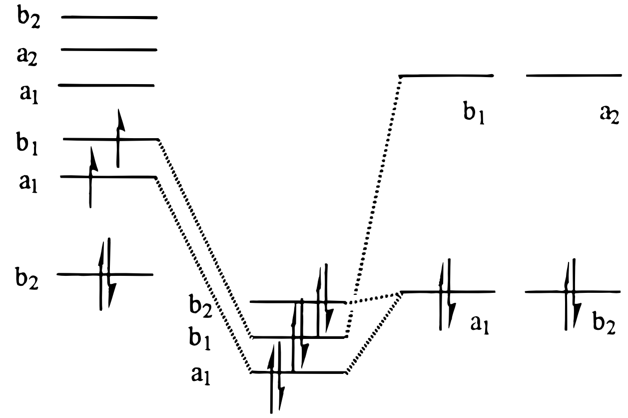

Figure 4. Energy level diagram of TiH_2 and C_2H_2 forming molecular $H_2TiC_2H_2$.

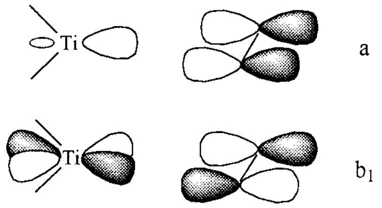

Figure 5. Schematics of the bonding orbitals of TiH_2 and C_2H_2.

the similar dihydride dihydrogen metal complexes.[30] TiH_2 is a bent molecule[31] with a $^3B_1$ ground state. The dipole moment of the molecule indicates a positive charge on the Ti atom. Initially considering the Ti end of H_2Ti as approaching a C_2H_2 triple bond, the diffuse π-electrons of C_2H_2 would be polarized toward the Ti metal center. A molecular orbital energy level diagram for this process is presented in Figure 4. This representation shows overlap between the a_1 orbital of TiH_2 and the π-bonding a_1 orbital of C_2H_2 and overlap between the b_1 orbital of TiH_2 and the π*-nonbonding b_1 orbital of C_2H_2. A schematic representation of the orbital interactions is provided in Figure 5 where the a_1 and b_1 orbitals of Ti are d_{z^2} and d_{xz} atomic orbitals, respectively. The reaction energy for our model process ($TiH_2 + C_2H_2$) with the B3LYP/TZV is -48.4 kcal/mol, whereas the reaction energy for the matrix isolation based process of a bare $Ti(^3F)$ atom reacting with C_2H_4 with the same method and basis is -10.7 kcal/mol.[32] A similar description can be made for the five-member ring $H_2TiC_4H_4$ and will not be presented in this work. The energy of reaction, however, for butadiene with a bare $Ti(^3F)$ atom to yield titanacyclopentadiene with the B3LYP/TZV is -76.8 kcal/mol. This value is based on the difference in the computed energy of the product and reactants and does not consider zero-point energy corrections.

Bonding in the four-membered ring, $HTiC_3H_3$, can be considered in many ways. Perhaps the simplest pathway is to consider a HTi ($^4B_1$) fragment inserting into a planar-C_{2v} C_3H_3 ($^4B_1$). With this simple picture we can construct an energy level diagram where the singly occupied symmetry orbitals b_2, a_1, and a_2 from each fragment pair up. This idealized picture could also be applied to a CH fragment to yield cyclobutadiene and SiH fragment to yield silacyclobutadiene. The ground-state geometry of these latter two molecules is of D_{2h} and C_s symmetry, respectively, and consists of localized double bonds. The delocalization in the Ti-bearing molecule is due to the availability of the Ti d_{xy} atomic orbital to the a_2 molecular orbital as shown in Figure 6. The overlap between the HTi d orbital and the C_3H_3 π-system allows electron delocalization and constitutes a molecule with aromatic character. Though currently of interest,[33] we do not wish to argue the nature of aromaticity here but present a system that is apparently aromatic. The energy of reaction of allene with a bare $Ti(^3F)$ atom to yield titanacyclobutadiene with the B3LYP/TZV is -32.7 kcal/mol. As with titanacyclopentadiene, zero-point energy corrections are not included.

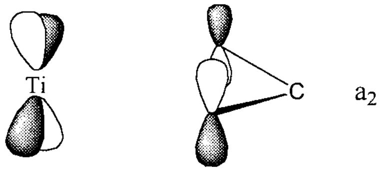

Figure 6. Schematics of the a_2 bonding orbitals of TiH and C_3H_3.

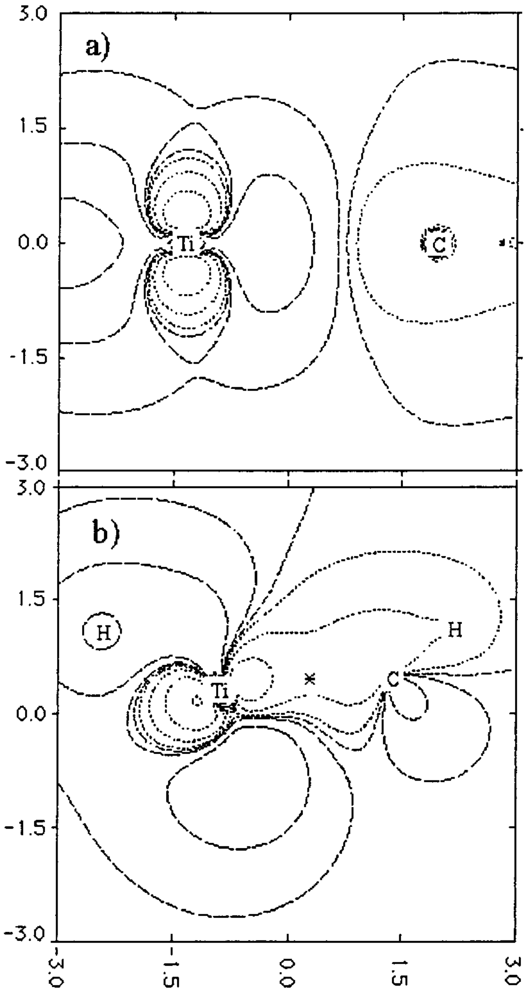

Figure 7. (a) Contour diagram of the HOMO orbital of the planar conformer of $HTiC_5H_5$. The chosen plane is perpendicular to the molecular plane and exhibits the Ti atom and the para-C atom. (b) Contour diagram of the same orbital in the boat-shaped conformation of $HTiC_5H_5$. The "*" indicates a bond critical point between Ti and C.

Titanabenzene is isovalent to benzene and silabenzene. A number of studies on silabenzene[34] have been performed and indicate that the geometry of the molecule is planar. In our study the first three molecules are planar whereas the ground state of titanabenzene is calculated to have a boat-shaped or Dewar conformation. This is not consistent with benzene or silabenzene. So why is this six-member ring not planar? From Mulliken charges, the Ti atom is positive and is therefore polarizing electrons from the π-network of the ring, similar to placing a positive charge in the molecular plane of benzene. From the NRT results in Figure 2, the double bonds of both the five- and six-member rings are localized to the C−C bonds adjacent to the Ti−C bonds. In the case of the six-member ring, the first resonance structure suggests a lone pair of electrons on the para-C atom and the second structure denotes a bond connecting the para-C atom with the Ti atom. Expecting less interaction between Ti and the para-C atom, NRT of the planar $HTiC_5H_5$ decreases the resonance contribution by 1.4% and gives a bond order of 0.13. The para-C atom "out-of-plane" p orbital is thus liberated to interact with an available d orbital on Ti. The folding of the molecule from planar to boat form reduces the Mulliken charge on the Ti atom from $+0.90e$ to $+0.75e$ where the electrons are coming from the para-C atom. The bonding between the para-C atom and the Ti atom therefore consists of a bent σ-bond across the ring. A cross-sectional contour plot of the orbital of interest in the planar and Dewar structure is shown in parts a and b of Figure 7, respectively. Figure 7a is a contour diagram of the nonbonding valence molecular orbital on the Ti and the para-C atom in the planar conformation. Figure 7b is a contour diagram of the same orbital in the Dewar conformation, revealing the overlap of orbitals to form the bent σ-bond.

Conclusion

In summary of the present work, $H_2TiC_2H_2$, $HTiC_3H_3$, and $H_2TiC_4H_4$ are planar molecules of C_{2v} symmetry. The six-member ring has a boat-shaped structure caused by σ-bonding between the para-C atom and a Ti d orbital. According to NRT results, double bonds are primarily localized away from the Ti center, with the exception of $HTiC_3H_3$. The ground singlet state of titanacyclobutadiene shows aromatic character, which is contradictory to cyclobutadiene and silacyclobutadiene. The triplet state of titancyclobutadiene is calculated to be 14.4 kcal/mol above the singlet with the B3LYP functional. Bader analysis of critical points shows considerable bond strain in the Ti−C bonds and very little bond strain in the C−C bonds.

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Supporting Information Available: Four tables listing results of various methods for $H_2TiC_4H_4$, $HTiC_3H_3$, and $HTiC_5H_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

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