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Structures and Bonding of the Sandwich Complexes $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ ($E = CH, N, P, As, Sb$): A Theoretical Study[†]

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Quantum chemical calculations using gradient-corrected DFT at the BP86/TZ2P level of the compounds $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ ($E = CH, N, P, As, Sb$) are reported. The nature of the metal–ligand bonding has been analyzed with an energy decomposition method, and the results are compared with $[Fe(\eta^5\text{-}E_5)_2]$. The bonding in both series of complexes is more covalent than electrostatic. The energy decomposition analysis shows that the dominant orbital interactions in the negatively charged titanium species come from the (e_2') Ti $\rightarrow$ $[(\eta^5\text{-}E_5)_2]^{2-}$ back-donation (δ bonding) while the covalent bonding in the iron complexes come mainly from (e_1'') $(Cp^-)_2 \rightarrow Fe^{2+}$ donation (π bonding). The nature of the metal–ligand interactions does not change very much for different ligands cyc-E_5 within the two series of compounds. The calculated bond dissociation energies for breaking one metal–ligand bond of the molecules $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ shows for E the order P > As > Sb ≫ N ≫ CH. The central message of this work is that the complexes $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ are δ bonded molecules.

Introduction

The recent synthesis and X-ray structure analysis of the first homoleptic sandwich complex with a pentaphospholyl ligand, $[Ti(\eta^5\text{-}P_5)_2]^{2-}$, which was reported by Urnéžius et al.,[1] has given a new impetus to the versatile chemistry of metallocenes.[2] Transition metal (TM) complexes with one η^5-bonded group-15 ligand cyclo-E_5 ($E = P, As$) are known since the pioneering work of Scherer,[3] but all attempts to isolate homoleptic species $[TM(\eta^5\text{-}E_5)_2]$ were not successful prior to this work. Recently, theoretical studies were published by us which focused on metallocenes with π-heterocyclic ligands.[4,5] The isoelectronic nitrogen analogue of ferrocene, i.e., $[Fe(\eta^5\text{-}N_5)_2]$, was predicted to be an energy-rich but kinetically stable compound.[4] This work was recently extended to the heavier group-15 analogues $[Fe(\eta^5\text{-}E_5)_2]$ and $[FeCp(\eta^5\text{-}E_5)]$ ($E = P, As, Sb$).[5] It was shown that the Fe−(η^5-E_5) bonding energies have the largest values when $E = P$ but also the other π-heterocyclic complexes were predicted to be stable compounds. A bonding analysis using an energy partitioning scheme was also carried out. The calculated data were used to quantify the metal−ligand interactions in terms of covalent and electrostatic bonding and to determine the relative strength of the different orbital interactions.[4,5]

In this paper we report about quantum chemical DFT calculations of the title compounds $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ ($E = CH, N, P, As, Sb$). The work is a continuation of our systematic studies of transition metal complexes with π-heterocyclic[4,5] and other ligands.[6] The goal of this project is to provide quantitative information about the nature of the chemical bond using a rigorously defined quantum chemical partitioning of the interaction energy. The results which we obtained so far in the field of transition metal[4−6] and main group[7]

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complexes have recently been summarized in a review.[8] The focus of the present work is the strength and the nature of the Ti−(η^5-E_5) interactions. We were intrigued by the results of the orbital correlation analysis of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ presented by Urnėžius et al.[1] The authors suggest that there are critical differences between the nature of the bonding of the organic (Cp) versus inorganic (cyclo-P_5) metal−ligand bonding. The ligand π orbitals of cyclo-P_5 were found to be lower in energy than those of the Cp ligand. It was concluded that "Cp serves more as a donor and P_5 as an acceptor".[1] Our recent theoretical studies of ferrocene and the inorganic analogues $[Fe(\eta^5\text{-}E_5)_2]$ and $[FeCp(\eta^5\text{-}E_5)]$ have shown, however, that the Fe−(η^5-E_5) and Fe−Cp interactions are very similar to each other.[4,5] It will be interesting to see if the suggestion of Urnėžius et al.,[1] which was based on a qualitative orbital interaction diagram, is supported by a quantitative analysis of the bonding energy. Therefore, we calculated also $[TiCp_2]^{2-}$ and the other members of the series $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ (E = N, Sb, As) and we compared the results with the data for ferrocene and $[Fe(\eta^5\text{-}E_5)_2]$. Another topic which we address in this work is the strength of the electrostatic attraction in the complexes. Urnėžius et al. speculated that "Our success in obtaining such a complex in the form of a charged species suggests that electrostatics may also play an important role in the stabilization of monomers containing $[(P_5)_2M]^z$ units".[1] We shall see that the electrostatic effects play only an indirect role for the strength of the metal−ligand bonding by raising the energy levels of the orbitals.

Methods

The geometries have been optimized at the gradient-corrected DFT level using the exchange functional of Becke[9] and the correlation functional of Perdew[10] (BP86) in conjunction with uncontracted Slater-type orbitals (STOs) as basis functions.[11] Relativistic effects have been considered by the zero-order regular approximation (ZORA).[12] The basis sets for titanium and iron have triple-ζ quality augmented by one set of 6p functions. Triple-ζ basis sets augmented by two sets of d-type polarization functions have been used for the main group elements. The $(n-1)s^2$, $(n-1)p^6$, and $(n-2)d^{10}$ core electrons of the main group elements and the $(1s2s2p)^{10}$ core electrons of Ti and Fe were treated by the frozen-core approximation.[13a] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[13b] We calculated the vibrational frequencies of the optimized structures to see if they are minima on the potential energy surface (PES). All calculations have been carried out with the program package ADF.[13,14]

The metal−ligand bonding interactions have been analyzed with the energy decomposition scheme of the program ADF,[14,15] which is based on the EDA method of Morokuma[16] and the similar ETS method of Ziegler.[17] For the energy partitioning analysis the interaction energy ΔE_{int} of $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ with D_{5h} symmetry was calculated and decomposed for the bonding between the metal atom with the electron configuration $Ti(e_2')^4$ and the ligand fragment $[(cyc\text{-}E_5)_2]^{2-}$. The energy partitiong analysis was also performed using the metal fragment $TM(\eta^5\text{-}E_5)^-$ and the ligand $(\eta^5\text{-}E_5)^-$ in the $^1A_1'$ and $^1A_1$ ground state, respectively. The instanteneous interaction energy ΔE_{int} can be divided into three components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (1)$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments which are calculated with a frozen electron density distribution in the geometry of the complex. It can be considered as an estimate of the *electrostatic* contribution to the bonding interactions. The second term in eq 1, ΔE_{Pauli}, gives the repulsive four-electron interactions between occupied orbitals. The last term gives the stabilizing orbital interactions, ΔE_{orb}, which can be considered as an estimate of the *covalent* contributions to the bonding. Thus, the ratio $\Delta E_{elstat}/\Delta E_{orb}$ indicates the electrostatic/covalent character of the bond. The covalent term can be partitioned further into contributions by the orbitals which belong to different irreducible representations of the interacting system. This makes it possible to calculate e.g. the contributions of σ and π bonding to a covalent multiple bond.[8] Technical details about the ETS method can be found in the literature.[15]

The bond dissociation energy (BDE) ΔE_e is given by the sum of ΔE_{int} and the fragment preparation energy ΔE_{prep}:

$$\Delta E_e = \Delta E_{prep} + \Delta E_{int} \qquad (2)$$

ΔE_{prep} is the energy which is necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state which they have in the optimized structure.

Geometries

We optimized the geometries of the complexes $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ (E = CH, N, P, As, Sb) in the electronic singlet state with staggered (D_{5d}) and eclipsed (D_{5h}) conformations of the cyclic ligands. The molecules have also been optimized in the electronic triplet state without symmetry constraints using structures with staggered and eclipsed conformations of the ligands as starting geometries. Table 1 gives the

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Table 1. Calculated Bond Lengths (Å) and Relative Energies (kcal/mol) of $[Ti(E_5)_2]^{2-}$ Complexes and Fragments at BP86/TZ2P

molecule	symmetry	state	Ti−E	Ti−X[a]	E−E	i[b]	E_{rel}
$Ti(Cp)_2^{2-}$	D_{5h}	$^1A_1'$	2.280	1.912	1.460	c	0.0
$Ti(Cp)_2^{2-}$	D_{5d}	$^1A_{1g}$	2.287	1.921	1.459	c	1.9
$Ti(Cp)_2^{2-}$	D_{5d}	$^3A_{1g}$	2.350	2.018	1.427	c	−27.0
$Ti(N_5)_2^{2-}$	D_{5h}	$^1A_1'$	2.145	1.781	1.405	0	0.0
$Ti(N_5)_2^{2-}$	D_{5d}	$^1A_{1g}$	2.150	1.788	1.404	1	0.9
$Ti(N_5)_2^{2-}$	C_{2v}	$^3A_1$	2.225		1.365	0	24.9
			2.279		1.393		
			2.313		1.418		
$Ti(P_5)_2^{2-}$	D_{5h}	$^1A_1'$	2.577	1.775	2.196	0	0.0
$Ti(P_5)_2^{2-}$	D_{5d}	$^1A_{1g}$	2.620	1.847	2.185	1	5.2
$Ti(P_5)_2^{2-}$	C_{2v}	$^3A_1$	2.720		2.168	0	46.8
			2.641		2.197		
			2.773		2.217		
$Ti(As_5)_2^{2-}$	D_{5h}	$^1A_1'$	2.802	1.878	2.445	0	0.0
$Ti(As_5)_2^{2-}$	D_{5d}	$^1A_{1g}$	2.774	1.834	2.447	1	7.6
$Ti(Sb_5)_2^{2-}$	D_{5h}	$^1A_1'$	3.089	1.929	2.837	0	0.0
$Ti(Sb_5)_2^{2-}$	D_{5d}	$^1A_{1g}$	3.087	1.926	2.837	1	9.0
$Ti(Cp)^-$	C_{5v}	$^1A_1$	2.333	1.991	1.429	0	
$Ti(N_5)^-$	C_{5v}	$^1A_1$	2.004	1.894	1.376	0	
$Ti(P_5)^-$	C_{5v}	$^1A_1$	2.386	1.414	2.259	0	
$Ti(As_5)^-$	C_{5v}	$^1A_1$	2.524	1.316	2.532	0	
$Ti(Sb_5)^-$	C_{5v}	$^1A_1$	2.765	1.185	2.937	0	

[a] X is the midpoint of the E_5 ring. [b] Number of imaginary frequencies. [c] SCF did not converge.

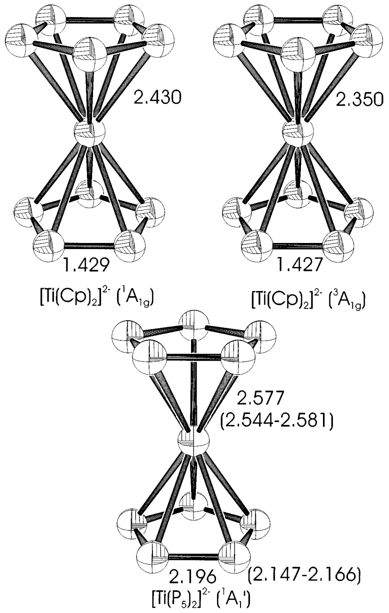

Figure 1. Calculated equilibrium geometries at BP86/TZ2P of the energetically lowest lying singlet and triplet species of $[Ti(Cp)_2]^{2-}$ and the singlet state of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$. Interatomic distances are given in Å.

calculated bond lengths. The equilibrium geometries of the energetically lowest lying singlet and triplet species of $[Ti(Cp)_2]^{2-}$ and the singlet state of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ are shown in Figure 1.

The calculation of the vibrational frequencies showed that the titanium metallocene complexes $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ in the electronic singlet state which have an eclipsed (D_{5h}) form are energy minima while the staggered (D_{5d}) forms are transition states ($i = 1$). This is in agreement with the X-ray structure analysis of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$, which gave a geometry where the two P_5 rings are eclipsed.[1] The Cp rings of ferrocene have also an eclipsed conformation while the group-15 heterocyclic analogues $[Fe(\eta^5\text{-}E_5)_2]$ (E = N, P, As, Sb) are predicted to have a staggered equilibrium geometry.[4,5] Figure 1 shows that the calculated bond lengths of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ are in very good agreement with the experimental values. The energy difference between the staggered and eclipsed conformations of $[Fe(\eta^5\text{-}E_5)_2]$ increases when the heteroatom E becomes heavier N < P < As < Sb (Table 1). The calculation of the vibrational frequencies of the parent metallocene complex $[Ti(Cp)_2]^{2-}$ using numerical second derivatives failed because of SCF convergence problems. This may be caused by the fact that the triplet state of $[Ti(Cp)_2]^{2-}$ is lower in energy than the singlet state. Table 1 shows that the triplet state with a staggered conformation of the Cp ligands is 27.0 kcal/mol below the lowest lying singlet state. This result is in agreement with the experimental observation that $[Cr(Cp)_2]$ which is isoelectronic with $[Ti(Cp)_2]^{2-}$ has a triplet electronic ground state.[19] The geometry optimization of triplet $[Ti(Cp)_2]^{2-}$ was carried out without symmetry constraints, and therefore, we think that the optimized structure is a minimum on the potential energy surface. The triplet states of the heteroanalogues $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ (E = N, P) are higher in energy than the singlet states (Table 1). The triplet states of $[Ti(\eta^5\text{-}As_5)_2]^{2-}$ and $[Ti(\eta^5\text{-}Sb_5)_2]^{2-}$ are probably also higher in energy than the singlet states and have therefore not been calculated by us.

Bonding Analysis

Figure 2 shows a qualitative orbital correlation diagram of the interactions between a d^4 and d^6 metal atom TM and a (cyc-E_5)$_2$ ligand in D_{5d} symmetry yielding the complexes [TM(cyc-E_5)$_2$] with 16 and 18 electrons, respectively. This is the standard MO correlation diagram for ferrocene which is discussed in many textbooks.[20] The difference between the correlation diagrams of a d^4 and d^6 metal atom is that the d_{z^2} (a_1') AO in the latter atom is occupied while it is

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(18) See Figure 2 in ref 1.

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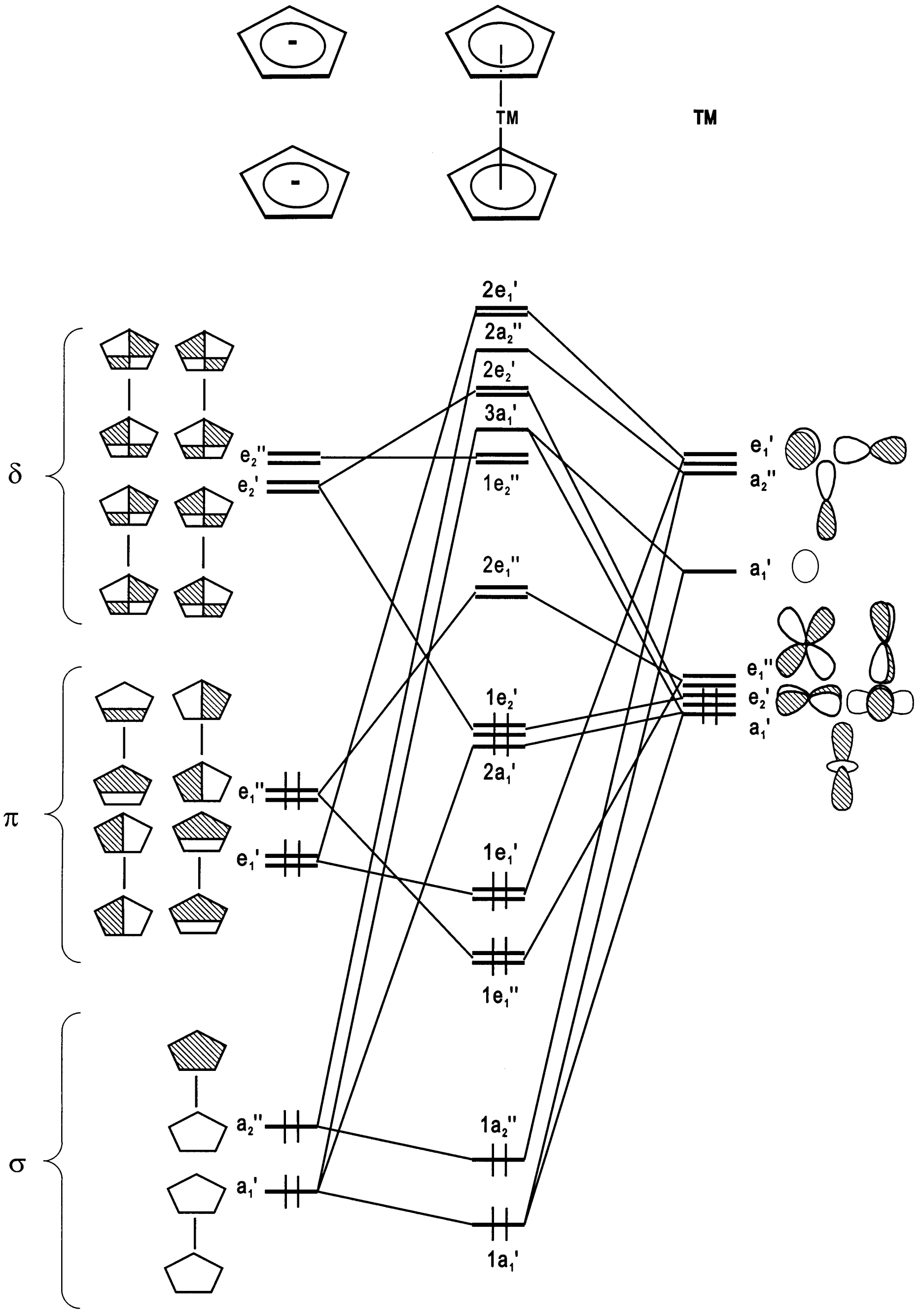

Figure 2. Qualitative orbital correlation diagram of the interactions between a d^4 and d^6 metal atom TM and a (cyc-E_5)$_2$$^{2-}$ ligand in D_{5h} symmetry. The d_{z^2}(a_1') AO of TM(d^4) and, thus, the highest lying $2a_1'$ MO of a 16 electron complex [TM(η^5-E_5)] are empty. The symmetry assignments σ, π, and δ refer to the metal−ligand bonds in the complex.

empty in the former atom. This means that the $2a_1'$ MO of [TM(cyc-E_5)$_2$] is empty in the 16 electron complex.

There is general agreement that the most important orbital interactions in ferrocene arise from the (e_1'') (Cp^-)$_2$ → Fe^{2+} donation.[21] Our quantitative analysis of the metal−ligand bonding in [$FeCp_2$] and [Fe(η^5-N_5)$_2$] with D_{5d} symmetry showed that the e_{1g} donation, which is equivalent to e_1'' donation in D_{5h} symmetry, contributes with ~65% to the total orbital interactions.[4,21] In the paper by Urnėžius et al.[1] it was argued that the π orbitals of cyc-P_5 are energetically lower lying than those of Cp and, therefore, the strongest metal−ligand interactions in the 16 electron complex [Ti(η^5-P_5)$_2$]$^{2-}$ would take place between the e_2' orbital set of the metal and the ligand (energy matching).[18] This means that the strongest donor−acceptor interactions in the latter complex should come from the (e_2') Ti → [(η^5-P_5)$_2$]$^{2-}$ back-donation. Since e_2' symmetry is equivalent to δ bonding and e_1'' symmetry is equivalent to π bonding, the above conclusion would mean that [Ti(η^5-P_5)$_2$]$^{2-}$ is a δ bonded molecule and ferrocene is a π bonded molecule.

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Table 2. Energy Decomposition Analysis of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{E}_5)_2]^{2-}$ in D_{5h} Symmetry Using the Fragments $\mathrm{Ti(e_2{}')^4}$ and $[(\text{cyc-}\mathrm{E}_5)_2]^{2-}$ with Energy Values in kcal/mol

term	E = CH	E = N	E = P	E = As	E = Sb
ΔE_{int}	−238.7	−255.4	−359.7	−349.5	−341.3
ΔE_{Pauli}	204.9	257.0	334.7	240.8	194.7
ΔE_{elstat}[a]	−141.9 (32.0)	−112.2 (21.9)	−272.8 (39.3)	−227.7 (38.6)	−204.3 (38.7)
ΔE_{orb}[a]	−301.6 (68.0)	−400.1 (78.1)	−421.6 (60.7)	−362.7 (61.4)	−331.7 (61.3)
$A_1{}'$[b] (σ)	−10.2 (3.4)	−17.7 (4.4)	−10.1 (2.4)	−8.7 (61.4)	−14.9 (61.3)
$A_2{}'$	0.00	0.00	0.00	0.00	0.00
$E_1{}'$[b] (π)	−4.7 (1.6)	−4.8 (1.2)	−3.7 (0.9)	−3.6 (1.0)	−5.2 (1.6)
$E_2{}'$[b] (δ)	−231.7 (76.8)	−315.0 (78.7)	−358.1 (84.9)	−320.2 (88.3)	−286.9 (86.5)
$A_1{}''$	0.00	0.00	0.00	0.00	0.00
$A_2{}''$[b] (σ)	−3.1 (1.0)	−3.6 (0.9)	−3.0 (0.7)	−3.2 (0.9)	−6.2 (1.9)
$E_1{}''$[b] (π)	−50.6 (16.8)	−56.1 (14.0)	−45.1 (10.7)	−25.9 (7.1)	−18.1 (5.5)
$E_2{}''$[b] (δ)	−1.4 (0.5)	−2.9 (0.7)	−1.6 (0.4)	−1.1 (0.3)	−0.4 (0.1)
s	−13.3 (4.4)	−21.3 (5.3)	−13.1 (3.1)	−11.9 (3.3)	−21.1 (6.4)
p	−55.3 (18.4)	−60.9 (15.2)	−48.8 (11.6)	−29.5 (8.1)	−23.3 (7.1)
d	−233.1(77.3%)	−317.9 (79.4)	−359.7 (85.3)	−321.3 (88.6)	−287.3 (86.6)

[a] The value in parentheses gives the percentage contribution to the total attractive interactions. [b] The value in parentheses gives the percentage contribution to the total orbital interactions.

Table 2 gives the results of the energy decomposition analysis of the complexes $[\mathrm{Ti}(\eta^5\text{-}\mathrm{E}_5)_2]^{2-}$ (E = CH, N, P, Sb, As) using symmetry-adapted orbitals from the D_{5h} point group. The interacting fragments are $\mathrm{Ti(e_2{}')^4}$ and $[(\text{cyc-}\mathrm{E}_5)_2]^{2-}$. The same fragments were chosen by Urnéžius et al.[1] The calculated interaction energies between the frozen fragments have large negative values which indicate strong attraction. Note that the largest value is calculated for E = P ($\Delta E_{\text{int}} = -359.7$ kcal/ mol) and that the lowest values are calculated for E = CH ($\Delta E_{\text{int}} = -238.7$ kcal/mol) and E = N ($\Delta E_{\text{int}} = -255.4$ kcal/mol). This indicates that the carbon and nitrogen complexes have the weakest metal−ligand bonds, while the bonds in the heavier heterometallocenes $[\mathrm{Ti}(\eta^5\mathrm{As}_5)_2]^{2-}$ and $[\mathrm{Ti}(\eta^5\text{-}\mathrm{Sb}_5)_2]^{2-}$ are only slightly weaker than in the phosphorus complex. The metal−ligand bonding between $\mathrm{Ti(e_2{}')^4}$ and $[(\text{cyc-}\mathrm{E}_5)_2]^{2-}$ is largely covalent. The calculated data suggest that the ΔE_{orb} term contributes between 60.7% (E = P) and 78.1% (E = N) to the attractive interactions. The relatively low degree of electrostatic attraction in $[\mathrm{Ti}(\eta^5\mathrm{P}_5)_2]^{2-}$ is at variance with the suggestion of Urnéžius et al.[1] that electrostatics may play an important role in the stabilization of the complex. We want to point out that the comparatively weak bonding in $[\mathrm{Ti}(\eta^5\text{-}\mathrm{N}_5)_2]^{2-}$ comes from the relatively small electrostatic term ($\Delta E_{\text{elstat}} = -112.2$ kcal/mol) while the orbital interactions are rather strong ($\Delta E_{\text{orb}} = -400.1$ kcal/mol).

The most important result given in Table 2 concerns the contributions of the orbital interactions which have different symmetry to the ΔE_{orb} term. The calculated data support the statement of Urnéžius et al.[1] that the strongest metal−ligand orbital interactions in $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ come from the $\mathrm{e_2{}'}$ orbitals. The energy analysis suggests that the $(\mathrm{e_2{}'})$ Ti → $[(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ back-donation contributes 84.9% to the ΔE_{orb} term. The $\mathrm{e_1{}''}$ orbitals, which were found to be the most important contributors to the orbital interactions in ferrocene,[4,21] contribute only 10.7% in in $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ (Table 2). It follows that the most important metal−ligand bond in $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ is indeed a δ bond. However, the energy analysis shows that the $\mathrm{e_2{}'}$ orbitals are also the most important orbitals for the ΔE_{orb} term of in $[\mathrm{Ti(Cp)_2}]^{2-}$![22] The orbital interactions of the $\mathrm{e_2{}'}$ orbital give 76.8% of the total covalent interactions in the latter complex. This is at variance with the suggestion of Urnéžius et al.,[1] who concluded that the difference between ferrocene and $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ is the nature of the ligand. The results in Table 2 indicate that the nature of the metal−ligand bonding in $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ is not very different from that in $[\mathrm{Ti(Cp)_2}]^{2-}$. The data suggest that the different orbital interactions in $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ and $[\mathrm{Fe(Cp)_2}]$ are rather caused by the nature of the metal and/or the charge of the complex.

To prove this hypothesis we compared the results of the energy analysis of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{E}_5)_2]^{2-}$ with the data of $[\mathrm{Fe}(\eta^5\text{-}\mathrm{E}_5)_2]$ (E = CH, N, P, Sb, As) which have been published by

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[21] Most textbooks discuss the orbital correlation diagram of metallocenes $[\mathrm{TM(Cp_2)}]$ using orbitals which belong to the D_{5d} group (staggered conformation) although the parent compound ferrocene has a D_{5h} equilibrium geometry. The two conformations are very close in energy, and the orbital correlation diagrams are very similar except that the symmetry labels of the orbitals are different. For the purpose of comparing the results of this work with our previous study,[4] we give the pairs of orbitals in D_{5d} and D_{5h} symmetry which correspond to each other: $\mathrm{a_{1g}} \leftrightarrow \mathrm{a_1{}'}$; $\mathrm{a_{2u}} \leftrightarrow \mathrm{a_2{}''}$; $\mathrm{e_{1g}} \leftrightarrow \mathrm{e_1{}''}$; $\mathrm{e_{1u}} \leftrightarrow \mathrm{e_1{}'}$; $\mathrm{e_{2g}} \leftrightarrow \mathrm{e_2{}'}$; $\mathrm{e_{2u}} \leftrightarrow \mathrm{e_2{}''}$. The energy decomposition analysis of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{E}_5)_2]^{2-}$ and $[\mathrm{Fe}(\eta^5\text{-}\mathrm{E}_5)_2]$ in D_{5h} and D_{5d} symmetry give very similar results for the contributions of the energy terms ΔE_{elstat}, ΔE_{Pauli}, and ΔE_{orb} and for the contributions of the orbitals having a different symmetry in the latter term.

[22] One reviewer argued that it would be invalid to assert that $\mathrm{Cp^-}$ and $\mathrm{P_5{}^-}$ engage in equivalent δ bonding to titanium when $[\mathrm{Ti(Cp)_2}]^{2-}$ has a triplet ground state while $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ is a singlet. We want to emphasize that the goal of the analysis is to elucidate the difference of the bonding behavior between the two ligands when they bind to a metal which has the same electron configuration. The analysis of the metal−ligand bonding in triplet $(^3\mathrm{A_1{}'})$ $[\mathrm{Ti(Cp)_2}]^{2-}$ should be carried out with the fragments $(\mathrm{Cp^-})_2$ and Ti with the electron configuration $\mathrm{Ti(a_1{}')^2(e_2{}')^{\alpha\alpha}}$. A comparison of the results with the analysis of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$ given in Table 2 would would mean that the bonding to a metal which has different electron configurations is considered. This is not meaningful for the purpose of comparing the intrinsic differences between the two ligands. We want to point out that the analysis of the bonding situation in $[\mathrm{Fe(Cp)_2}]$ and $[\mathrm{Fe}(\eta^5\text{-}\mathrm{P}_5)_2]$ which both have a singlet ground state showed also that the two ligands have similar bonding properties. A result, which is interesting in the context of the question which was raised by the reviewer, has been reported by us in ref 6f. There it is shown that the preference of ferrocene for π bonding is also found when the EPA is carried out with the neutral fragments Fe and $\mathrm{Cp_2}$ in the triplet states.

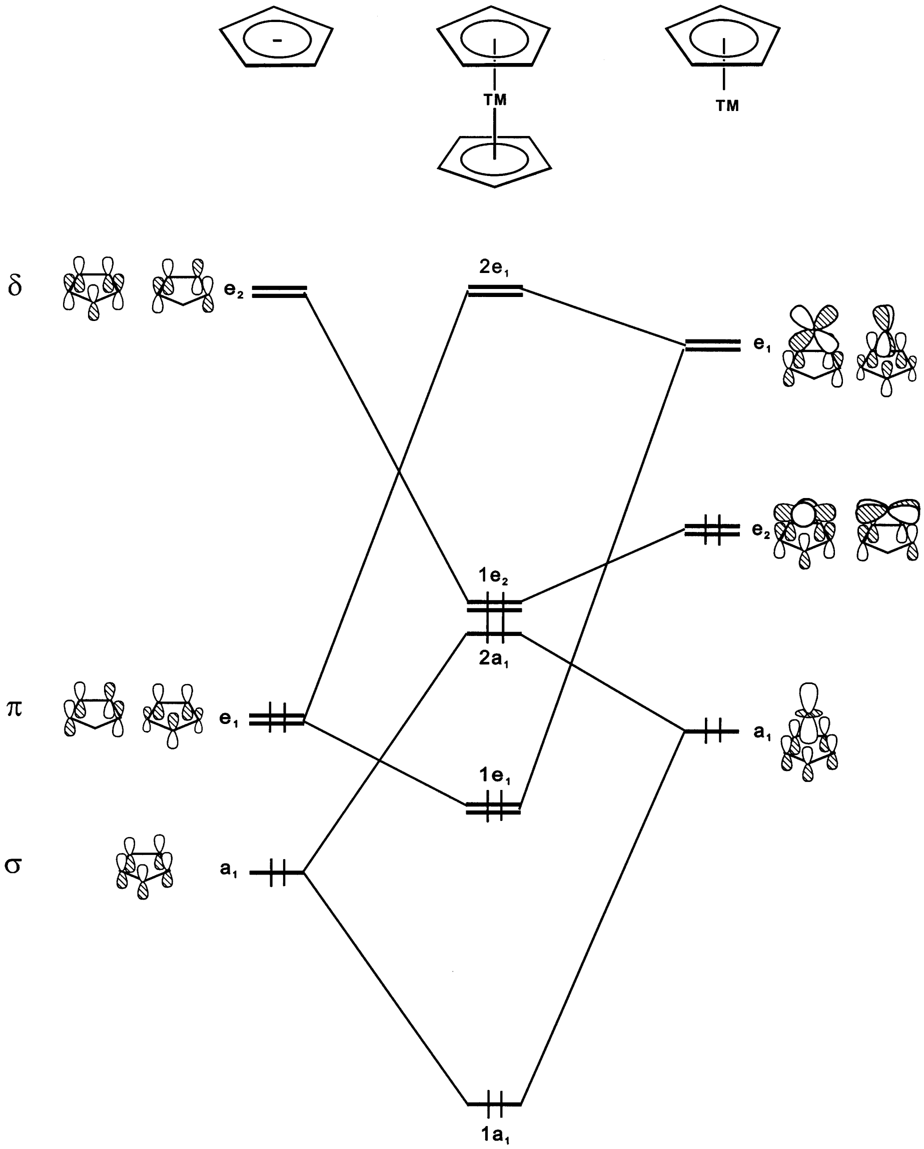

Figure 3. Qualitative orbital correlation diagram for the interactions between cyclo-E_5^- and $[TM(\eta^5\text{-}E_5)]$ in C_{5v} symmetry. Only those orbitals which are relevant for the metal−ligand bonding are shown. The a_1 MO of $[TM(\eta^5\text{-}E_5)]$ and, thus, the $2a_1$ MO of 16 electron complexes $[TM(\eta^5\text{-}E_5)_2]$ are empty. The symmetry assignments σ, π, and δ refer to the metal−ligand bonds in the complex.

us before.[5] The bonding analysis of the neutral iron complexes was carried out in terms of interactions between the fragments cyclo-E_5^- and $[Fe(\eta^5\text{-}E_5)]^+$. A qualitative orbital correlation diagram for the interactions between cyclo-E_5^- and $[TM(\eta^5\text{-}E_5)]$ which shows only the orbitals which are relevant for the metal−ligand bonding is given in Figure 3. The fragment $[TM(\eta^5\text{-}E_5)]$ has C_{5v} symmetry, which means that there can only be orbitals which have a_1, a_2, e_1, and e_2 symmetry. There are no relevant valence orbitals in the molecules which have a_2 symmetry. The σ interactions of the a_1 orbitals should not lead to a significant stabilization because the a_1 ligand orbital is much lower in energy than the e_1 orbital. The crucial difference between the ΔE_{orb} term of the neutral iron complexes $[Fe(\eta^5\text{-}E_5)_2]$ and the negatively charged titanium species $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ is the strength of the e_1 (π) and e_2 (δ) orbital interactions. The former interactions should be strong when the orbitals of $[TM(\eta^5\text{-}E_5)]$ are low in energy yielding better energy matching of the e_1 orbitals while the latter interactions should become stronger when the orbitals of the metal fragment are energetically high lying. Table 3 gives the results of the energy decomposition analysis of the two series of compounds.

The calculated orbital contributions to the ΔE_{orb} term support the qualitative arguments. The largest stabilization energy of the iron complexes which have a positively charged $[Fe(\eta^5\text{-}E_5)]^+$ metal fragment with low-lying orbitals comes always from the e_1 orbitals which contribute between 63.8% and 69.4% to the total covalent bonding energy. There is a continuous increase of the relative $\Delta E(e_1)$ values from $[Fe(\eta^5\text{-}Cp)_2]$ to $[Fe(\eta^5\text{-}Sb_5)_2]$, but the differences are not very large. We want to point out that the nature of the metal−ligand bonding in $[Fe(\eta^5\text{-}E_5)_2]$ changes very little for different E species. The calculations suggest that the $(\eta^5\text{-}E_5)-[Fe(\eta^5\text{-}E_5)]^+$ interactions have a slightly higher electrostatic

Table 3. Energy Decomposition Analysis of $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ and $[Fe(\eta^5\text{-}E_5)_2]$ in C_{5v} Symmetry Using the Fragments $[Ti(\eta^5\text{-}E_5)]^-/(\eta^5\text{-}E_5)^-$ and $[Fe(\eta^5\text{-}E_5)]^+/(\eta^5\text{-}E_5)^-$ with Energy Values in kcal/mol

	Ti					Fe				
Term	E = CH	E = N	E = P	E = As	E = Sb	E = CH	E = N	E = P	E = As	E = Sb
ΔE_{int}	−30.5	−27.5	−39.5	−33.3	−29.4	−237.6	−198.0	−199.5	−183.8	−165.1
ΔE_{Pauli}	116.7	132.7	178.5	198.2	195.1	172.4	149.7	190.2	221.6	220.8
$\Delta E_{elstat}{}^a$	−22.4 (15.2)	−3.7 (2.3)	−63.0 (28.9)	−84.5 (36.5)	−87.4 (38.9)	−238.5 (58.2)	−184.3 (53.0)	−207.3 (53.2)	−223.1 (55.0)	−205.1 (53.1)
$\Delta E_{orb}{}^a$	−124.8 (84.8)	−156.5 (97.7)	−154.9 (71.1)	−147.0 (63.5)	−137.2 (61.1)	−171.5 (41.8)	−163.4 (47.0)	−182.5 (46.8)	−182.3 (45.0)	−180.9 (46.9)
$A_1{}^b$ (σ)	−8.5 (6.8)	−12.7 (8.1)	−16.5 (10.7)	−18.9 (12.9)	−25.5 (18.6)	−25.0 (14.6)	−22.4 (13.7)	−28.1 (15.4)	−29.1 (16.0)	−35.7 (19.7)
A_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$E_1{}^b$ (π)	−30.6 (24.5)	−34.8 (22.3)	−48.8 (31.5)	−49.6 (33.7)	−52.0 (37.9)	−109.3 (63.8)	−106.1 (65.0)	−120.7 (66.1)	−123.7 (67.8)	−125.6 (69.4)
$E_2{}^b$ (δ)	−85.7 (68.7)	−109.0 (69.6)	−89.6 (57.8)	−78.5 (53.4)	−59.6 (43.5)	−37.1 (21.6)	−34.9 (21.3)	−33.7 (18.5)	29.6 (16.2)	−19.6 (10.8)
ΔE_{prep}	83.0	44.4	27.4	27.5	30.5	2.8	13.1	28.0	23.3	46.3
ΔE (=D_e)	52.5	16.9	−12.1	−5.8	1.1	−234.8	−184.9	−171.5	−160.5	−118.8

[a] The value in parentheses gives the percentage contribution to the total attractive interactions. [b] The value in parentheses gives the percentage contribution to the total orbital interactions.

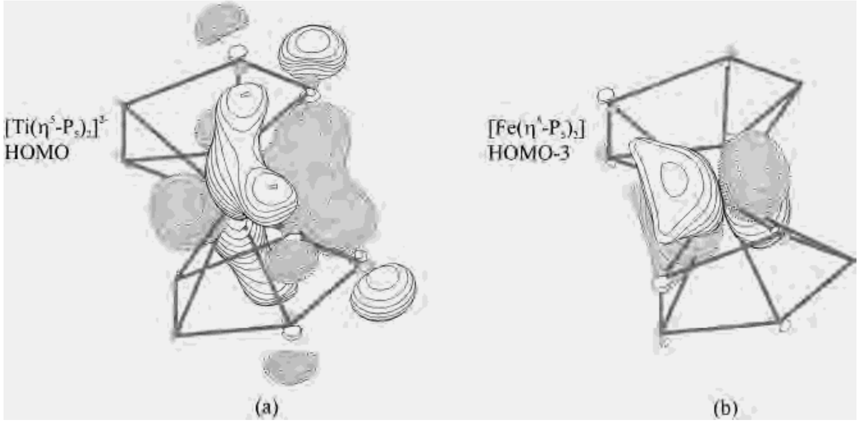

Figure 4. Plot of the highest lying occupied e_2' orbitals of (D_{5h}) $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ and $[Fe(\eta^5\text{-}P_5)_2]$: (a) HOMO of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$; (b) HOMO-3 of $[Fe(\eta^5\text{-}P_5)_2]$.

(53.2−58.2%) than covalent character. The lowest degree of covalent bonding is calculated for ferrocene.

The energy decomposition results for the titanium complexes $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ differ significantly from those of $[Fe(\eta^5\text{-}E_5)_2]$. Table 3 shows that the covalent bonding term ΔE_{orb} is much larger than ΔE_{elstat} for all titanium complexes. In the nitrogen complex $[Ti(\eta^5\text{-}N_5)_2]^{2-}$, the calculations indicate that the $(\eta^5\text{-}N_5)^-$−$[Ti(\eta^5\text{-}N_5)]^-$ interactions are nearly exclusively covalent. Thus, the electrostatic attractions play a larger role for the stabilization of the neutral complexes $[Fe(\eta^5\text{-}E_5)_2]$ than in $[Ti(\eta^5\text{-}E_5)_2]^{2-}$. It may be argued that the higher degree of electrostatic metal−ligand bonding in the former compounds comes from the choice of the fragments $[Fe(\eta^5\text{-}E_5)]^+$ and $(\eta^5\text{-}E_5)^-$ which have opposite charges that could lead to large values for the charge attraction. However, a recent energy partitioning analysis of the metal−ligand bonding in ferrocene using neutral fragments Fe and Cp in the triplet states and charged fragments Fe^{2+} and Cp^- in the singlet state showed that the relative contributions of ΔE_{elstat} and ΔE_{orb} change very little.[6f] It has been shown earlier by us that the charge of the fragments has a very strong influence of the energy levels of the orbitals which in turn may even enhance the orbital interactions more than the electrostatic interactions.[6a]

A second difference between the neutral iron complexes and the charged titanium species concerns the most important orbital term. Table 3 shows that the largest contribution to ΔE_{orb} comes always from the e_2 orbitals, i.e., from the electron donation of the HOMO of $[Ti(\eta^5\text{-}E_5)_2]^-$ to the LUMO of $(\eta^5\text{-}E_5)^-$. The latter orbital interaction is always stronger than the e_1 term, although the $\Delta E(e_2)$ contribution to the total orbital interaction energy decreases from 69.6% in $[Ti(\eta^5\text{-}N_5)_2]^{2-}$ to 43.5% in $[Ti(\eta^5\text{-}Sb_5)_2]^{2-}$ while the $\Delta E(e_1)$ contribution increases from 22.3% to 37.9%. The contributions of the a_2 orbitals are always less than the e_1 and e_2 values. Thus, the most important metal−ligand bonds in $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ are δ bonds while the metal−ligand bonds in $[Fe(\eta^5\text{-}E_5)_2]$ have π symmetry.

The large contribution of the metal−ligand δ bonding in in $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ is also revealed by the shape of the occupied orbitals. Figure 4a shows a plot of the e_2' HOMO of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$. There is a large overlap between the d(e_2') AO of the metal and the π orbitals of the ring. Figure 4b gives for comparison the corresponding e_2' orbital of $[Fe(\eta^5\text{-}P_5)_2]$ which is the HOMO-3. It becomes obvious that the latter MO is mainly a metal lone-pair orbital without large contributions of the ligand π orbitals. This is supported by the mixing coefficients of the fragment orbitals which is given by the ETS method. The contribution of the d(e_2') AO of Ti to the e_2' HOMO of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ is 33.6% while 60.2% come from the valence π orbitals of P_5.[23] The contribution of the Fe orbitals to the HOMO-3 of $[Fe(\eta^5\text{-}P_5)_2]$ is 69.0% while only 21.9% come from $(P_5)_2$.

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(23) Further contributions which then give 100% come from lower lying orbitals of the same symmetry.

The calculated energy values of $\Delta E(e_1)$ and $\Delta E(e_2)$ of the complexes [Ti(η^5-P$_5$)$_2$]$^{2-}$ and [Fe(η^5-Cp)$_2$] thus agree with the suggestion of Urnėžius et al.[1] that the inorganic ligand (η^5-P$_5$) serves as an electron acceptor in the former compound while Cp serves as an electron donor in the latter. However, the difference is *not* because the ligands are different. The difference comes from the fact that the titanium complex carries two negative charges while ferrocene is a neutral compound.

Finally we want to comment on the relative stabilities of the [Ti(η^5-E$_5$)$_2$]$^{2-}$ series for different E species which are predicted by the calculations. We want to point out that the chemical stabilities of the complexes are strongly influenced by the counterions whose effects are not considered here. Therefore, the calculated values should be judged with caution. Nevertheless, the calculated values of the interaction energy ΔE_{int} and the bond dissociation energy ΔE_{e} ($=-D_{\mathrm{e}}$) provide useful information about the trend of the intrinsic stabilities. The ΔE_{int} values in Table 3 indicate that the net interaction energy is only weakly stabilizing (compared with the values for [Fe(η^5-E$_5$)$_2$]) because the attractive electrostatic and covalent forces are largely compensated by the Pauli repulsion. The ΔE_{int} values give a stability trend of [Ti(η^5-E$_5$)$_2$]$^{2-}$ with P > As > Sb > CH > N. The values of the preparation energy ΔE_{prep} of the heavier ligand atoms P, As, and Sb are not very different from each other, and therefore, they do not alter the predicted trend of the stability of these compounds. However, the ΔE_{prep} values of [Ti(η^5-N$_5$)$_2$]$^{2-}$ and [Ti(Cp)$_2$]$^{2-}$ are much higher and, therefore, the dissociation of a ligand becomes exothermic. It should be noted that [Ti(Cp)$_2$]$^{2-}$ has a triplet ground state and that the nitrogen complex [Ti(η^5-N$_5$)$_2$]$^{2-}$ is thermodynamically highly unstable because the fragmentation of the cyclic N$_5$ ligand into N$_2$ is highly exothermic.[4] The calculated bond dissociation energies D_{e} indicate that the phosphorus and arsenic complexes are intrinsically stable with respect to dissociation of one ligand. Since the phosphorus complex [Ti(η^5-P$_5$)$_2$]$^{2-}$ could be prepared, it seems possible that also the arsenic analogue [Ti(η^5-As$_5$)$_2$]$^{2-}$ could be isolated while it will be difficult to synthesize [Ti(η^5-Sb$_5$)$_2$]$^{2-}$.

Summary and Conclusion

The energy decomposition analysis of the complexes [Ti(η^5-E$_5$)$_2$]$^{2-}$ and [Fe(η^5-E$_5$)$_2$] (E = CH, N, P, As, Sb) shows that the metal−ligand bonding in both series of complexes is more covalent than electrostatic. The dominant orbital interactions in the negatively charged titanium species come from the (e_2') Ti → [(η^5-E$_5$)$_2$]$^{2-}$ back-donation (δ bonding) while the covalent bonding in the iron complexes comes mainly from (e_1'') (Cp$^-$)$_2$ → Fe^{2+} donation (π bonding). The nature of the metal−ligand interactions does not change very much for different ligands cyc-E$_5$ within the two series of compounds. The calculated bond dissociation energies for breaking one metal−ligand bond of the molecules [Ti(η^5-E$_5$)$_2$]$^{2-}$ shows for E the order P > As > Sb $\gg$ N $\gg$ CH.

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