

Relation between topology and stability of bent titanocenes

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Abstract Bent metallocenes are a class of organometallic compounds that are widely used as catalysts in olefin polymerization procedures. We found a linear relation between the relative stability of bent titanocenes and the average delocalization index (DI) for Ti–C (from the cyclopentadienyl ring) atomic pairs within the evaluated compounds. As a consequence, the stability of the bent titanocenes can be estimated from their topologies. However, secondary interactions between the ligands of some of the bent titanocenes reduce the coefficient of determination for the average DI–stability relation.

Keywords QTAIM · DFT · Bent titanocene · Stability · Delocalization index

Introduction

Metallocenes are organometallic coordination compounds in which a transition metal is bonded to two η^5 -cyclopentadienyl (Cp) anions that lie in parallel planes [1, 2]. In 1951, the first metallocene was synthesized—ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$ [3]. Soon afterwards, a group of metallocene derivatives (such as Cp_2TiCl_2 and Cp_2ZrCl_2) containing a metal ion capable of binding up to three ligands in addition to both Cp groups were discovered by Wilkinson and Birmingham [4]. These compounds were called “bent metallocenes” because the Cp groups bend away from the additional ligands [5].

The first generation of Ziegler–Natta catalysts were used in the synthesis of crystalline and amorphous polyolefins [6]. By 1957, Natta had used Cp_2TiCl_2 (along with trimethyl aluminum, a co-catalyst in olefin polymerization) to obtain polyethylene [7]. Thereafter, a second generation of Ziegler–Natta catalysts consisting of group 4 bent metallocenes were utilized for olefin polymerization [8]. These are usually activated by a co-catalyst, methylaluminoxane (MAO), in a reaction that generates aluminoxane anions and metallocene cations, which are the actual active species during polymerization [9–12]. Bent metallocenes have two types of ligands: two π -ligands (usually substituted or unsubstituted cyclopentadienyl groups) and two σ -ligands (usually chlorine or methyl groups), giving them a pseudotetrahedral geometry [13–16]. In these catalysts, the π -bonded ligands strongly influence the stereo- and regio-regularity of the polymers produced [17–21], and voluminous (or large) σ -bonded alcoholato ligands affect either the molecular weight or the regio-regularity of the resulting polypropylenes [22–25].

Among the π -ligands usually studied in metallocene chemistry, cyclopentadienyl (Cp), indenyl (Ind), fluorenyl (Flu), tetrahydroindenyl (Thind), and arylindenyl (ArInd) are the most common. They can also be connected to one another by a bridge, forming a stereorigid metallocene or *ansa*-metallocene, or they can undergo free rotation along the metal center, forming a nonrigid metallocene [9]. The main types of bridges are: isopropylidene ($\text{Me}_2\text{C}<$), ethylene ($-\text{C}_2\text{H}_4-$), and dimethylsilane ($\text{Me}_2\text{Si}<$) groups. Synthesis of *ansa*-metallocenes with certain π -ligands (e.g., indenyl or tetrahydroindenyl) yields three isomeric forms: one meso and two racemic [26].

Molecular orbital (MO) and experimental studies of bent metallocenes have been done by different research groups [27–31]. The quantum theory of atoms in molecules (QTAIM) has been used to study coordination compounds, including metallocenes [30–33]. In a recent work, we studied

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the topological nature of titanocenes with a wide range of point group symmetries (Cp_2Ti , Cp_2Fe , Cp_2TiCl_2 , and $\text{Ind}_2\text{TiCl}_2$) in order to evaluate the chemical interactions between the metal center and its ligands. In addition, we established a direct relation between titanocene stability and the number of bond paths between the metal and π -ligand [34]. In this work, we extended the QTAIM and DFT study to a series of bent titanocenes with π -ligands larger than cyclopentadienyl whose point group symmetries are similar or very close to each other. In this case, the relation between topology and stability turned out to be different from that found in the previous work.

Methodology

The geometries of the studied species were optimized according to the Berny algorithm using energy-represented DIIS in redundant internal coordinates [35, 36]. Vibrational analysis of the optimized geometries of selected points on the potential energy surface was carried out in order to determine whether the resulting geometries are true minima or transition states by checking for the existence of imaginary frequencies. The calculations were performed at the B3LYP/6-311++G(2d,2p) level [37, 38] using the Gaussian 09 package [39]. Energy values are given in terms of the electronic energy, which was obtained from self-consistent field calculations of the molecular system. The difference between the electronic energies of the products and reagents in the synthesis of each metallocene is the electronic energy of the corresponding formation reaction.

The electronic density was derived from the Kohn–Sham orbitals and further used in QTAIM calculations performed by the AIM2000 software package [40]. The algorithm of AIM2000 that searches for critical points is based on the Newton–Raphson method, which relies heavily on the starting point chosen [41]. Iterations to find critical points begin with nuclear positions, mean values of maxima pairs, and mean values of maxima triples, which are followed by iterations from chosen starting grid points where a critical point might exist.

Integrations of the atomic basins were performed in natural coordinates using the default integration options. All integrations yielded orders of magnitude of 10^{-3} to 10^{-4} for the Laplacian of the charge density ($\nabla^2\rho$) in the calculated atomic basin. Atomic energies were calculated using the atomic virial approach. The atomic virial approach [$-2T(\Omega)=V(\Omega)$, where Ω is the atomic basin, T is the kinetic energy, and V is the potential energy] is identical to the virial theorem for a total system [42]. All calculated bond paths were mirrored by their corresponding virial paths, except for chlorine–hydrogen AILs. According to the atomic virial approach, mirroring of bond paths by virial paths is indicative of bonded interactions.

All of the studied molecular graphs followed the Poincaré–Hopf rule ($n - b + r - c = 1$), where n is the number of nuclear attractors, b is the number of bond critical points, r is the number of ring critical points, and c is the number of cage critical points [43].

The type of chemical bond or interaction between two atoms can be classified according to the following topological information: (1) the value of the charge density of the critical point (ρ_b); (2) the value and the sign of the Laplacian of the charge density; (3) the ratio $|\lambda_1|/\lambda_3$, where λ_1 and λ_3 are eigenvalues of the Hessian matrix of the charge density; (4) the ratio G_b/ρ_b , where G_b is the kinetic energy density; and (5) the total energy density (H_b) at the bond critical point. When $\nabla^2\rho > 0$, ρ_b is relatively low ($\rho_b < 6 \times 10^{-2}$ a.u.), the ratio $|\lambda_1|/\lambda_3 < 1$, the ratio $G_b/\rho_b > 1$ or close to 1, and H_b has a positive value that is close to zero, the chemical interaction is defined as “closed shell” (which applies, for example, to hydrogen bonds, ionic bonds, and van der Waals interactions [42]).

The delocalization index (DI) is a measure of the number of electrons that are shared or exchanged between two atoms (or basins), and it is derived by integrating the Fermi hole density [44, 45]. The localization index (LI) is the number of unshared electrons within each atomic basin [44, 45].

Our previous work that investigated the relation between DI and formal bond order [46] implicitly showed that the conventional (Lewis model) number of electrons associated with one or more traces (or lines) representing chemical bonds [47] is not correct. According to the Lewis model, single, double, and triple C–C bonds have two, four, and six electrons in the valence bonding region, respectively, regardless of the Coulombic and Fermi repulsions among them. Nonetheless, DI calculations indicate that there are actually one, two, and three shared electrons, on average, in single, double, and triple C–C bonds, respectively [46]. This discrepancy can be understood by noting that QTAIM is based on quantum physics, while the Lewis model is based on an empirical (though useful) model which disregards the Coulombic and Fermi electronic repulsions involved in a chemical bond.

The 16- and 18-electron rule, introduced by Nevil Sidgwick in 1923, is consistent with a large body of experimental evidence [48], but it is an empirical rule based on the Lewis model. Therefore, it is to be expected that the 16- and 18-electron rule and the delocalization index between the transition metal atom and each donor atom from a ligand do not agree numerically, as we noted in our previous work on metallocenes [34].

Results and discussion

Bent titanocenes with π -ligands larger than cyclopentadienyl were studied in this work in order to extend our previous

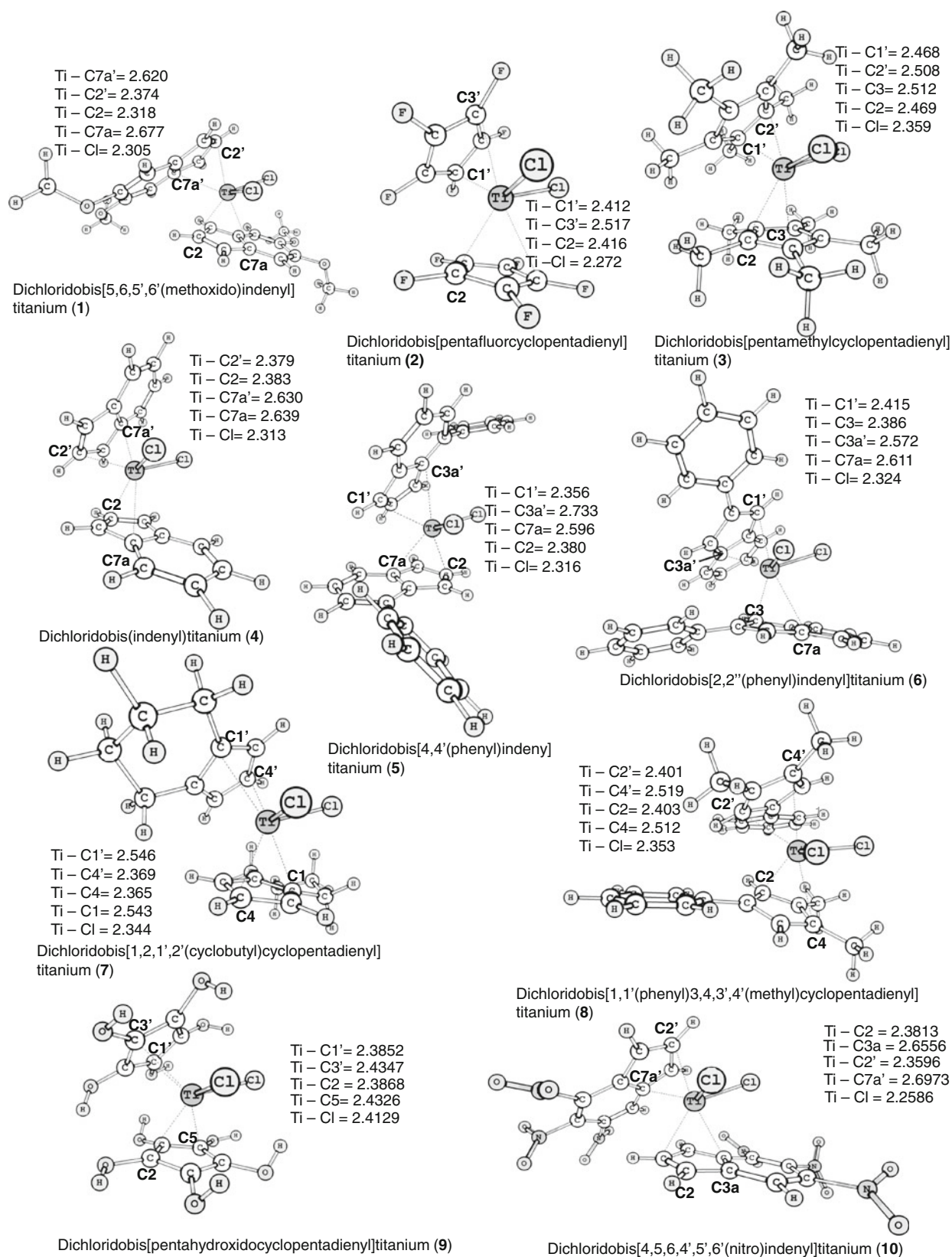


Fig. 1 IUPAC names, optimized geometries, selected Ti-C interatomic distances, (in Å) and Ti-Cl bond length, (in Å), of bent titanocenes 1–10

topological analysis on titanocenes [34]. The optimized geometries (each corresponding to a local minimum of the potential energy surface) of the studied bent titanocenes 1–10, along with some of their geometrical parameters and their IUPAC names [49], are shown in Fig. 1. The molecular graphs

of 1–10 are shown in Fig. 2, along with the average topological values at the bond critical points between the Ti atom and a C atom from the π -ligand.

Bent titanocenes 5 and 6 are isomers that differ in the position of the phenyl substituent in the indenyl ligand. In 5, the phenyl

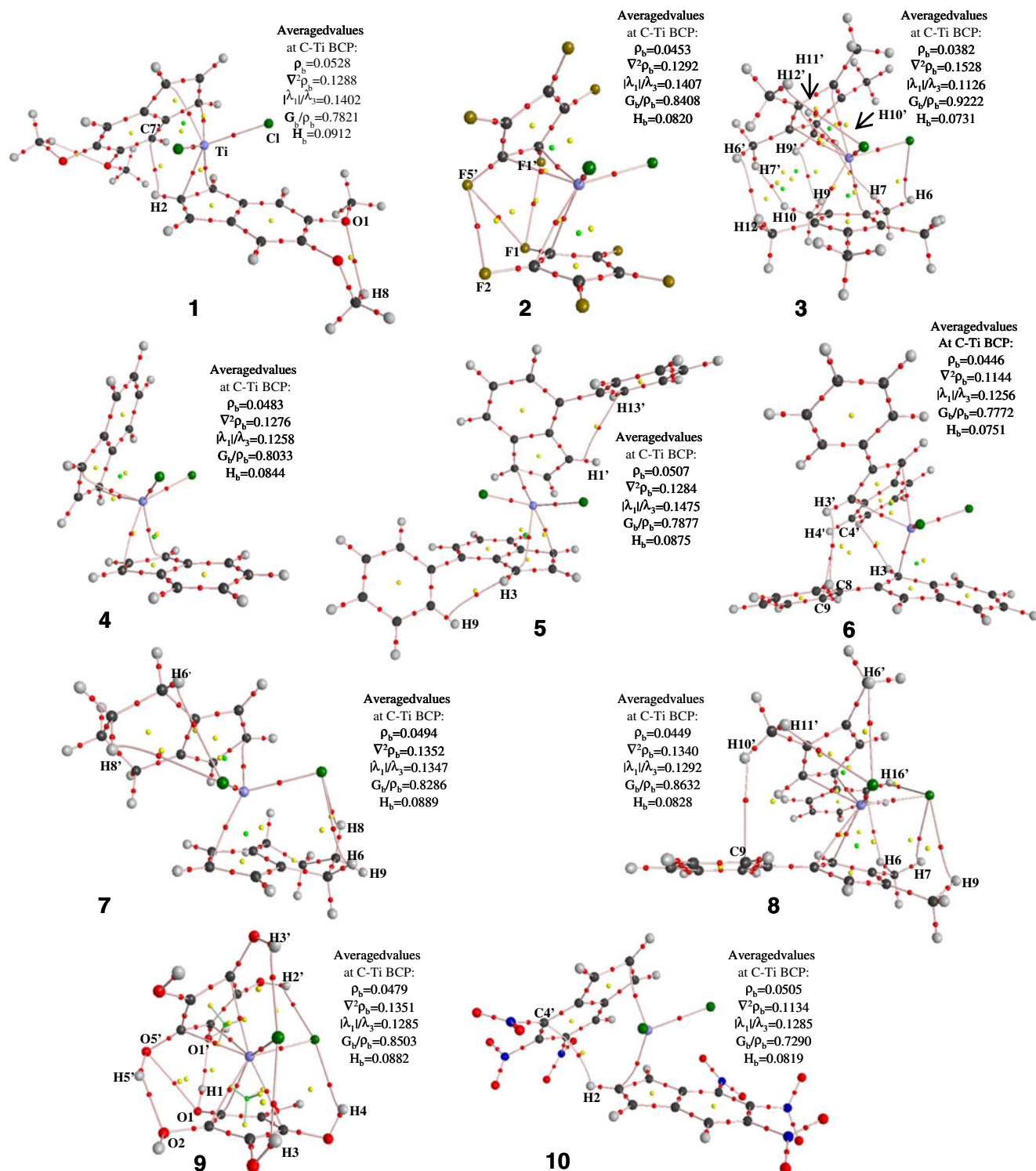


Fig. 2 Molecular graphs of bent titanocenes 1–10 along with their average topological properties (charge density ρ_b , Laplacian of charge density $\nabla^2 \rho_b$, ratio $|\lambda_1/\lambda_3|$, ratio G_b/ρ_b , and total energy density H_b , in a.u.) at the bond critical points between the Ti atom and a C atom from the π -ligand

substituent is attached at carbon 4 in the indenyl ligand; in **6**, the phenyl substituent is attached to carbon 2 in the indenyl ligand.

From Fig. 2, we can see that the topological data for the bond critical points of Ti–C bond paths involving π -ligands are characteristic of closed-shell interactions, as also observed in studies of other metallocenes [34].

The bent titanocenes **2**, **3**, **6**, and **8–10** have secondary interactions which involve atoms from different π -ligands (Fig. 2). These secondary interactions are weaker than other bonds in titanocene. They are indicated by F–F bond paths in **2**; H–H bond paths in **3**; C–H bond paths in **6** and **8** and one H–Cl bond path in **8**; H–O, O–O and H–Cl bond paths in **9**, and an H–C bond path in **10**.

The H(methylenic)–Cl atomic interaction lines (AILs) of **7** and the H(methylic)–Cl AILs of **3** and **8** are not bond paths, since they do not have corresponding virial paths, except for one H(methylic)–Cl atomic interaction in **8** (Fig. 3). Indeed, these interactions are found to be repulsive when the atomic energies of these hydrogen atoms are compared to those from equivalent nonparticipating hydrogen atoms. These AILs are therefore not regarded as bond paths because bond paths must be mirrored by corresponding virial paths [42], meaning that there are no secondary interactions involving chlorine and hydrogen atoms in **3**, **7**, and **8**, with one exception in **8**.

Moreover, the virial graphs of **1** and **5** indicate that there are no secondary interactions in these compounds.

As a consequence, the analysis of the results shown in Figs. 2 and 3 exemplifies the importance of analyzing the corresponding virial graph of a particular molecular graph in order to check whether a bond path exists, as some atomic interaction lines in the molecular graph may not be bond paths.

Table 1 shows the formation reactions for bent titanocenes **1–10**, their closest point group symmetries, their electronic energies of formation, the number of bond paths between Ti and C atoms, and the average DI value of Ti and C atomic pairs (averaged over all carbon atoms of the substituted cyclopentadienyl ring). The difference between the lowest and highest values of the average DI is 0.058 (Table 1), which represents an overall DI value of 0.29 electrons. The electronic energies of **1–10** in Table 1 are indicative of their stabilities: the more negative the energy, the more stable the corresponding bent titanocene.

By analyzing the electronic energies of formation of isomers **5** and **6**, we found that isomer **5** is more stable than **6**. The only structural difference between them is the position of the phenyl substituent in the indenyl ligand, which makes isomer **5** 5–6 kcal mol⁻¹ more stable. However, both isomers have the same number of Ti–C bond paths, which

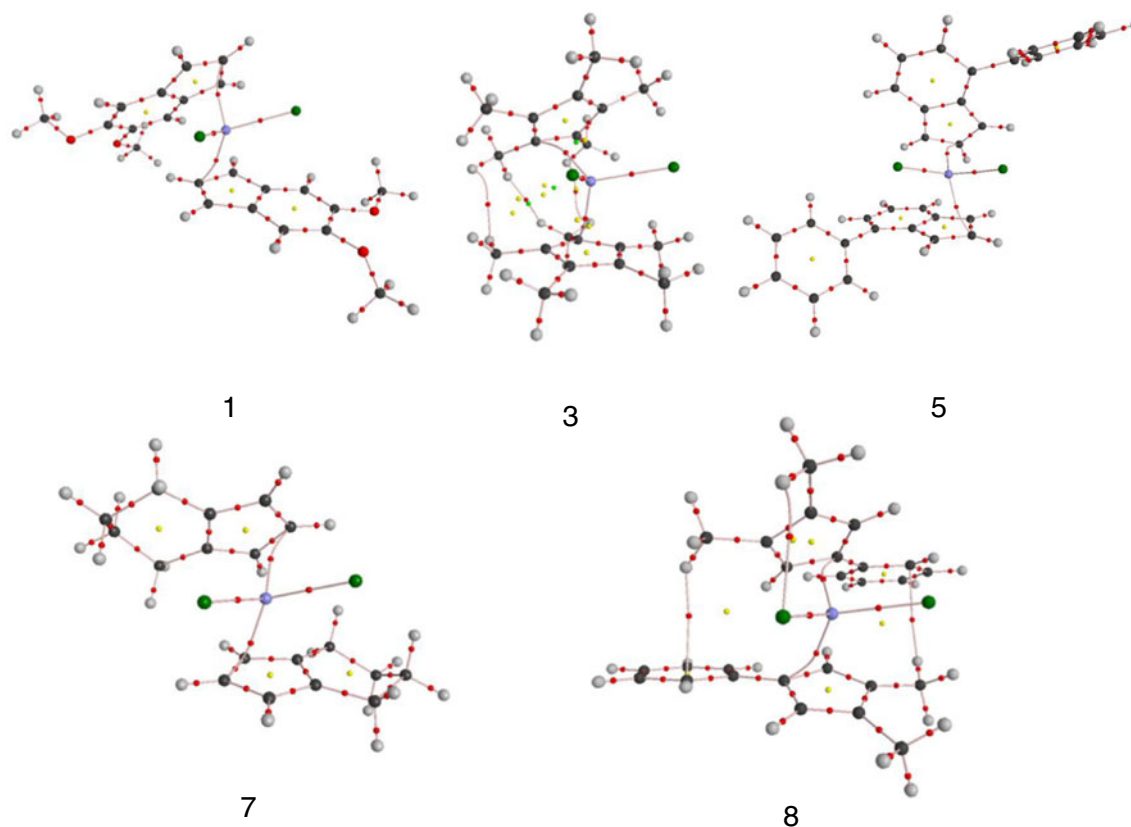


Fig. 3 Virial graphs of the titanocenes **1**, **3**, **5**, **7**, and **8**

Table 1 Formation reactions of bent titanocenes **1–10**, their point group symmetries, their electronic energies of reaction (in kcal mol⁻¹), the number of bond paths for the Ti–C atomic pair, and the average DI value involving Ti and C atoms from the cyclopentadienyl ring

Bent titanocene formation reaction	Molecule	Point group symmetry	ΔE (kcal mol ⁻¹)	Average Ti–C DI ^a	Number of bond paths ^b
TiCl ₄ +2Li(IndC ₂ H ₆ O ₂)→(IndC ₂ H ₆ O ₂) ₂ TiCl ₂ +2LiCl	1	C ₁	-3.39	0.229	4
TiCl ₄ +2Li(CpF ₅)→(CpF ₅) ₂ TiCl ₂ +2LiCl	2	C ₁	4.02	0.222	4
TiCl ₄ +2Li(CpC ₅ H ₁₅)→(CpC ₅ H ₁₅) ₂ TiCl ₂ +2LiCl	3	C ₁	-9.35	0.248	6
TiCl ₄ +2Li(Ind)→(Ind) ₂ TiCl ₂ +2LiCl	4	C ₂	4.89	0.226	4
TiCl ₄ +2Li(IndPh)→(IndPh) ₂ TiCl ₂ +2LiCl	5	C ₁	5.77	0.233	3
TiCl ₄ +2Li(IndPh)→(IndPh) ₂ TiCl ₂ +2LiCl	6	C ₁	10.35	0.222	3
TiCl ₄ +2Li(CpC ₄ H ₈)→(CpC ₄ H ₈) ₂ TiCl ₂ +2LiCl	7	C ₂	-9.22	0.250	2
TiCl ₄ +2Li(CpPhC ₂ H ₆)→(CpPhC ₂ H ₆) ₂ TiCl ₂ +2LiCl	8	C ₂	-9.73	0.245	4
TiCl ₄ +2Li(Cp(OH) ₅)→[Cp(OH) ₅] ₂ TiCl ₂ +2LiCl	9	C ₂	-45.80	0.261	6
TiCl ₄ +2Li(Ind(NO ₂) ₃)→[Ind(NO ₂) ₃] ₂ TiCl ₂ +2LiCl	10	C ₁	29.36	0.203	2

^a Involving only C atoms of the substituted cyclopentadienyl ring

^b Involving only Ti–C atomic pairs

contradicts the direct association of the number of Ti–C/Fe–C bond paths with titanocene/ferrocene stability that we found in our previous work [34].

Figure 4a shows that there is no linear relation between $\Delta E_{\text{reaction}}$ and the total number of Ti–C bond paths. However, in our previous work, where the studied ferrocene, titanocene, and bent titanocenes had very different point group symmetries [Cp₂Fe (D_{5h}), Cp₂Ti (C_{2v}), Cp₂TiMe₂ (C_{2v}) and Ind₂TiMe₂ (C₂)], there was a linear relation between the number of Ti–C bond paths and their stabilities [34]. The lack of a linear relation between $\Delta E_{\text{reaction}}$ and the total number of Ti–C bond paths can be observed in bent titanocenes **1**, **2**, **4**, and **8**, which have the same number of Ti–C bond paths but completely different stabilities (Table 1). A possible reason for the different relations observed in the two studies may be identified from a comparison of the structural differences among the metallocenes studied in our previous work and those among the titanocenes investigated in this work. Titanocenes **1–10** have large π -ligands and their point group symmetries are either very close to each other or are similar (Table 1). However, as mentioned above, the point group symmetries of the metallocenes from [34] are very different, and their π -ligands are relatively small, except for those from Ind₂TiMe₂.

On the other hand, we found a linear relation between $\Delta E_{\text{reaction}}$ and the averaged DI of Ti–C atomic pairs (averaged over all C atoms of the substituted cyclopentadienyl ring)—see Fig. 4b—for bent titanocenes **1–10**. As the average Ti–C DI increases, the stability of the bent titanocene tends to increase. Since the DI indicates the number of electrons shared by an atomic pair, it means that increasing the average Ti–C DI strengthens the interaction between the Ti and π -ligands, which yields a more stable titanocene.

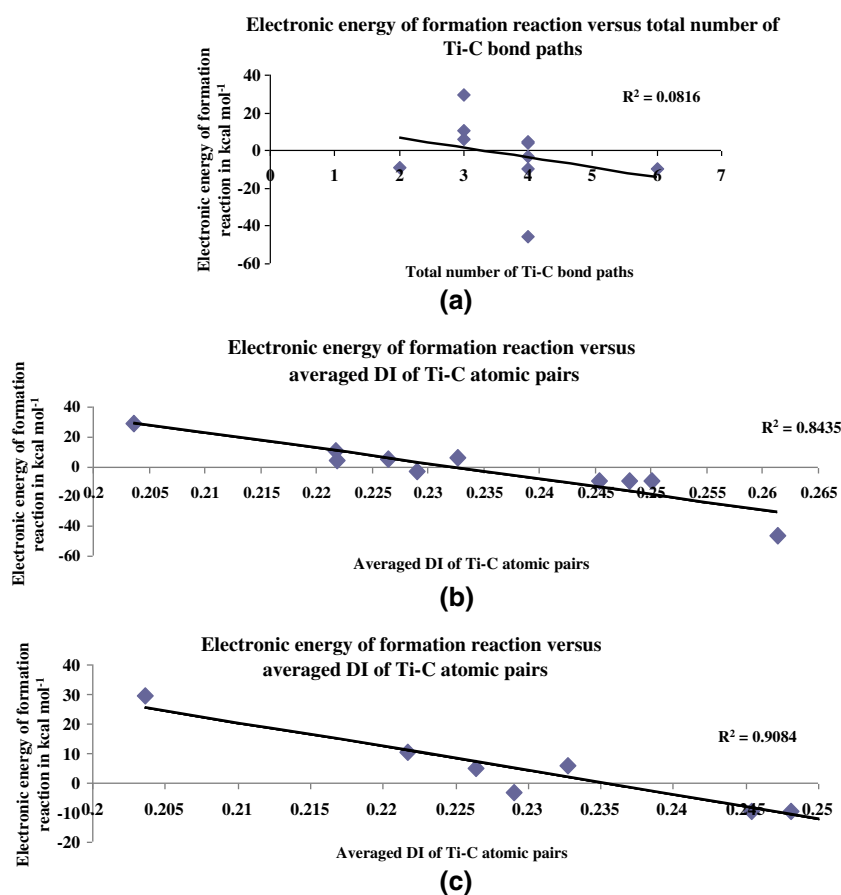
However, secondary interactions in some of the studied compounds (Fig. 2) reduce the coefficient of determination of the linear relation between $\Delta E_{\text{reaction}}$ and the average DI of Ti–C atomic pairs. These secondary interactions in bent titanocenes exert some influence over the stability of the whole molecule because they provide extra stabilization for the π -ligands (see Table 2) that is not accounted for in the Ti–C delocalization indices, thus affecting the linear relation between $\Delta E_{\text{reaction}}$ and the average DI. When we remove the data for bent titanocenes **2** and **9** (with relatively moderate F–F and O–H interactions, respectively) from the plot, the coefficient of determination increases (Fig. 4c).

No linear relation was observed between other topological data and the stabilities of the studied bent titanocenes. Neither the average ρ_b nor the average $\nabla^2\rho_b$ of Ti–C bonds showed any linear relation to the stabilities of compounds **1–10**. Even combinations of them that included the number of Ti–C bond paths failed to show any linear relation with the stabilities of the bent titanocenes.

One particular aspect of the bent titanocenes studied in this work is that most of them have secondary interactions involving the π -ligands (Fig. 2). On the other hand, none of the compounds studied in our previous work (Cp₂Fe, Cp₂Ti, Cp₂TiMe₂, and Ind₂TiMe₂) have secondary interactions involving the π -ligands. Probably, secondary interactions do not occur in the metallocenes studied in our previous work because their π -ligands are not as voluminous (or large) as the π -ligands of the bent titanocenes studied in this work.

Table 2 gives the atomic energy values for **2**, **3**, **6**, **8**, **9**, and **10**, including the secondary interactions (the atomic energies of the atoms involved in the secondary interactions; the atomic energies of their equivalent atoms in the corresponding bent titanocene that do not participate in any secondary interactions; and the difference in atomic energy

Fig. 4 **a** Plot of the electronic energies of formation of **1–10**, in kcal mol⁻¹, versus their total numbers of Ti–C bond paths. **b** Plot of the electronic energies of formation of **1, 3–8**, and **10**, in kcal mol⁻¹, versus their average DIs for Ti–C atomic pairs. **c** Plot of the electronic energies of formation of **1–10**, in kcal mol⁻¹, versus their average DIs for Ti–C atomic pairs



between the equivalent participating and nonparticipating atoms for the same bent titanocene). The atoms listed in Table 2 that participate in secondary interactions can be viewed in Fig. 2. The atomic energy differences shown in Table 2 indicate that the great majority of atoms involved in secondary interactions have smaller energies than their equivalent atoms that do not participate in any secondary interactions; in other words, most of the bond paths associated with secondary interactions are attractive. In the case of titanocene **9**, the atomic energy of the H1 atom is probably influenced by the O1–O5' secondary interaction, where O1 is the oxygen atom bonded to H1. For the bond path involving H(methylic) and C1 atoms in **8** (Fig. 3), there is no equivalent nonparticipating methylic hydrogen to the H(methylic) atom that does participate in a secondary interaction, because the latter is the only H in the methyl group that is close to a vicinal methylic H atom, which possibly leads to van der Waals repulsion between them.

If we consider only the secondary interactions that have a stabilizing effect (i.e., those with negative ΔE values), the magnitude of the stabilizing interaction for each atom involved in the secondary interaction ranges from -0.0720 a.u. (47.34 kcal mol⁻¹) to -0.0030 a.u. (1.88 kcal mol⁻¹), except for one value (-0.0002 a.u.). This implies that the secondary interactions have a significant influence on the stability of the

studied bent titanocenes by approaching Ti and π -ligands through interaction between π -ligands. Since these secondary interactions are not related to the average Ti–C DI, they affect the linear relation between the DIs and stabilities of the studied metallocenes, meaning that the corresponding coefficient of determination becomes smaller than expected.

The direct relation between topology and stability identified in this work can be used when designing novel bent titanocenes, as the relation allows the relative stability of the bent titanocene to be predicted from its average Ti–C delocalization index. For instance, if we replace the fluorine atoms in **2** with electron-releasing hydroxyl groups, we find that the average Ti–C DI of dichloridobis[pentahydroxycyclopentadienyl]titanium **9** is higher than that of **2**. According to their stabilities (see Table 1), **9** is more stable than **2**, according to the expected tendency. On the other hand, when dichloridobis(indenyl)titanium **4** is converted to dichloridobis(4,5,6-trinitroindenyl)titanium **10** by replacing the hydrogen atoms with electron-withdrawing nitro groups, the average Ti–C DI decreases, so titanocene **10** is less stable than **4** (Table 1). We also note that the presence of an electron-releasing group attached to the Cp ring increases the stability of the bent titanocene, because it increases the interaction of the π -ligand with the titanium atom (as demonstrated by the average Ti–C DI), while the presence of an electron-withdrawing group on the ring decreases its stability by weakening the π -

Table 2 Atomic energies (in Hartrees) of the atoms participating in secondary interactions in the bent titanocenes **2**, **3**, **6**, **9**, and **10**, the atomic energies of the equivalent atoms without any secondary

interactions in the bent titanocenes, and the difference in atomic energy between the equivalent participating and nonparticipating atoms for the same bent titanocene

Bent titanocene	Secondary interaction	Atom	Energy (Hartrees)		Bent titanocene	Secondary interaction	Atom	Energy (Hartrees)	
			$E(\Omega)$	ΔE				$E(\Omega)$	ΔE
2	F1–F1'	F1	-100.22	-0.0300	6	H3–C4'	H3	-0.6092	-0.0083
		F5 ^a	-100.19				H1 ^c	-0.6009	
		F1'	-100.19	0.0000			C4'	-37.952	-0.0340
		F5 ^a	-100.19				C7 ^c	-37.918	
2	F1–F5'	F1	-100.22	-0.0300	8	H10'–C9	H10'	-0.6197	-0.0061
		F5 ^a	-100.19				H9 ^d	-0.6136	
		F5'	-100.21	-0.0200			C9	-37.975	-0.0170
		F5 ^a	-100.19				C9 ^d	-37.958	
2	F2–F5'	F2	-100.20	-0.0100	8	H6–C13'	H6	-0.6195	0.0000
		F5 ^a	-100.19				H8 ^d	-0.6195	
		F5'	-100.21	-0.0200			C13'	-37.977	-0.0190
		F5 ^a	-100.19				C9'	-37.958	
3	H7–H10'	H7	-0.6331	-0.0089	9	O1'–H1	O1'	-75.644	0.0225
		H8 ^b	-0.6242				O4 ^e	-75.667	
		H10'	-0.6253	-0.0030			H1	-0.3514	0.0172
		H11 ^{ab}	-0.6223				H5 ^e	-0.3686	
3	H9–H9'	H9	-0.6298	-0.0079	9	O1–O5'	O1	-75.677	-0.0160
		H11 ^b	-0.6219				O5 ^e	-75.661	
		H9'	-0.6341	-0.0118			O5'	-75.679	-0.0120
		H11 ^{ab}	-0.6223				O4 ^e	-75.667	
3	H10–H7'	H10	-0.6347	-0.0128	9	O2–H5'	O2	-75.654	-0.0090
		H11 ^b	-0.6219				O5 ^e	-75.645	
		H7'	-0.6353	-0.0127			H5'	-0.3577	0.0030
		H8 ^{ab}	-0.6226				H4 ^e	-0.3607	
3	H12–H6'	H12	-0.6328	-0.0112	9	(H3'–Cl)*	H3'	-0.3676	-0.0069
		H14 ^b	-0.6216						
		H6'	-0.6287	-0.0061			H4 ^e	-0.3607	
		H8 ^{ab}	-0.6226						
6	H3'–C8	H3'	-0.6071	-0.0051	9	(H2'–Cl)*	H2'	-0.3609	-0.0002
		H1 ^{cc}	-0.6020						
		C8	-37.965	-0.0100			H4 ^e	-0.3607	
		C8 ^{cc}	-37.955						
6	H4'–C9	H4'	-0.6149	-0.0042	10	H2–C4'	H2	-0.5956	-0.0121
		H7 ^{cc}	-0.6107				H1 ^f	-0.5835	
		C9	-37.960	0.0088			C4'	-37.906	-0.0702
		C9 ^{cc}	-37.947				C7 ^{ff}	-37.836	

^{a–d} are the nonparticipating atoms equivalent to those participating in secondary interactions in bent titanocenes **2**, **3**, **6**, and **8–10**.

* Chlorine atom without an equivalent atom that does not participate in any secondary interaction

ligand–titanium interaction. Therefore, the average number of electrons shared between the π -ligand and the titanium atom is a very important influence on the stability of the titanocene.

Two relations between the topology and relative stability of metallocenes/bent titanocenes can thus be discerned. When the species show a wide range of point group symmetries, there is a linear relation between the number of Ti–

C bond paths and the relative stability. However, when the bent titanocenes have rather similar point group symmetries, there is a linear relation between the average DI for Ti–C atomic pairs and the relative stability. Moreover, we can use the plots shown in Fig. 4b or c to estimate the relative stabilities of bent titanocenes by calculating their average Ti–C DIs.

Conclusions

Most of the studied bent titanocenes (which were identified as local minima on the potential energy surface) have secondary interactions that link atoms between the π -ligands of each titanocene. The great majority of these secondary interactions are attractive according to their atomic energy values. Some chlorine–hydrogen atomic interaction lines are not bond paths because they are not mirrored by corresponding virial paths, and these chlorine–hydrogen pairs do not have secondary interactions.

No linear relation between the number of Ti–C bond paths and the relative stability was found when bent titanocenes with voluminous π -ligands were considered. This absence of a linear relation may be due to the rather similar point group symmetries of the studied bent titanocenes.

On the other hand, we found a linear relation between the average DI of Ti–C (from the cyclopentadienyl ring) atomic pairs and relative stability for the studied bent titanocenes. In another words, we found that the average number of electrons shared between the π -ligand and titanium atom is a very important parameter for determining and predicting the stability—a thermodynamic property—of a titanocene. However, the secondary interactions that occur in some of the studied bent titanocenes reduce the coefficient of determination of the average DI–stability relation, since they indirectly increase the interaction between the π -ligand and the titanium atom in a different manner to that accounted for by the Ti–C delocalization index.

The stabilities of bent titanocenes can be estimated from their topological data. In addition, we believe that topology (DI or bond path)–stability relations can also be obtained for metallocenes with a central metal ion that is not titanium.

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