Theoretical studies on titanium pentafulvene complexes

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Abstract

A series of six titanium pentafulvene complexes are thoroughly investigated using the B3LYP/6-31G(d) level of theory. Excellent agreement with the available structural data is obtained. Relevant structural parameters indicate that a gradual change of the fulvene ligand coordination to the titanium center. Depending on the nature of the exocyclic fulvene substituents dianionic η^5, η^1-and olefinic η^6-coordination modes are found. This behavior is further supported by NBO and AIM population analyses which predict differences in the bond nature meanly of the contacts between titanium and the exocyclic carbon atom. In an excitation study, several theoretical approaches are evaluated against the available recorded UV–Vis spectra of the six complexes. The "best" approach, time-dependant DFT calculations reproduce the experimental UV data reasonably well, although systematically slightly too small values (abut 50 cm^{-1}) are obtained. The other levels of theory are significantly more erratic. It could further be testified that the absorption maxima correspond to a ligand-to-metal charge transfer from the HOMO to the LUMO+1 of the complexes.
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1. Introduction

The chemistry of complexes containing π-acceptor ligands is of fundamental interest to both preparative [1,2] and theoretical [3–5] point of view. In such a way, the coordination chemistry of complexes containing six-electron donor ligands like benzene [6,7] marks a milestone in this field. On the other hand, due to the stronger π-acceptor properties of pentafulvenes [8] as potential six electron donors, complexes thereof becomes more and more attractive.

Fulvenes are hydrocarbons with fully-unsaturated odd-membered rings, in which through-conjugation is maintained by the presence of an exocyclic CC double bond [8]. The complex chemistry of these ligands, particularly
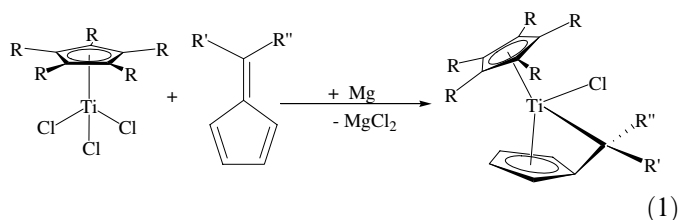
of late transition metal pentafulvene complexes, is well developed [9–16]. On the other hand, growing theoretical interests in structure and bonding relationships is dedicated to this complex type. Starting from investigations of the free ligand [17–19] particularly in order to understand its spectroscopic properties [20–22] the bonding situation of fulvene transition metal complexes has been thoroughly analyzed [14,23–27].

Generally, pentafulvene complexes of early transition metals are available by thermolysis of methyl substituted cyclopentadienyl derivatives [28–38]. On the other hand, free pentafulvenes are often used as starting materials in a direct [39,40] or indirect way [41,42] for the preparation of ansa-metallocenes, as well as heteroatom substituted σ–π chelating systems [43,44].

However, the efficient procedure of direct reductive complexation of pentafulvenes to LTiCl fragments (L: C_5H_5, C_5Me_5) allows a broad variation of the substitution patterns particularly in the exocyclic position of the fulvene ligand used (Eq. (1)) [45].

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$$(1)$$

In such a way, the monocyclopentadienyltitaniumpentafulvene chlorides (**2**–**5**) [46–48] as well as derivatives there of (e.g., **1**) becomes available in acceptable yields (Table 1, Fig. 1).

Fulvene complexes with transition metals which have been investigated by means of X-ray techniques are frequently reported in the literature: Common to most of them is the bending of the exocyclic substituents towards the metals centers and the more or less elongation of the exocyclic C–C bond lengths. Pentafulvenes can be bond to transition metals in several different modes (Fig. 2). In unusual examples, fulvenes can act as η^2-ligands, through the exocyclic double bond (Form **A**: $[Pd(\eta^2\text{-}C_5Me_4=CH_2)(PMe_3)_2]$ [49] and $[Rh(\eta^2\text{-}C_5H_4=CPh_2)(CO)_2Cl]$ [50]) as well as through one double bond of the five-membered ring (Form **B**: $[Pt(\eta^2\text{-}C_5H_4=CPh_2)(PPh_3)_2]$ [51]). η^4-Modes (**C**) are found in $[Fe(\eta^4\text{-}C_5H_4=CPh_2)(CO)_3]$, $[(COD)Ni(\eta^4\text{-}C_5H_4=CPh_2)]$ [52] or $[CpCo(\eta^4\text{-}C_5H_4=CPh_2)]$ [53]. More commonly, fulvene ligands act as six-electron donors (**D**). In the case of early transition metals, the bonding situation is best described as π–η^5:σ–η^1 coordination mode (**E**) [24,54]. Alternatively also trimethylene methane like π^4, η^2-coordination modes (**F**) are described [55].

Experimental studies with titanium complexes **1**–**6**, including UV–Vis and NMR investigations as well as crys-
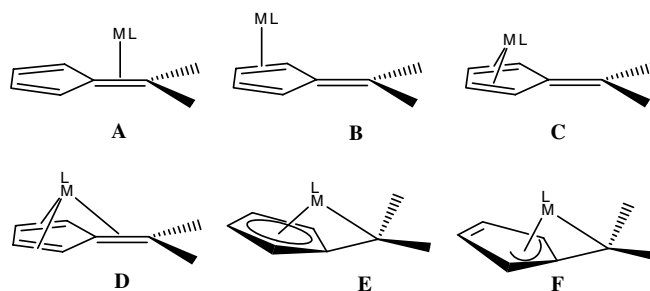

Fig. 2. Possible coordination modes of pentafulvene metal complexes.

tallographic data, indicate that these complexes exist in a coordination between the dianionic (**E**) and an olefinic form (**D**) [46–48,56]. We therefore set out to theoretically analyze this situation using geometry optimizations, excited states calculations and population analyses. Particularly, we wish to present the influence of the nature of the exocyclic substituents.

2. Computational details

All calculations were performed with GAUSSIAN 98 [57]. Pople's basis set 6-31G(d) [58,59] and density functional theory (DFT) with the B3LYP functional [60,61] was used for the optimizations of the ground state geometries. The nature of all stationary points as true minima was confirmed by calculating harmonic frequencies. Population analyses were performed with the NBO [62,63] and the AIM2000 [64–66] packages.

Excited states calculations were performed employing configuration interaction with single excitations (CIS) [67] and time-dependent [68–70] TD-DFT methodologies. The basis set for these calculations was the same as for the optimization of the ground states.

3. Experimental details

Preparation of **1**: a solution of 1.764 g (5 mmol) of **3** [46] in 20 mL Et$_2$O is added to 3.28 ml (5.25 mmol) MeLi (1.6 M in Et$_2$O) at −78 °C. The mixture is warmed up under stirring to room temperature and stirred for 1 h at 25 °C. The solvent is evaporated to dryness and the residue is extracted with 20 mL n-pentane. The remaining LiCl is filtered, the filtrate is reduced to 10 mL and cooled to −20 °C, leading to **1** as microcrystalline turkeys solid (yield 1.081 g, 65 %, de > 98%). {^{1}H} NMR (500 MHz, C$_6$D$_6$, 300 K) δ −0.74 (s, 3H, CH$_3$), 0.91 (s, 9H, C(CH$_3$)$_3$), 1.33 (s, 1H, H6), 1.67 (s, 15H, C$_5$(CH$_3$)$_5$), 3.28 (m, 1H, H2), 4.61 (m, 1H, H3), 6.01 (m, 1H, H4), 6.62 (m, 1H, H5). ^{13}C NMR (125.8 MHz, C$_6$D$_6$, 300 K) δ 12.5 (C$_5$(CH$_3$)$_5$), 33.8 (C(CH$_3$)3), 34.7 (C$_5$(CH$_3$)$_5$), 42.6 ($^1J_{CH}$ = 118.7 Hz, CH$_3$), 111.9 ($^1J_{CH}$ = 140.2 Hz, C6), 113.4 ($^1J_{CH}$ = 170.5 Hz, C3), 118.0 ($^1J_{CH}$ = 169.6 Hz, C2), 118.2 ($^1J_{CH}$ = 170.5 Hz, C4), 118.6 (C$_5$(CH$_3$)$_5$), 123.4 ($^1J_{CH}$ = 175.2 Hz, C5), 131.0 (C1). IR (KBr, cm^{-1}) v 2951 (m), 2905 (m), 2866 (m), 1493 (s), 1451 (s), 1375 (s), 1364 (s),

Table 1
Summary of selected monocyclopentadienyltitaniumpentafulvene complexes

	Yield (%), m.p. (°C)	Color	Remarks	
1	65, 87 (dec.)	Turquoise	de ⩾98%	[48][a]
2	48, 92	Dark green	de ⩾98%	[46]
3	68, 118	Dark green	de ⩾98%	[46]
4	45, 138	Green		[47]
5	61, 102	Green-yellow	de ⩾98%	[46,48]
6	57, 164	Brown-yellow		[47]

[a] This paper.

Fig. 1. Definition of the investigated titanium fulvene compounds.

1260 (m), 1244 (m), 1086 (vs), 1051 (Vs), 1026 (vs), 947 (m), 810 (vs), 789 (vs), 702(s). UV–Vis (*n*-pentane, nm, 10^3 cm^2 mol^{-1}) λ_{max} (ε) = 615 (80). MS (EI, *m/z*, rel. int.) = 316 (65) [M−CH$_4$]$^+$, 135 (30) [Cp*], 119 (18), 104 (10), 97 (36), 85 (39), 69 (60), 57 (100) [C$_4$H$_9$]$^+$, 41 (58); MS (CI, *i*-butane): *m/z* (rel. int.) = 333 (40) [MH]$^+$.

4. Results and discussion

4.1. Geometries

The titanium complexes investigated herein are those for which experimental data are available. A list is given in Fig. 1. Comparison of calculated geometrical values with experimental results can give valuable information about the existing bonding situation. Important geometrical variables are the distances between the metal center and the exocyclic atom C6, the exocyclic C1–C6 bond length and the bond lengths in the fulvene ligand ring.

Another useful value is the angle Θ defining the deviation of the exocyclic atom C6 out of the fulvenic plane (Fig. 3). Changes of this angle also indicate changes in the bonding situation of either olefinic or dianionic complexation.

In order to evaluate the reliability of the chosen method, calculated selected geometrical data were compared with the available X-ray structures, namely the complexes **2**, **3** and **6**. Table 2 gives a list of these values with the available experimental data in parentheses. All data show excellent
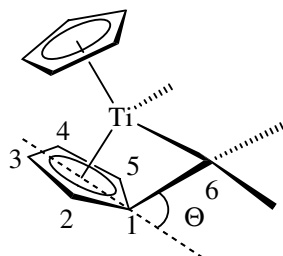

Fig. 3. Definition of atom numbering and the out-of-plane angle Θ.

agreement between theory and experiment, including the – in this context – important Ti–C6 and C1–C6 distances, with a very slight underestimation of the bond lengths. Also the angles Θ of the three complexes in this comparison fit with the crystal structure data. In conclusion it can be seen that the chosen level of theory for the description of the complexes studied herein is appropriate. It confirms findings for similar systems [71,72]. Unpublished calculations using the HF/6-31G(d,p) level are in significantly worse agreement, in particular for system **6**, where almost no bonding between the fulvene ligand and the titanium core is predicted.

The DFT-calculated results of all complexes **1**–**6** are listed in Table 2, as an example is the structure of **2** shown in Fig. 4. As a first finding, the bond length of the Ti–C6 contact tends to increase going from left to right: **1** has the shortest length (2.341 Å), and it is elongated to 2.621 Å in complex **6**. In general, the complexes with monosubstituted pentafulvenes (**1**–**3**) have similar distances, while the latter three complexes have significantly longer contacts. These disubstituted fulvene complexes have an increased steric demand that complicates the interaction with the titanium centre and therefore leads to the observed extension. As a consequence of this trend, the C1–C6 bond is also affected: its length is reduced from **1** to **6** (1.449–1.435 Å), in accordance with the above finding. The double bond character of the C1–C6 bond is therefore larger when coordination of C6 to the titanium centre is weaker. For comparison, the uncoordinated fulvenes of the complexes have C1–C6 bond lengths ranging between 1.362 and 1.373 Å.

Another important aspect is the deviation angle Θ at the fulvene. This angle is around 35° for the monosubstituted fulvene complexes **1**–**3**, but is reduced to 30° (**4** and **5**) and 26.2° in **6**. This reduction is an additional effect of the weakening of the Ti–C6 interaction and also indicates an increasing participation of the olefinic η^6 coordination mode.

The conclusion of the theoretical investigations of the fulvene complex structures is a gradual change from the

Table 2
Selected geometrical data of complexes **1**–**6**, B3LYP/6-31G(d)-optimized values (experimental values for **2**, **3** and **6** in parentheses)

|	**1**	**2**	**3**	**4**	**5**	**6**
Ti–C6	2.341	2.341 (2.367)	2.363 (2.355)	2.464	2.463	2.621 (2.535)
Ti–C1	2.161	2.160 (2.155)	2.162 (2.151)	2.171	2.173	2.200 (2.183)
Ti–C2	2.294	2.297 (2.286)	2.289 (2.279)	2.316	2.323	2.261 (2.262)
Ti–C5	2.335	2.308 (2.291)	2.321 (2.293)	2.275	2.288	2.333 (2.313)
Ti–C3	2.498	2.495 (2.443)	2.487 (2.446)	2.484	2.488	2.426 (2.424)
Ti–C4	2.523	2.485 (2.446)	2.502 (2.452)	2.449	2.474	2.471 (2.452)
C1–C6	1.449	1.439 (1.434)	1.439 (1.432)	1.443	1.437	1.435 (1.428)
C1–C2	1.445	1.448 (1.443)	1.446 (1.431)	1.445	1.443	1.452 (1.446)
C1–C5	1.445	1.447 (1.440)	1.445 (1.440)	1.449	1.452	1.442 (1.433)
C2–C3	1.413	1.413 (1.394)	1.412 (1.401)	1.409	1.411	1.418 (1.403)
C4–C5	1.411	1.410 (1.400)	1.410 (1.394)	1.418	1.414	1.409 (1.389)
C3–C4	1.414	1.413 (1.405)	1.412 (1.395)	1.413	1.412	1.412 (1.380)
Θ	34.8	34.3 (35.6)	35.4 (35.6)	31.1	30.6	26.2 (29.2)
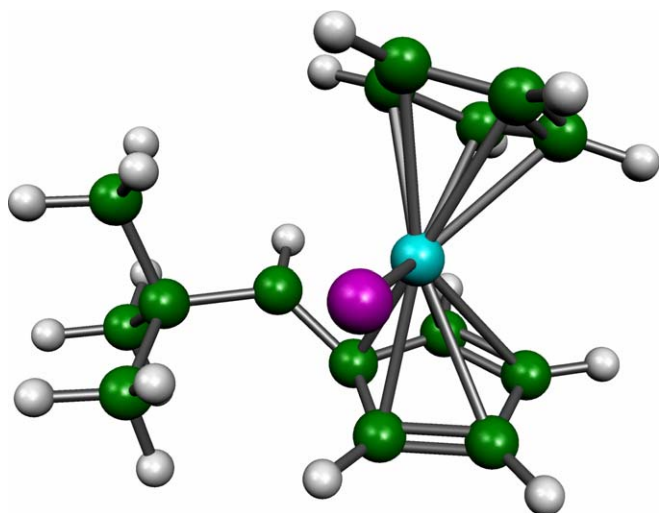
Fig. 4. The B3LYP/6-31G(d)-optimized structure of **2**.

dianionic η^5:η^1 form **E** to the olefinic η^6 complex form **D** when going from complex **1** to **6**, as shown in Fig. 5. This is in accordance with the before mentioned experimental investigations.

4.2. Excited states calculations

All of the complexes **1**–**6** show a distinct color, and their UV–Vis spectra have been recorded [46,47,56]. It therefore seems straightforward to theoretically investigate the excitation behavior which allows the correct reproduction of excitation energies and gives information on the nature of the excitation.

The excited states calculations were performed with different theoretical approaches in order to obtain information on the merits of every method. Based on the B3LYP/6-31G(d)-optimized geometries, the configuration interaction method employing single excitations only (CIS) and the time-dependent DFT approach were used
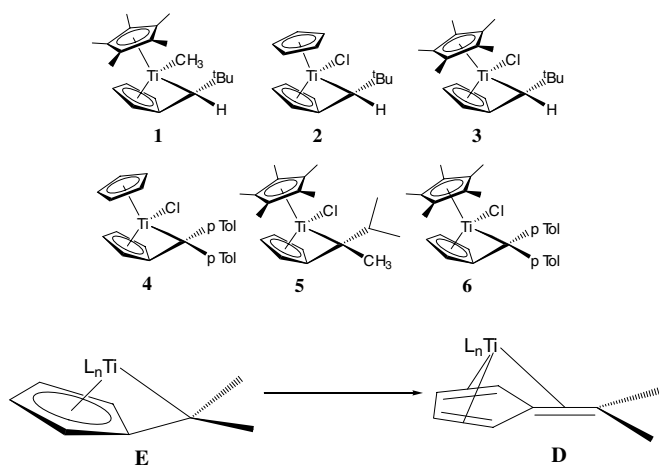
herein [73]. Additionally, the TD-HF method with a HF/6-31G(d,p) geometry has been tested. Fig. 6 gives a graphical overview of the calculated results and the experimental data [48]. Common to all experimental UV–Vis spectra is the existence of only one charge-transfer band in the UV region. In general, the trend of increasing absorption maxima for the investigated complexes is reproduced by all methods, but all methods seem to systematically underestimate the absorption maxima, at least to some extend (Table 3). While the TD-HF approach gives the most erratic data, the TD-DFT results agree quite well with the experimental measurements and can correctly reproduce the ordering and values of the absorptions, although on average 50 cm^{-1} too small. The CIS approach is somewhat less reliable in this respect, giving larger deviations and a huge error of almost 150 cm^{-1} for complex **1**. The similar-
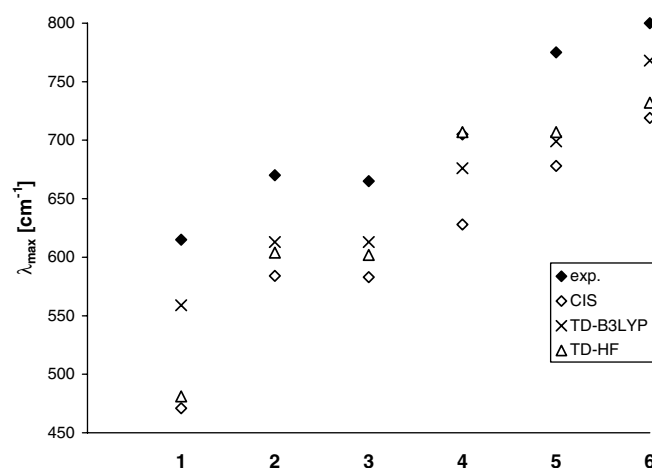

Fig. 6. Experimental and calculated absorption maxima of complexes **1**–**6**.

Table 3
Comparison of experimental and calculated absorption maxima (cm^{-1})

λ_{max}	**1**	**2**	**3**	**4**	**5**	**6**
Exp.	615	670	665	705	775	800
CIS	471	584	583	628	678	719
TD-HF	481	604	602	707	707	732
TD-B3LYP	559	613	613	676	699	768

Fig. 5. Different Ti–fulvene bonding modes in the series of complexes **1**–**6**, from dianionic to olefinic mode.
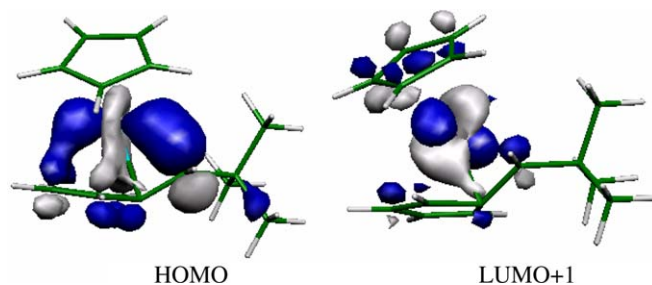

Fig. 7. Visualization of the HOMO and LUMO+1 orbitals of **2** showing the two orbitals involved in the excitation.

Table 4
Relevant natural population analysis partial charges and hybridization in complexes **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
NPA charges						
C6	−0.449	−0.389	−0.401	−0.191	−0.170	−0.176
Ti	1.522	1.420	1.452	1.435	1.461	1.467
Hybridization sp^x						
C6 (in C1–C6 bond)	2.39	2.30	2.28	2.27	2.26	2.11
C1 (in C1–C6 bond)	1.71	1.70	1.69	1.72	1.67	1.71
C6 (in Ti–C6 bond)	8.10	9.78	9.45	14.25	12.53	19.69

ity of UV absorptions of complexes **2** and **3** is confirmed by all three methods.

All methods agree in their conclusion about the excitation behavior of the complexes. The absorption maxima increase, resulting in an easier excitation. A closer look at the nature of these excitations by means of population analyses of the complexes revealed that all excitations have the same nature: an electron from the HOMO of the complex is excited in the LUMO+1 orbital. The HOMO is formed mainly from the Ti–C6 bond orbital, while the unoccupied orbital can best be described as a d orbital at the titanium centre (Fig. 7). The excitation is therefore a ligand-to-metal charge transfer (LMCT).

The structural investigations above indicate a change from a dianionic to an olefinic coordination of the fulvene ligand to the metal. In Table 4 are listed the results of the natural bond orbital analysis.

The partial charges at C6 reflect the change from mono- to disubstituted fulvenes, the last three entries with small charges belong to the latter category. Apart from the obvious influence of a chlorine substituent instead of a methyl group (in **1**) and that of a Cp* instead of Cp (**2** and **3**, respectively), the variations of the Ti partial charges are not sensitive enough to allow for a valid assessment. While the hybridization of the C1 atom (in the C1–C6 bond) remains almost constant throughout the series, there are several effects at C6: the hybridization of this atom in the C1–C6 bond diminishes, effectively freeing p orbital contribution which in turn can be located in the C6–Ti bond. This results in an increased olefinic coordination form of the latter complexes, confirming the structural findings of the gradual change from the dianionic coordination.

Temperature-dependent NMR spectra indicate free rotation of the fulvene ligand in complex **6**, and hence only a weak interaction between the two fragments, while the remaining systems do not exhibit a rotational motion. The NBO analysis however shows a Ti–C6 bond in each complex, including **6**. To verify the interactions, all the complexes were analyzed with AIM, but all disubstituted complexes **4**–**6** reveal no bonding interaction between Ti and C6. These seemingly different findings point at a difficulty inherent to population analyses: depending on the method chosen for the investigation, one can get very different results and has to take precautions in evaluating them. In the present case, calculations with model systems demonstrate that the AIM approach underestimates interactions at bond lengths longer than 2.45 Å. The general picture of bonding interactions between C6 and Ti given by the NBO analysis is valid. The occurrence of a "formal" bond in complex **6** however does not rule out the experimentally observed free rotation.

5. Conclusions

B3LYP/6-31G(d) reproduces in excellent agreement the available structural data of pentafulvene titanium complexes. The calculations presented herein demonstrate a gradual change of the coordination mode of the fulvene ligand to the titanium centre from a dianionic η^5, η^1- to an olefinic η^6-coordination form. This is further supported by the analysis of geometrical features and population analyses. As a result of our excitation studies, the "best" approach (TD-B3LYP) reproduces the experimental UV data reasonably well, although systematically slightly too small values are theoretically obtained. It further testifies that the absorption maxima as shown in the recorded UV–Vis spectra correspond to a LMCT from the HOMO to the LUMO+1.

Acknowledgements

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