

# Are cyclopentadienyl complexes more stable than their pyrrolyl analogues?

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## Abstract

Metal- $\eta^5$ -cyclopentadienyl (M-Cp) and metal- $\eta^5$ -pyrrolyl (M-pyr) bond dissociation enthalpies in group 4 complexes were determined from DFT/B3LYP calculations with a VTZP basis set. Thermochemical cycles involving calculated enthalpies of ligand exchange reactions and experimental values of ligand electron affinities and M-Cl bond dissociation enthalpies were applied to  $[M(\eta^5\text{-X})Cl_3]$  piano stool complexes (M = Ti, Zr, Hf; X = pyr, Cp), allowing a comparative study of those metal-ligand bond strengths. The results indicate that both ligands establish weaker bonds with Ti than with the heavier elements, Zr and Hf. Very similar bond dissociation enthalpies were obtained for pyrrolyl and cyclopentadienyl (within  $1 \text{ kcal mol}^{-1}$ ), suggesting that the well known difference in reactivity between those families of complexes should derive from kinetic rather than thermodynamic causes. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Pyrrolyl; Cyclopentadienyl; Group 4; Bond dissociation enthalpies; Molecular orbital calculations; DFT

## 1. Introduction

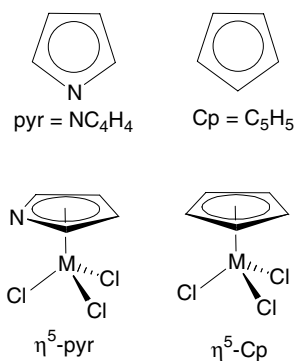
Despite the similarities between cyclopentadienyl (Cp =  $C_5H_5$ ) and pyrrolyl (pyr =  $NC_4H_4$ ), a striking difference is found in the development of their chemistry as ligands for transition metals. In fact, both ligands are isoelectronic and geometrically similar (Scheme 1), and both can coordinate a metal centre as  $\pi$  ligands in a  $\eta^5$  mode. However, complexes with pyrrolyl or substituted pyrrolyl ligands (pyr') are relatively scarce while cyclopentadienyl ligand is ubiquitous in organometallic chemistry. Furthermore, complexes with Cp, or substituted derivatives of this ligand (Cp'), play an important role in organometallic chemistry [1], with relevant applications in areas as different as catalysis [2] and cancer therapy [3,4].

Besides the historical reason for the preference of cyclopentadienyl as a ligand (related to the discovery of ferrocene structure), it has been claimed that pyrrolyl metal complexes are intrinsically unstable [5–7], explaining why they are so difficult to handle, compared to their Cp analogues. Nevertheless, continuing efforts have been made to explore the potentialities of pyr' ligands, as shown by some examples of recent theoretical [8] and experimental results [9,10]. The elegant work of Parkin et al. [10] is of particular notice since it represents the first series of structurally characterized Zr complexes with pyrrolyl coordinated in the two more important modes,  $\eta^5$ -pyr' and  $\sigma$ -pyr'.

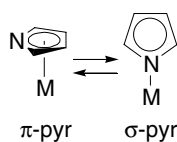
Our group has a long standing interest in pyrrolyl organometallic chemistry, namely in the synthesis of new pyrrolyl complexes and in the theoretical understanding of those species [11–17]. In the course of this work, we have focused our attention on the study of the metal-pyr' bond for the two limiting coordination modes of that ligand,  $\eta^5$ -pyr' and  $\sigma$ -pyr', and also on

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Scheme 1.



Scheme 2.

the mechanism for the interconversion between the two (Scheme 2), for tungsten [14] and zirconium complexes [15]. Very recently, in a comparative study of the interconversion process in Scheme 2 for  $[M(\text{pyr})\text{Cl}_3]$  complexes of the three metals of group 4 [16], we developed a strategy that allows the calculation of  $M-(\eta^5\text{-pyr})$  and  $M-(\sigma\text{-pyr})$  bond dissociation enthalpies, based on thermochemical cycles combining DFT [18] results and experimental values. In the present work, we extend that strategy to cyclopentadienyl complexes and use an improved theoretical model to compare the bond dissociation enthalpies,  $D(M-X)$ , for the two ligands in  $[M(\eta^5\text{-X})\text{Cl}_3]$  complexes ( $X = \text{pyr}, \text{Cp}$ ), with group 4 transition metals,  $M = \text{Ti}, \text{Zr},$  and  $\text{Hf}$ . The results allow a comparison of the  $M-X$  bond strengths, and the discussion of the reactivity for the two families of complexes. The application of the same methodology to other metals and different  $\pi$  ligands is straightforward and is currently under study.

## 2. Results and discussion

The performance of the computational model (see Section 4) is well established by previous works for both pyr [14–16] and Cp [19] complexes. The optimized geometries obtained for the six complexes,  $[M(\eta^5\text{-X})\text{Cl}_3]$  ( $X = \text{pyr}, \text{Cp}; M = \text{Ti}, \text{Zr}, \text{Hf}$ ), correspond to typical piano stool species. As an example, the results for the Ti species are shown in Fig. 1, with the more relevant bond lengths.

The geometries of the two complexes in Fig. 1 are very similar. With respect to the Ti–Cl bonds, the mean distance is 2.21 Å for the pyr complex and 2.22 Å for the

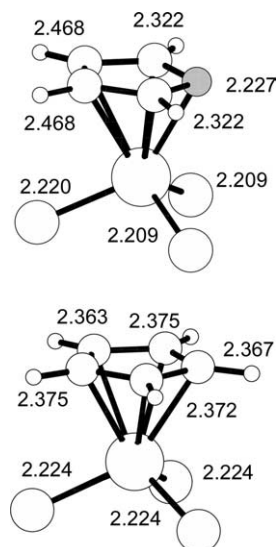


Fig. 1. Optimized geometries (B3LYP) of the Ti complexes,  $[\text{Ti}(\eta^5\text{-X})\text{Cl}_3]$ , for  $X = \text{pyr}$  (top) and  $X = \text{Cp}$  (bottom). The bond lengths to the metal are given (Å), and the N atom is shaded.

Cp species. The mean  $\text{ct}_X\text{-Ti-Cl}$  angle is the same in both molecules ( $115^\circ$ ,  $\text{ct}_X$  being the ring centroid), within the typical values for piano stool complexes [20]. However, the ring coordination geometry is slightly different in the two molecules. In the Cp case, all carbon atoms have practically the same Ti–C bond length (within 0.01 Å), affording a good example of nearly perfect  $\eta^5$  coordination of a Cp ring. In the pyr complex, a slight distortion of the pyr coordination towards a  $\eta^3 + \eta^2$  mode is noted, with the corresponding shortening of the Ti–N bond with respect to the Ti–C ones. This is typical of pyrrolyl complexes [11], representing a tilting of the ring, and can be measured, for example, by the slipping parameter,  $\Delta$ , originally introduced to characterise the coordination geometry of C<sub>5</sub> rings [21]. In an extension of its use to pyrrolyl rings,  $\Delta$  may be defined as the difference between (a) the mean distance from the metal to the nitrogen and the two adjacent carbons, and (b) the mean distance from the metal to the two remaining carbon atoms. This parameter has been widely used before to characterise the coordination geometry of pyrrolyl rings in organometallic complexes, and its value for the pyr complex of Fig. 1 (0.18 Å) is characteristic of pyr  $\pi$  complexes [14–16]. Despite the slight distortion from a perfect  $\eta^5$  coordination found in the pyr complex and absent in the Cp species ( $\Delta = 0$ ), the overall coordination of the two ligands is similar in the two molecules, as is shown by the mean distance from the metal to the five ring atoms, 2.36 and 2.37 Å for the pyr and the Cp species, respectively. Similar conclusions result from the comparison of the optimized geometries of the pyr and the Cp complexes obtained for the heavier elements, Zr and Hf. The

coordinates for all the optimized geometries are given as Supporting Information.

It is interesting to compare the optimized geometry of [TiCpCl<sub>3</sub>] with the experimental solid state structure determined by means of X-ray crystallography [22]. In fact, this is the only complex in the present study for which a X-ray structure is available, as is shown by a Cambridge Structural Database (CSD) [20] survey. The experimental values of 2.31 and 2.22 Å for Ti–C and Ti–Cl mean distances, respectively, and 115 ° for the ct<sub>Cp</sub>–Ti–Cl mean angle, compare well with the computed values, given above.

The strategy used for the calculation of the M–X bond dissociation enthalpies,  $D(\text{M–X})$ , in the [M( $\eta^5$ -X)Cl<sub>3</sub>] complexes is described by the thermochemical cycle of Scheme 3. The reaction on the left side of the cycle is a ligand exchange reaction where the  $\pi$  ligand in the [M( $\eta^5$ -X)Cl<sub>3</sub>] species is exchanged by a chloride, forming the corresponding tetrachloro complex, MCl<sub>4</sub>, and free anion, X<sup>-</sup>. The enthalpy of this reaction,  $\Delta H_{\text{R}}$  is the only quantity in the cycle obtained by means of DFT/B3LYP [23–25] calculations. The tetrachloro complexes, MCl<sub>4</sub>, and the free ligands were optimized using the same theoretical level applied to the [M( $\eta^5$ -X)Cl<sub>3</sub>] complexes (see Section 4). In fact, this is the main advantage of the method. The bond dissociation enthalpies,  $D(\text{M–X})$ , are derived from the enthalpy variation of a simple reaction involving only closed shell molecules with conservation of the number of electron pairs. A direct calculation of  $D(\text{M–X})$  yielding accurate results would require higher level theoretical methods, able to provide a very good description of electron correlation [26]; the computational cost associated with the application of such methods normally precludes their use for the study of many systems of practical interest.

The bottom reaction in the cycle is the dissociation of one ligand from the tetrachloro complex, MCl<sub>4</sub>, producing MCl<sub>3</sub> and a chlorine atom. The corresponding enthalpies used in the present study are 83, 112 and 114 kcal mol<sup>-1</sup>, for Ti, Zr and Hf, respectively [27].

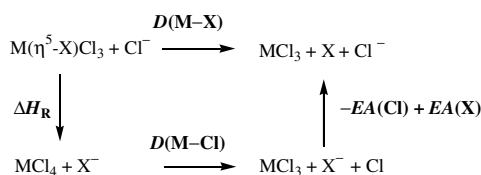
Finally, the reaction on the right side of Scheme 3 corresponds to a one electron exchange between the anionic ligand, X<sup>-</sup>, and a chlorine atom, resulting in the neutral radical, X, and a chloride anion, Cl<sup>-</sup>. The

enthalpy involved is the difference between the electron affinities (EA) of the two species, X and Cl. Experimental values for the adiabatic electron affinities (EA) of all the intervening species can also be found in the literature: 83 kcal mol<sup>-1</sup> (Cl) [28], 55 kcal mol<sup>-1</sup> (pyr) [29], and 41 kcal mol<sup>-1</sup> (Cp) [30].

Eq. (1), also shown in Scheme 3, is derived from the thermochemical cycle and allows the calculation of the desired bond dissociation enthalpies,  $D(\text{M–X})$ . The values obtained are presented in Table 1.

To the best of our knowledge, there are no experimental values for bond dissociation enthalpies of  $\eta^5$ -pyr or  $\eta^5$ -Cp in group 4 metal complexes and, thus, the calculated results cannot be tested by direct comparison with experimental data. However, the same theoretical method proved successful in the determination of Ir–halogen bond enthalpies [31], and allowed the comparative study of the slippage process between  $\pi$ -pyr' ( $\eta^5$ ) and  $\sigma$ -pyr' in [M(pyr)Cl<sub>3</sub>] complexes with group 4 metals (Ti, Zr and Hf) [16]. Furthermore, basis set convergence, in size, seems to be attained for the studied systems, since the differences between the  $D(\text{M–X})$  values here reported (B3LYP/VTZP) and the ones obtained with a smaller basis set (VDZP) are within 3 kcal mol<sup>-1</sup>, for both pyr [16] and Cp.

It is important to stress that even if the absolute values of Table 1 are affected by some systematic error, both the trends of  $D(\text{M–Cp})$  and  $D(\text{M–pyr})$  for the three metals (columns in Table 1) and, especially, the comparison between the two  $\pi$  ligands, pyrrolyl and cyclopentadienyl, for each metal (rows in Table 1), should be reliable. Although the results for M = Hf may be affected by relativistic effects, these are expected to be taken into account, at least partially, by the basis set used for the metals (see Section 4). Consequently, this work is focused on the *comparison* of the bond dissociation enthalpies for a given ligand in complexes with the different metals, and on the *relative* values of the bond enthalpy for the two ligands (pyr and Cp) for each metal. This avoids most systematic errors related to the theory level used. It also takes care of solvent effects, which are



$$D(\text{M-X}) = \Delta H_{\text{R}} + D(\text{M-Cl}) - EA(\text{Cl}) + EA(\text{X}) \quad (1)$$

Scheme 3.

Table 1

Bond dissociation enthalpies (kcal mol<sup>-1</sup>),  $D(\text{M–X})$ , for the [M( $\eta^5$ -X)Cl<sub>3</sub>] complexes (X = pyr, Cp)<sup>a</sup>

Metal (M)	X Ligand (pyr = NC <sub>4</sub> H <sub>4</sub> , Cp = C <sub>5</sub> H <sub>5</sub> )	
	pyr	Cp
Ti	69	70
Zr	101	100
Hf	102	101

<sup>a</sup> Obtained from Eq. (1), in Scheme 3, using the DFT calculated  $\Delta H_{\text{R}}$  and the following experimental values (kcal mol<sup>-1</sup>):  $D(\text{M–Cl})$  = 83 (Ti), 112 (Zr), 114 (Hf) [27],  $EA(\text{Cl})$  = 83 [28],  $EA(\text{pyr})$  = 55 [29] and  $EA(\text{Cp})$  = 41 [30].

more likely to be cancelled out when relative values are considered.

The values of  $D(\text{M}-\text{Cp})$  in the metallocenes  $\text{MCp}_2$ , obtained in the gas phase by Optiz, using electron impact ionization mass spectrometry, may be used for a gross comparison with the ones calculated here for the  $[\text{M}(\eta^5\text{-Cp})\text{Cl}_3]$  complexes, taking into consideration the differences between the species involved. The  $D(\text{M}-\text{Cp})$  enthalpies, determined for the stepwise dissociation of each one of the two Cp ligands in the neutral ( $\text{MCp}_2$ ) and in the cationic homoleptic metallocenes,  $\text{MCp}_2^+$  ( $\text{M} = \text{Co}, \text{Mn}$ ), are within the following ranges: 64–112 kcal mol<sup>-1</sup> for  $\text{M} = \text{Co}$  [32], and 49–74 kcal mol<sup>-1</sup> for  $\text{M} = \text{Mn}$  [33]. It is important to stress that these results provide only an order of magnitude for comparison with the bond enthalpies of Table 1, given the dissimilarities of the complexes, both in terms of geometry as well as in the nature of the transition metal.

Two main conclusions can be drawn from the values in Table 1. The first is that  $D(\text{Ti}-\text{X}) < D(\text{Zr}-\text{X}) \approx D(\text{Hf}-\text{X})$  and this trend is very similar for pyr and Cp. Incidentally, the same trend is observed when the experimental  $\text{M}-\text{Cl}$  mean bond dissociation enthalpies for  $\text{MCl}_4$  (see above) are compared [27c]. The second, and perhaps more interesting conclusion, is that the  $\text{M}-(\eta^5\text{-X})$  bond strengths for pyrrolyl and cyclopentadienyl are almost identical! This similarity is in keeping with the geometric features obtained in the optimized structures for the respective complexes (see above), which are also quite similar, and with a simple molecular orbital analysis of the  $\text{M}-(\eta^5\text{-X})$  bonds, comparing Cp [19] and pyr [14,15]. In both cases the bond is based on three orbital interactions, corresponding to three formal 2-electron donations to the metal, and involving orbitals of the ligand  $\pi$  system with essentially the same topological characteristics. Another aspect that parallels the close resemblance of the two  $\text{M}-(\eta^5\text{-X})$  bonds are the metal charges on the optimized complexes,  $[\text{M}(\eta^5\text{-Cp})\text{Cl}_3]$ , obtained by means of a Natural Population Analysis (NPA) [34]. The values calculated for the two complexes with the same metal are equal within 0.02 electrons, showing that both ligands have roughly the same donating capability.

The results above indicate that, from a thermodynamic point of view, the  $\text{M}-\text{Cp}$  and the  $\text{M}-\text{pyr}$  bonds are equally stable in the complexes considered. The well known differences in reactivity between the two families of complexes should thus derive from on kinetic factors. One possible explanation for the higher reactivity of pyr complexes, is the interchange process between the two coordination modes of the pyr ligand,  $\pi$ -pyr and  $\sigma$ -pyr (see Scheme 2), that was shown to be reasonably easy to occur even at room temperature, at least for group 4 metal complexes [15,16]. In fact, the slippage of the pyrrolyl from a  $\pi$  coordination ( $\eta^5$ ) to a  $\sigma$  mode, yields an electronically deficient metal centre and a coordin-

atively unsaturated molecule, thus opening a way to an enhanced reactivity and possible decomposition. There is no equivalent of such a process in a Cp complex because in this ligand there is no heteroatom lone pair capable of establishing a  $\sigma$  bond to the metal, comparable to the one existing in a  $\sigma$ -pyr species. In fact, repeated attempts to optimize  $\sigma$ , or  $\eta^1$ , Cp complexes of the type  $[\text{M}(\text{Cp})\text{Cl}_3]$  always ended up in the  $\eta^5$  species.

### 3. Conclusions

The calculated bond dissociation enthalpies,  $D(\text{M}-\text{X})$ , for the group 4 metal complexes,  $[\text{M}(\eta^5\text{-X})\text{Cl}_3]$ , with pyrrolyl and cyclopentadienyl  $\pi$  ligands (X), increase in the order  $\text{Ti} < \text{Zr} \approx \text{Hf}$ , for both ligands.

For practical purposes, equal bond dissociation enthalpies are obtained for the  $\text{M}-(\eta^5\text{-X})$  bonds of cyclopentadienyl and pyrrolyl. This implies that the known instability of pyrrolyl complexes, when compared to their cyclopentadienyl analogues, should be due to kinetic causes.

### 4. Computational details

All calculations were performed using the GAUSSIAN 98 software package [35], and the B3LYP hybrid functional. That functional includes a mixture of Hartree–Fock [26a] exchange with DFT [18] exchange–correlation, given by Becke’s three parameter functional [23] with the Lee, Yang and Parr correlation functional, which includes both local and non-local terms [24,25]. The Stuttgart/Dresden ECP (SDD) basis set [36] augmented with a f-polarization function [37] was used for the metals, and a standard 6-311G(d,p) basis set [38] for the remaining elements. All geometries were optimized without symmetry constraints. The enthalpies were obtained at 298.15 K and 1 atm, by conversion of the zero point corrected electronic energies with the thermal energy corrections based on the calculated structural and vibrational frequency data. The atomic charges on the optimized molecules were obtained by means of a Natural Population Analysis (NPA) [34].

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### Appendix A. Supplementary data

Tables of atomic coordinates for all the optimized species. Ordering information is given on any current

masthead page. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.02.010.

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(c) The application of the same theory level used in this work (B3LYP/VTZP) for the direct calculation of  $D(M-X)$  (top step of the thermochemical cycle of Scheme 3) yields values 10–32 kcal mol<sup>-1</sup> lower than the ones obtained through the cycle and presented in Table 1.
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