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# Structure and dynamics in unsymmetrically substituted five-coordinate iridacyclopentadiene complexes<sup>†</sup>

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The structure and dynamics of five-coordinate iridacyclopentadiene–chlorido and –hydrido complexes of the form  $[(\text{PH}_3)_2\text{Ir}(\text{CY}=\text{CYCY}'=\text{CY}')\text{X}]$  ( $\text{X}=\text{Cl}$  or  $\text{H}$  and  $\text{Y}=\text{F}$  and/or  $\text{H}$ ) are investigated by M06-2X/Def2-TZVPP density functional theory computation. For the symmetrically substituted ring systems ( $\text{Y}=\text{Y}'=\text{H}$  and  $\text{Y}=\text{Y}'=\text{F}$ ) the minimum energy chlorido structures are Y-shaped trigonal bipyramids; whereas the hydrido complexes favor a T-structure. Both the symmetrically and unsymmetrically ( $\text{Y}=\text{H}$ ,  $\text{Y}'=\text{F}$ ) substituted hydrido complexes exhibit double well potentials for the hydrido ligand wag motion within the metallacycle ring plane, the depths of the well depending on the degree of steric, and electronic interactions within the particular constitutional isomer. Copyright © 2014 John Wiley & Sons, Ltd.

**Keywords:** iridacyclopentadiene; metallacyclopentadiene; computation; dynamics; hydrido

The buta-1,3-dien-1,4-diyl ligand is important as both a reactive ligand in alkyne cyclotrimerization reactions<sup>[1]</sup> and as a “spectator” ligand<sup>[2]</sup> in transition metal catalysts. Considerable attention has therefore been directed toward understanding the structure, properties, and reactivity of metallacyclopentadiene complexes. Interest in iridacyclopentadienes dates from Collman’s synthesis of five-coordinate  $[(\text{PPh}_3)_2\text{Ir}(\text{CR}=\text{CR}=\text{CR})\text{Cl}]$  (**1**,  $\text{R}=\text{CO}_2\text{CH}_3$ ),<sup>[3]</sup> which was later shown to exist in the solid state as a distorted trigonal bipyramid with unequal C–Ir–Cl angles (Fig. 1).<sup>[4]</sup> Related complexes, such as  $[(\text{PPh}_3)_2\text{Ir}(\text{biph})\text{Cl}]$  (**2**,  $\text{biph}=\text{biphenyl-2,2'-diyl}$ ),<sup>[5]</sup> also exist in the solid state as distorted trigonal bipyramidal structures.<sup>[6]</sup>

Maseras, Eisenstein, and Crabtree have defined the parameter  $\phi=[1/2(\omega_1+\omega_2)-\omega_1]$  the deviation of five-coordinate metallacyclopentadiene structures from an ideal Y-geometry, where  $\phi=[1/2(\omega_1+\omega_2)-\omega_1]$ ,  $\omega_1$  is the  $\text{C}_{\text{cis}}-\text{Ir}-\text{X}$  angle and  $\omega_2$  is the  $\text{C}_{\text{trans}}-\text{Ir}-\text{X}$  angle (Fig. 2).<sup>[7]</sup> The symmetrically substituted complexes **1** and **2** exhibit Y/T-geometries in the solid state with  $\phi=5^\circ$  and  $10^\circ$ , respectively.

In order to further develop the chemistry of iridacyclopentadienes<sup>[8]</sup> we sought to establish the structures and properties of iridacycles in which the  $\alpha$ -carbons (C1, C4) within a buta-1,3-dien-1,4-diyl ligand bear different substituents. Here we report M06-2X/Def2-TZVPP density functional theory computations on the prototype metallacycle systems represented by structures **3**–**5** (Fig. 3). The results reveal a significant structural dependence on both the nature of the metallacycle substituents and the nature of the  $\kappa^1$  ligand (halido or hydrido). In the case of the hydrido complexes, **3**-H–**5**-H, double well potentials are identified for the wag motion of the hydrido ligand within the plane of the metallacycle ring.

For all iridacyclopentadiene complexes described herein the metallacycle ring is planar and the buta-1,3-dien-1,4-diyl ligand exhibits alternating single [C(2)–C(3)] and double bond [C(1)–C(2) and C(3)–C(4)] lengths. In the case of the symmetric iridium–chlorido systems, **3**-Cl and **4**-Cl, the chlorido ligand is located within the plane of the metallacycle ring, and the calculated minimum energy structures are of pure Y geometry,

with  $\phi=0^\circ$  (indicated as **3**-Cl-I and **4**-Cl-I in Table 1).<sup>[9]</sup> The potential energy surface for these chlorido structures is very flat. In particular, twisting about the Ir–PH<sub>3</sub> bonds generates nearly identical energy structures with essentially no energetic cost. The Ir–Cl bond distance in **3**-Cl-I (2.421 Å) is 0.032 Å longer than in **4**-Cl-I (2.389 Å), consistent with a higher degree of pi-donation by the chlorido ligand in the complex bearing the more electronegative fluorine ring substituents. Alternative Y/T- or pure T-structures were not found; however, in the case of **4**-Cl a higher energy minima corresponding to a distorted trigonal bipyramidal structure with *cis* PH<sub>3</sub> ligands was located at 5.2 kcal higher energy (**4**-Cl-IV, Table 1).

For the unsymmetrically substituted metallacycle **5**-Cl the minimum energy structure is best described as a Y/T-structure (**5**-Cl-III) with C(1)–Ir–Cl and C(4)–Ir–Cl angles

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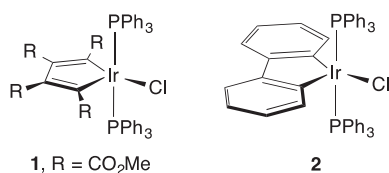
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**Figure 1.** Representative examples of structurally characterized five-coordinate iridacyclopentadienes

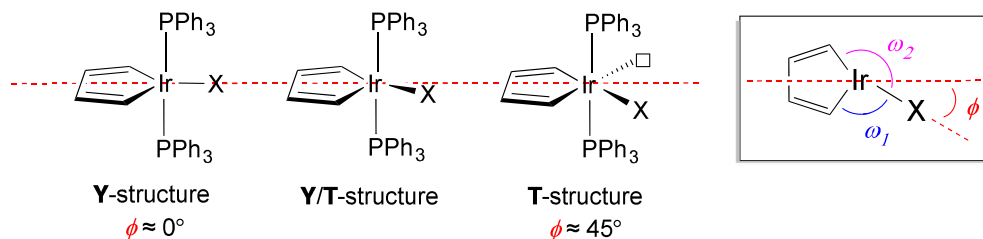
of 152.1° and 131.5°, and  $\phi = 10.3^\circ$  Fig. 4). The chlorido ligand is located within the metallacycle ring mean plane but displaced away from the metallacycle carbon (C1) bearing a fluorine substituent. In all attempts to find a minimum with the chlorido ligand on the side nearest the fluorine ring substituent, the starting structure optimizes to the other form to alleviate the steric repulsion between a fluorine lone pair and a chlorido ligand lone pair. As was the case for **4-Cl**, a distorted trigonal bipyramidal structure with cis-PH<sub>3</sub> ligands, was located at higher energy (**5-Cl-IV**, 5.5 kcal). This higher energy isomer has the metallacycle carbon bearing the fluorine substituent in an axial position and metallacycle carbon (C4) bearing the hydrogen substituent in the equatorial plane (Fig. 4, right panel). The distorted trigonal bipyramidal structures **4-Cl-IV** and **5-Cl-IV** exhibit remarkably acute equatorial P – Ir – C angles of 74.3° and 74.7°, respectively. Related non-metallacycle structures have been observed previously for 5-coordinate iridium complexes in which the acute angle within the equatorial plane is opposite a pi-donor ligand (Z),<sup>[10]</sup> and Eisenstein has determined that the pi-donating ligand plays a determining role in stabilizing the electronically unsaturated metal center by engaging in partial M – Z multiple bonding.<sup>[11]</sup> A comparison of **4-Cl-I** to **4-Cl-IV**, and of **5-Cl-III** to **5-Cl-IV** suggests greater pi-back bonding from the chloride ligand in the cis-phosphine structures than in the trans phosphine structures. The Ir – Cl bond distance in **4-Cl-IV** is 0.036 Å shorter than in **4-Cl-I** and the Ir – Cl distance in **5-Cl-IV** is 0.039 Å shorter than in **5-Cl-III**.

Eisenstein has previously noted that replacing a weak sigma-donor, good pi-donor chlorido ligand in Ir(biph)Cl (PH<sub>3</sub>)<sub>2</sub> with a hydrido ligand converts the Y-structure to a

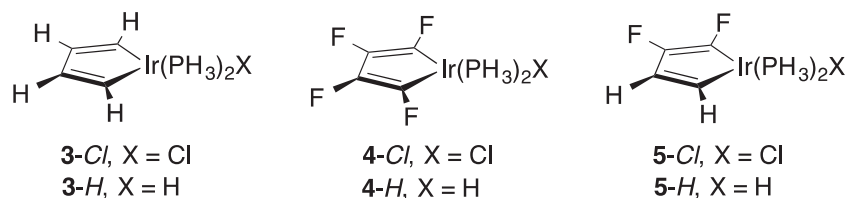
T-structure.<sup>5b</sup> In the metallacycles examined here, changing the nature of the X ligand from chlorido to hydrido leads to the symmetric iridium systems, **3-H** and **4-H**, which both adopt homomeric Cs symmetric ground state structures, as shown in Table 1: **3-H-II/3-H-III** and **4-H-II/4-H-III**, respectively. For both complexes, the ground state structures are separated by C<sub>2v</sub> symmetric transition states (**3-H-I** and **4-H-I**), leading to a symmetric double well potential for the hydrido wag motion within the mean plane of the metallacycle ring (Fig. 5). The barrier to interconversion from the two identical forms on the respective potential surfaces is essentially the same (2.1 vs 1.8 kcal/mol, respectively) whether the peripheral ring substituents are hydrogen or fluorine (Fig. 5, left panel).

The unsymmetric complex, **5-H**, introduces a much different minimum energy structure (**5-H-V**) with cis-phosphine ligands and the hydrido ligand trans to a phosphine (Fig. 6). In addition, there are now three structures with the hydrido ligand positioned within the metallacycle ring plane (**5-H-II**, **5-H-II'**, **5-H-III**), none of which is a pure Y-structure. Two of these structures, **5-H-II** and **5-H-III**, are essentially T-structures with nearly identical  $\phi$  values of 39.2° and 39.4°, respectively. The structure with the hydrido ligand proximal to fluorine F<sub>pro</sub> (**5-H-II**) is 2.7 kcal higher in energy than the isomer with the hydrido ligand proximal to a ring hydrogen H<sub>pro</sub> (**5-H-III**). The third structure with the hydrido ligand located in the metallacycle plane (**5-H-II'**, 6.3 kcal) is the transition state structure connecting **5-H-II** and **5-H-III**. As such, an unsymmetric double well potential is obtained for the hydrido wag motion in **5-H**, the depths of the well depending on the degree of steric and electronic interactions in the structure (Fig. 5). The hydrido wag transition state structure, separating the two minima, gives a barrier of 3.6 kcal from the lowest energy structure, and only 0.9 kcal/mol from the higher energy structure.

In summary, these results indicate that for five-coordinate iridacyclopentadiene–chlorido complexes, Y/T and T-structures **3-Cl-II/4-Cl-II** and **3-Cl-III/4-Cl-III** are high in energy compared to the pure Y-structures **3-Cl-I/4-Cl-I**, as previously observed in the calculations of Eisenstein on **3-Cl**. However, the introduction of an unsymmetrically substituted ring system, as in **5-Cl**, leads to



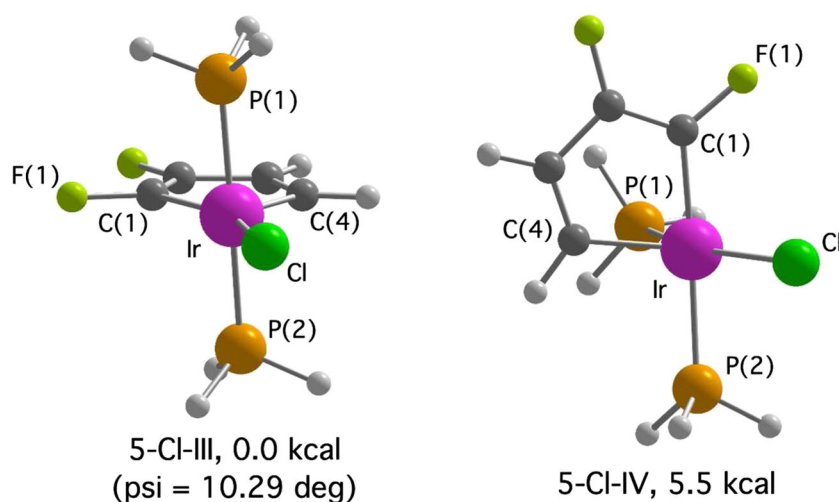
**Figure 2.** The position of the X ligand within the equatorial plane is defined by the parameter  $\phi$



**Figure 3.** Metallacyclopentadiene complexes used in the current study

**Table 1.** M06-2X/Def2-TZVPP computational results for iridium prototype systems **3** – **5**

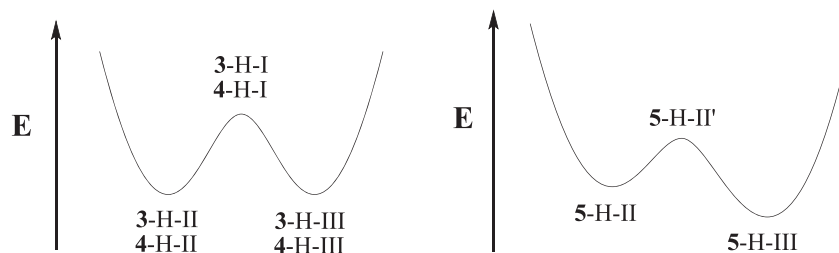
Complexes							
	I (Y-structure)	II (Y/T- or T-structure)	III (Y/T- or T-structure)	IV (cis-PH <sub>3</sub> -structure)			
No.	X	Y	Y'	I	II	III	IV
<b>3</b> -Cl	Cl	H	H	0.0 kcal	–	–	–
<b>4</b> -Cl	Cl	F	F	0.0 kcal	–	–	5.2 kcal
<b>5</b> -Cl	Cl	H	F	–	–	0.0 kcal	5.5 kcal
<b>3</b> -H	H	H	H	2.1 kcal	0.0 kcal $\phi = 39.5^\circ$	0.0 kcal $\phi = 39.5^\circ$	–
<b>4</b> -H	H	F	F	1.8 kcal	0.0 kcal $\phi = 39.2^\circ$	0.0 kcal $\phi = 39.2^\circ$	–
<b>5</b> -H	H	H	F	–	5.4 kcal ( <b>5</b> -H-II) $\phi = 39.2^\circ$ 6.3 kcal ( <b>5</b> -H-II') $\phi = 13.4^\circ$	2.7 kcal $\phi = 39.4^\circ$	see <b>5</b> -H-V 0 kcal (Fig. 6)

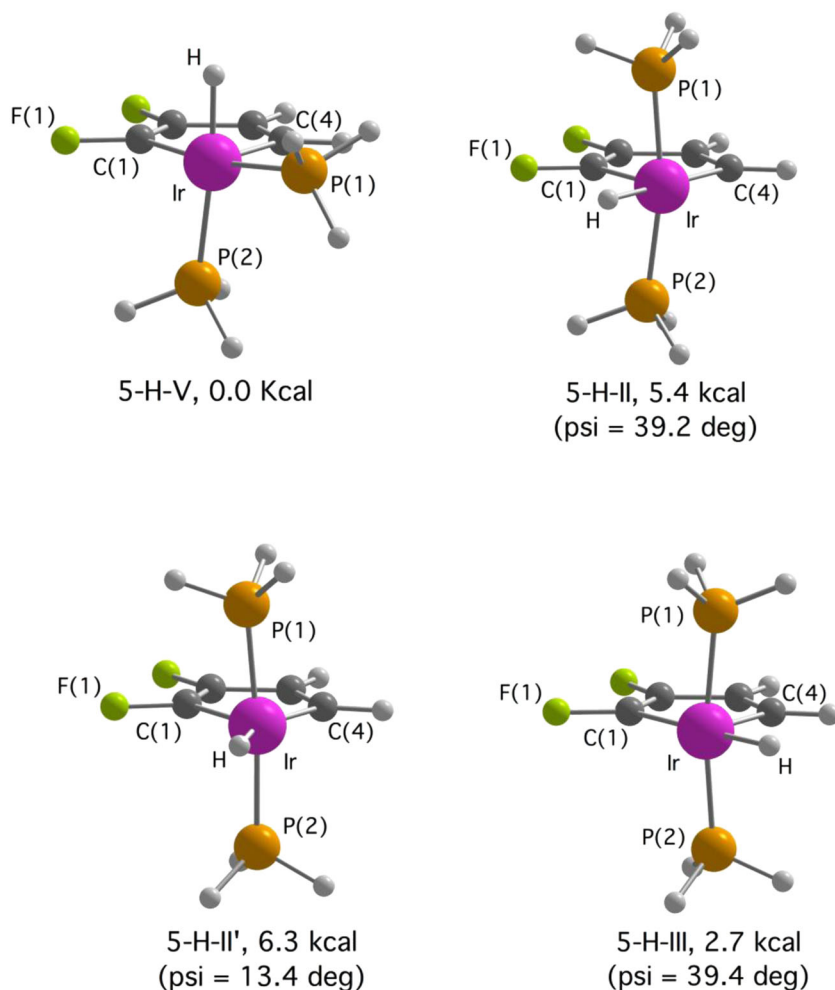
**Figure 4.** M06-2X/Def2-TZVPP computational results for **5**-Cl. Selected bond distances (Å) and angles (deg) for **5**-Cl-III: Ir – Cl 2.406, Ir – C(1) 1.986, Ir – C(4) 2.006, C(1) – C(2) 1.339, C(2) – C(3) 1.449, C(3) – C(4) 1.339; C1 – Ir – C(I) 152.1, C(4) – Ir – Cl 131.5. For **5**-Cl-IV: Ir – Cl 2.361, Ir – C(1) 2.027, Ir – C(4) 2.014, C(1) – C(2) 1.343, C(2) – C(3) 1.447, C(3) – C(4) 1.341; P(1) – Ir – C(4) 74.7, Cl – Ir – P(1) 155.7, Cl – Ir – C(4) 129.1, P(1) – Ir – P(2) 98.9

unfavorable fluoride–chlorido interactions that destabilize the Y-structure in favor of a Y/T-structure ( $\phi = 10.3^\circ$ ). Replacement of the chlorido ligand by hydrido favors T-structures ( $\phi = 39\text{--}40^\circ$ ), as in **3**-H-II/III and **4**-H-II/III, and a shallow double well potential exists for the hydrido ligand wag motion within the plane of the metallacycle ring. For the unsymmetrically substituted metallacycle–hydrido complex **5**-H an unsymmetrical double well potential exists with T-structures **5**-H-II and **5**-H-III interconverting via the Y/T-structure **5**-H-II'. Efforts are underway to prepare unsymmetrically substituted iridacyclopentadiene–chlorido and hydrido complexes with bulky ring substituents in order to establish structure–selectivity relationships for addition of a sixth ligand at iridium.

## COMPUTATIONAL METHODS

The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements as well as property calculations, were carried out using the GAMESS<sup>[12]</sup> software package. The hybrid metal density functional with kinetic energy density gradient, M06-2X,<sup>[13,14]</sup> was used together with the Def2-TZVPP basis set.<sup>[15]</sup> Full geometry optimizations were performed and uniquely characterized via second derivatives (Hessian) analysis to determine the number of imaginary frequencies (0 = minima; 1 = transition state), and effects of zero point energy. Visualization and analysis of structural and property results were obtained using Avagadro<sup>[16]</sup> and WEBMO.<sup>[17]</sup>

**Figure 5.** Double-Well Potentials for metallacycle hydrido complexes **3**–**5**-H



**Figure 6.** M06-2X/Def2-TZVPP computational results for **5-H**. Selected bond distances (Å) and angles (deg) for **5-H-V**: Ir – H 1.598, Ir – C(1) 2.045, Ir – C(4) 1.988, C(1) – C(2) 1.337, C(2) – C(3) 1.450, C(3) – C(4) 1.338; C(1) – Ir – H 87.8, C(4) – Ir – H 87.4, P(1) – Ir – P(2) 105.0. **5-H-II**: Ir – H 1.657, Ir – C(1) 1.962, Ir – C(4) 2.116, C(1) – C(2) 1.340, C(2) – C(3) 1.454, C(3) – C(4) 1.342; C(1) – Ir – H 101.1, C(4) – Ir – H 180.0, P(1) – Ir – P(2) 105.0. For **5-H-II'**: Ir – H 1.710, Ir – C(1) 1.978, Ir – C(4) 2.063, C(1) – C(2) 1.339, C(2) – C(3) 1.451, C(3) – C(4) 1.339; C(1) – Ir – H 129.0, C(4) – Ir – H 155.8, P(1) – Ir – P(2) 174.6. For **5-H-III**: Ir – H 1.647, Ir – C(1) 2.100, Ir – C(4) 1.998, C(1) – C(2) 1.340, C(2) – C(3) 1.452, C(3) – C(4) 1.338, C(1) – Ir – H 176.4, C(4) – Ir – C(1) 97.7, P(1) – Ir – P(2) 170.5

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