

## Tuning the tripodal rotational barrier in $\eta^6$ -chromiumtricarbonyl heteroarenes – A step towards torsional switches

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Received 12 October 2016; revised and accepted 27 May 2017

The current work focuses on manifold magnification of tripodal rotational barrier of  $\text{Cr}(\text{CO})_3$  which is haptotopically bound to the arene ring with variety of hetero substitution (boron/phosphorus). The study shows that the differential electronegativities of boron and phosphorus can be harnessed to manipulate the torsional barrier, enabling hundred 200-fold enhancement of barrier to nearly free tripodal rotation of  $\text{Cr}(\text{CO})_3$  in arene moiety. Insights obtained by density functional studies are supported by natural bond orbital analysis.

**Keywords:** Tripodal rotational barrier, Tricarbonyl chromium complexes, Carbonyl complexes, Chromium, Boron, Phosphorus, Density functional calculations, Natural bond orbital analysis, Torsional switches

Complexation of aromatic rings with  $\text{Cr}(\text{CO})_3$  has been a fantastic synthetic tool in the hands of the organic chemist in designing a variety of chiral reagents<sup>1-8</sup>. These highly versatile arene-chromium tricarbonyl compounds have potential applications ranging from organic synthesis<sup>9,10</sup>, molecular switches<sup>11,12</sup>, tunable molecular wires<sup>13</sup>, optical information storage devices<sup>14,15</sup> to non linear optical (NLO) materials<sup>16</sup>. Tripodal moiety pivoted to the aromatic ring centre rotates relatively freely (negligible rotational barrier)<sup>17</sup> and substituents on the ring influence both the conformation and the torsional barrier<sup>18</sup>. Electron donating substituents favour syn eclipsed orientation of  $\text{Cr}(\text{CO})_3$ , while electron withdrawing groups prefers the anti eclipsed orientation<sup>19</sup>. Remarkable barrier enhancement has been observed by multiple fluoro substitution<sup>20</sup>. Further, phosphabenzene also show similar magnification of torsional barrier<sup>21</sup>.

Similar to borazine ( $\text{B}_3\text{N}_3$ ), its phosphorus analogue ( $\text{B}_3\text{P}_3$ ) is a particularly good candidate with sufficient electronegativity difference and currently the studies are targeted on such BP analogues<sup>22-28</sup>. Heterocycles with embedded boron and phosphorus

atoms ( $\text{MesBPC}_6\text{H}_{11}$ )<sub>3</sub> have also been synthesised<sup>22</sup>. Further, ( $\text{MesBPtBu}$ )<sub>3</sub> has been complexed with tripodal  $\text{Cr}(\text{CO})_3$  to form  $\eta^6$ -complex<sup>23</sup>.

In the pursuit of conformational switches, the present study aims at incorporating push and pull strategy in enhancing the torsional barrier to tripodal rotation of  $\text{Cr}(\text{CO})_3$  relatively much higher. The prominent and befitting candidate for operating the push-pull effect would be those with large electronegativity differences. Therefore, in the present work different combinations of boron and phosphorus atoms are embedded in the benzene ring. We have critically examined the factors controlling the relative stabilities of these isomers, their rotational energy barriers as well as the alterations of structural and electronic factors due to skeletal substitutions. The NBO analyses have been carried out to have a deeper insight into the structure and stability of the complexes under study.

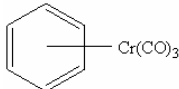
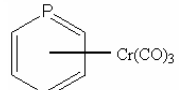
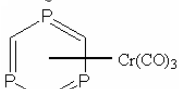
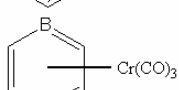
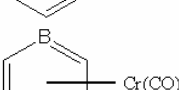
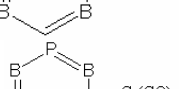
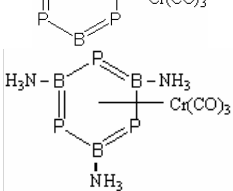
### Computational details

All calculations were performed with the GAUSSIAN-98 program<sup>29</sup>. Geometry optimizations utilized the B3LYP method<sup>30-33</sup> and the LANL2DZ basis set<sup>34</sup>. Previous studies have shown this to be an appropriate level of theory for chromium tricarbonyl complexed arenes<sup>35-41</sup>. All optimized structures were characterized by frequency analysis. Nucleus-independent chemical shifts (NICS)<sup>42</sup> were calculated at the geometrical centres of the ring atoms NICS(0), and also 1 Å above the ring NICS(1) using the gauge invariant atomic orbital (GIAO)<sup>43</sup> method at the B3LYP/6-311++g(d,p) using the geometries optimized at B3LYP/LANL2DZ level. NBO<sup>44-46</sup> calculations were carried out at B3LYP/LANL2DZ level.

### Results and discussion

The compounds chosen for conformational analysis (**I-VII**) are given in Table 1. Compound **I** is  $\eta^6$ -benzene tricarbonyl chromium while **II-VII** are skeletally hetero substituted ring analogues. **II** and **III** show the role of skeletal phosphorus on rotational barrier<sup>21</sup> while **IV** and **V** reveal the role of skeletal boron. **VI** and **VII** demonstrate the hand in hand effect of both boron and phosphorus. Further, **VII** projects the tuning of push effect of boron by stabilising lewis acid-base interaction. This can also

Table 1 — Conformational structures of systems (I-VII)

System	Structure	Nomenclature
I		$\eta^6$ -benzene tricarbonyl chromium
II		$\eta^6$ -phosphabenzene tricarbonyl chromium
III		$\eta^6$ -1,3,5-triphosphabenzene tricarbonyl chromium
IV		$\eta^6$ -borabenzene tricarbonyl chromium
V		$\eta^6$ -1,3,5-triborabenzene tricarbonyl chromium
VI		$\eta^6$ -1,3,5-triphospha-2,4,6-triborabenzene tricarbonyl chromium
VII		$\eta^6$ -1,3,5-triphospha-2,4,6-(triammine)borabenzene tricarbonyl chromium

reveal the possibility of tuning the barrier using lewis acid-base interaction strategy.

The computed conformational minima and their corresponding transition state with their rotational barrier to tripodal rotation are presented in Table 2. As has been reported earlier<sup>20,21</sup>, **I** has a negligible barrier (0.18 kcal/mol) and the phosphorus substitution increases the rotational barrier. Similar effect but larger in magnitude is rendered by skeletal boron. The 1,3,5-triphospha analogue (**VI**) has  $\Delta E_{\text{rot}}^\ddagger$  of 6.49 kcal/mol, while that of 1,3,5-tribora analogue (**V**) is three-folds larger ( $\Delta E_{\text{rot}}^\ddagger = 19.10$  kcal/mol) than the former. In **VI** where there is alternate boron and phosphorus, the barrier is very high ( $\Delta E_{\text{rot}}^\ddagger = 32.4$  kcal/mol). This is a remarkable barrier not obtained so far in any torsional variations. The negligible torsional barrier of just 0.2 kcal/mol in  $\eta^6$ -benzene tricarbonyl chromium has been now amplified to 32 kcal/mol by manipulating the differential electronegativity of hetero atoms in the ring skeleton. The quantum of energy as a rotational barrier is comparable with the activation energy of any bond breaking/making reaction. **VII** that shows a lewis acid-base interaction between  $\text{NH}_3$  and ring boron reduces the barrier by 12 kcal/mol compared to unsubstituted complex (**VI**) giving a scope for barrier tuning.

In minima conformation the  $\text{Cr}(\text{CO})_3$  moiety always prefers to anti eclipse the phosphorus atoms in phosphabenzene- $\text{Cr}(\text{CO})_3$  complexes (**II** and **III**) and syn eclipse the phosphorus atoms in their corresponding TSs. In borabenzene- $\text{Cr}(\text{CO})_3$  complexes, (**IV** and **V**), the  $\text{Cr}(\text{CO})_3$  fragment prefers to syn and anti eclipse with the boron in their minima and TS respectively. Similarly, in the case of complexes that have alternate boron and phosphorus, the  $\text{Cr}(\text{CO})_3$  moiety chooses to remain syn eclipsed with boron in their minima and with phosphorus in their TS. Thus, the conformational preference of the  $\eta^6$ -benzene tricarbonylchromium complexes (as staggered/syn/anti eclipsed) depends on the orientation of  $\text{Cr}(\text{CO})_3$  tripodal moiety, which in turn depends upon the nature of hetero atoms present in the benzene ring and difference in their electronegativities as compared to carbon atom.

Table 3 lists the energies of the frontier molecular orbitals and the hardness of both minima and the corresponding TSs. Generally, an activation barrier of reaction is related to its activation hardness<sup>47</sup>; larger the activation hardness, larger is the activation barrier. In the present study, the torsional barrier is strongly influenced by activation hardness. A good correlation

Table 2 — Rotational energy barrier ( $\Delta E_{\text{rot}}^{\ddagger}$ ) and optimized geometries of minima and transition state computed at B3LYP/LanL2DZ<sup>a</sup>

System	Minima	TS	$\Delta E_{\text{rot}}^{\ddagger}$ (kcal/mol)
I	Staggered 	Eclipsed 	0.18
II	Anti Eclipsed 	Syn Eclipsed 	2.65
III	Anti eclipsed 	Syn Eclipsed 	6.49
IV	Syn Eclipsed 	Anti Eclipsed 	5.16
V	Syn Eclipsed 	Anti Eclipsed 	19.10
VI	Syn Eclipsed with B 	Syn Eclipsed with P 	32.45
VII	Syn Eclipsed with B 	Syn Eclipsed with P 	20.42

<sup>a</sup>Ring carbons numbered 1–6 and 8, 9, 10 stand for the three carbonyl carbons of Cr(CO)<sub>3</sub> moiety.

Table 3 — Energies of frontier molecular orbitals of conformational minima and TS of **I-VII** at B3LYP/LANL2DZ level

System	Minima			TS			$\Delta\eta^\ddagger$ (eV) <sup>b</sup>	$\Delta E_{\text{rot}}^\ddagger$ (kcal/mol)
	HOMO	LUMO	$\eta$ (eV) <sup>a</sup>	HOMO	LUMO	$\eta$ (eV) <sup>a</sup>		
<b>I</b>	-0.22	-0.06	2.23	-0.22	-0.06	2.22	0.01	0.18
<b>II</b>	-0.23	-0.09	1.96	-0.23	-0.09	1.85	0.11	2.65
<b>III</b>	-0.25	-0.10	1.99	-0.25	-0.11	1.81	0.18	6.49
<b>IV</b>	-0.22	-0.12	1.44	-0.22	-0.12	1.28	0.16	5.16
<b>V</b>	-0.24	-0.15	1.25	-0.22	-0.16	0.82	0.44	19.10
<b>VI</b>	-0.26	-0.16	1.42	-0.24	-0.18	0.78	0.64	32.45
<b>VII</b>	-0.19	-0.03	2.16	-0.17	-0.03	1.95	0.22	20.42

<sup>a</sup> $\eta = [(LUMO-HOMO)/2]*27.2116$  eV; <sup>b</sup> $\Delta\eta^\ddagger = \eta_R - \eta_{TS}$ .

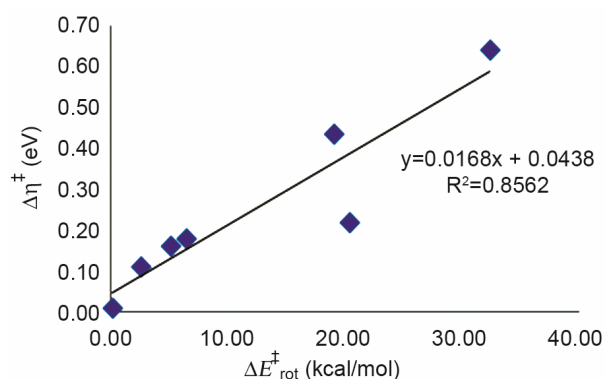
Table 4 — Selected second order hyperconjugative interactions  $E^2$  (kcal/mol) in complexed systems

System	Bonding interactions (Ring atoms/bonds $\rightarrow \sigma^*Cr-CO$ ) (kcal/mol)			Back bonding interactions (Cr-CO $\rightarrow$ Ring atoms) (kcal/mol)			Total loss in TS (kcal/mol)	$\Delta E_{\text{rot}}^\ddagger$ (kcal/mol)
	Minima	TS	Loss in TS	Minima	TS	Loss in TS		
	<b>II</b>	121.11	103.40	17.71	-	-		
<b>III</b>	120.05	78.73	41.32	-	-	-	41.32	6.49
<b>IV</b>	114.12	74.87	39.25	19.03	11.38	7.65	46.90	5.16
<b>V</b>	142.36	46.93	95.43	-	-	-	95.43	19.10
<b>VI</b>	56.85	4.72	52.13	117.13	78.10	39.03	91.16	32.45
<b>VII</b>	95.34	75.37	19.97	62.95	8.53	54.42	74.39	20.42

( $R^2 = 0.856$ ) between  $\Delta\eta^\ddagger$  &  $\Delta E_{\text{rot}}^\ddagger$  is a testimonial to the above fact (Fig. 1). The activation hardness  $\Delta\eta^\ddagger$  is maximum for system **VI** (0.64 eV) and hence tripodal rotation is found to be frontier orbital controlled.

Stability of conformations and their rotational barrier can be much explained through NBO studies. Table 4 collects prominent second order hyperconjugative interactions between ring to metal orbitals (bonding) and vice versa (back bonding). It is seen from Table 4 that in the systems **II**, **III** and **V** the bonding hyperconjugative interactions of ring  $\rightarrow \sigma^*$  metal orbitals are present and the sum total of all the bonding interactions indicates that the conformational minima of **II**, **III** and **V** have greater bonding interactions than their corresponding TS. This loss in interaction accounts for their larger barrier. Other systems, i. e., **IV**, **VI** and **VII** show both ring orbitals  $\rightarrow \sigma^*$  metal orbitals (bonding) and LP metal orbital  $\rightarrow$  LP ring atom orbital (back-bonding) interactions. There is a reduction in magnitude of both the interactions in the TSs. Hence, stability of the minima may be attributed to predominantly those interactions whose loss in TS results in large rotational barrier. In fact there is a good correlation between cumulative loss in second order hyperconjugative energy in TS relative to minima and rotational barrier ( $R^2 = 0.788$ ) (Fig. 2).

The charge transfer CT, stabilisation energy and aromaticity index NICS<sub>zz</sub> (0) and NICS<sub>zz</sub> (1) for all the minimum energy conformer of all the systems

Fig. 1 — Plot of  $\Delta\eta^\ddagger$  versus rotational energy barrier (kcal/mol)

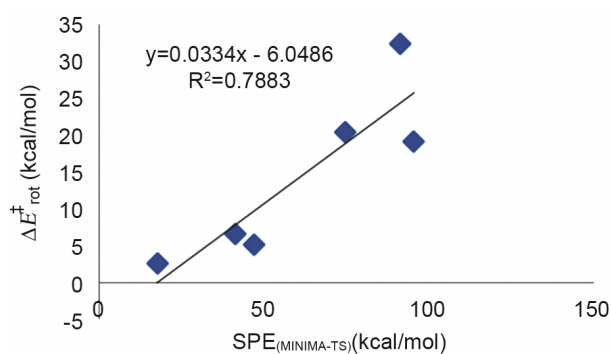
undertaken for study are listed in Table 5. It has been observed from Table 5 that the stabilisation energy increases from **I** to **VII** with **IV** as an exception indicating that they are stabilised upon  $Cr(CO)_3$  complexation. The magnitudes are higher for the systems **VI** and **VII** compared to all other systems under study, indicating an attainment of greater stability upon  $Cr(CO)_3$  complexation. This may be attributed to the cumulative effect of greater charge transfer (CT) from ring to  $Cr(CO)_3$  moiety and gain in aromaticity upon complexation. The charge transfer from ring to  $Cr(CO)_3$  moiety is greater for triphosphatirborabenzene complexed systems (**VI** and **VII**) compared to phosphabenzene/borinine tricarbonyl complexes (**II-V**). Also, it has been observed from the Table 5 that compared to

Table 5 — Charge transfer (CT), stabilisation energy (SE) and NICS<sub>zz</sub> computed for minimum energy conformers in the studied system<sup>a</sup>

System	SE <sup>b</sup> (kcal/mol)	CT (Ring→M)	M-Ω (Å)	NICS <sub>zz</sub> (ppm) <sup>c</sup>			
				NICS <sub>zz</sub> (0)		NICS <sub>zz</sub> (1)	
<b>I</b>	-44.00	0.30	1.85	-6.89	(-14.37)	-24.59	(-28.81)
<b>II</b>	-46.19	0.30	1.84	-5.13	(-12.04)	-21.52	(-26.05)
<b>III</b>	-52.88	0.27	1.85	-4.01	(-9.56)	-18.77	(-22.11)
<b>IV</b>	-33.98	0.36	1.85	-13.21	(-20.17)	-22.40	(-25.46)
<b>V</b>	-54.34	0.33	1.83	-24.61	(5.74)	-23.15	(6.14)
<b>VI</b>	-73.57	0.42	1.73	-13.19	(14.44)	-15.51	(14.36)
<b>VII</b>	-89.21	0.78	1.78	-20.47	(-13.48)	-14.32	(-13.38)

<sup>a</sup>All structures are fully optimized local minima (RB3LYP/LANL2DZ). <sup>b</sup>SE =  $E_{\text{complex}} - (E_{\text{arene}} + E_{\text{Cr(CO)}_3})$ .

<sup>c</sup>NICS<sub>zz</sub> computed at RB3LYP/6-311G++(d,p); NICS<sub>zz</sub> values of corresponding uncomplexed arene ring (in bracket).

Fig. 2 — Plot of REB versus SPE<sub>MINIMA-TS</sub> (kcal/mol)

phosphabenzene complex, the borinine complexes have higher quantum charge transfer from ring to metal moiety. CT is found to be maximum for **VII**, in which boron has NH<sub>3</sub> substituent. This may be due to electron donation via the lewis base to the electron deficient lewis acid.

The change in aromaticity was monitored by the NICS<sub>zz</sub><sup>20, 21, 48</sup>. Interesting effects on aromaticity is observed from the NICS<sub>zz</sub>(0) and NICS<sub>zz</sub>(1) values in Table 5. In general, systems **I** to **IV** show decrease in aromaticity upon complexation relative to their corresponding uncomplexed entity. This is in accordance with the reports that complexation with Cr(CO)<sub>3</sub> reduces the electron density of the ring<sup>17-19,48</sup>. However, systems **V**, **VI** and **VII** show a reverse trend; the uncomplexed rings of the systems **V** and **VI** are antiaromatic while that of **VII** is relatively less aromatic (NICS<sub>zz</sub>(0)) or comparable (NICS<sub>zz</sub>(1)) relative to their complexed ones. Probably this gain in aromaticity in their complexed counterparts (**V**, **VI** and **VII**) would have stabilised these heterocycles and hence they have high stabilisation energy as mentioned earlier.

In the present study, the differential electronegativities of boron and phosphorus atoms and their resulting push-pull attributes have been effectively exploited in designing torsionally biased

η<sup>6</sup>-hetero arene chromium tricarbonyl complexes with a very large rotational barrier of 32 kcal/mol relative to the negligible 0.2 kcal/mol of η<sup>6</sup>-benzene tricarbonyl chromium (η<sup>6</sup>-benzene-Cr(CO)<sub>3</sub>). This enormous increase in barrier (two hundred folds) is due to the alternate B, P positions in the ring and has been attributed to the stabilising bonding and back-bonding interactions. The conformations have been adopted so as to maximise the donor acceptor interactions and hence the pivoted Cr(CO)<sub>3</sub> always chooses to syn eclipse P and anti eclipse B.

### Acknowledgment

The authors sincerely thank Prof. P Venuvanalingam, CSIR Emeritus Professor, School of Chemistry, Bharathidasan University, Tiruchirappalli, Tamil Nadu, India for his suggestions. AK thanks University Grants Commission, New Delhi, India, for financial assistance (No. F-MRP-5586/15 (SERO/UGC)).

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