

Molecular mechanics modelling of triarylphosphine and phenyl rotation in the compound $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$)

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Abstract

The molecular mechanics package PCMODEL is used to calculate the global minimum structure of and the conformational energy profiles for $\text{P}(p\text{-tolyl})_3$ and phenyl rotation in the compound $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$). The results are in good agreement with published experimental data.

Key words: Rhodium; Molecular mechanics; Phenyl rotation; Phosphine rotation; Cyclopentadienyl; MMX

1. Introduction

Although the potential utility of molecular mechanics (MM) calculations in assessing the importance of steric effects on structures and reactions of organotransition metal compounds has long been appreciated [1], it is only recently that a variety of solutions to the problems of devising proper force fields for π -bonded ligands have been proposed [2]. We have previously assessed one of these options, the commercial MM software package PCMODEL, for its potential applicability to compounds of the types $\eta^5\text{-CpFe}(\text{CO})\text{LR}$ ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{L} = \text{CO}, \text{PPh}_3$; $\text{R} = \text{alkyl, acyl}$) [3], ($\eta^6\text{-arene}$) $\text{Cr}(\text{CO})_2(\text{PPh}_3)$ (arene = $\text{C}_6\text{H}_6, \text{C}_6\text{Me}_6$) [3c] and $\eta^5\text{-Cp}_2\text{Ti}(\text{SiHRR}')(\text{PMe}_3)$ ($\text{R}, \text{R}' = \text{H, Me, Ph}$) [3d], finding generally excellent agreement between computed ligand rotation conformational energy profiles and quantitative experimental information concerning ligand conformational preferences and/or barriers to rotation. We now describe the results of complementary computations on a compound of a second row transition metal, $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), of a type for which the barriers to rotation of the triarylphosphine and phenyl ligands have been determined, and for which X-ray crystal structure data are available [4].

2. Experimental details

All MM calculations were performed on a Sun SPARCStation 1 using MMX, the force field utilized by PCMODEL 4.0 [2h,3b,c]. The structure of $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$ was built using published X-ray data [4a], input and output procedures being carried out as previously described [3b,c]; ligand rotation was forced utilizing the dihedral driver function of PCMODEL. The dihedral (torsional) angle for $[\text{P}(p\text{-tolyl})_3]$ rotation was defined as $\text{C}(\textit{ipso})\text{-P-Rh-Br}$, that for phenyl rotation as $\text{C}(\textit{ortho})\text{-C}(\textit{ipso})\text{-Rh-Br}$.

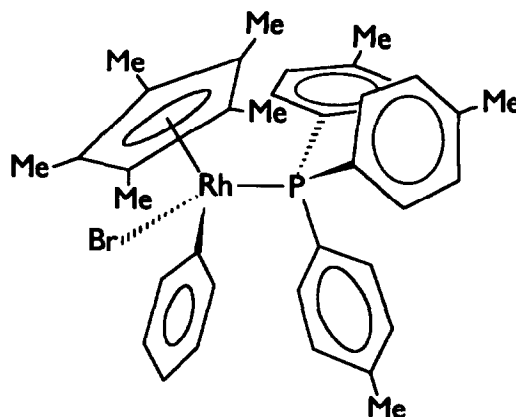


Fig. 1. Stick structure of $\text{Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$.

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3. Results and discussion

3.1. Structure minimizations

Jones and Kuykendall have reported the crystal structure of $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$, which is chiral at the rhodium atom and exists in the solid state as a 1:1 mixture of enantiomers [4a] in which the the *R*- and the *S*-stereoisomers (at Rh) are bound to $\text{P}(p\text{-tolyl})_3$ in the *M*- and *P*-configurations [5], respectively. The opposite relative preferences of chirality at PPh_3 and at the metal have been demonstrated for chiral iron complexes of the type $\eta^5\text{-CpFe}(\text{CO})(\text{PPh}_3)\text{R}$ [3c]. Structural data for both stereoisomers were read into PCMODEL [3b,c], and both were minimized in order to ascertain how well the program would reproduce the experimental structural dimensions. The structure of the compound is shown in Fig. 1.

The minimized *R,M*- and *S,P*-structures had very similar MMX energies (-24.38 , -24.81 kcal mol $^{-1}$, respectively), as anticipated, and a space-filling illustration of the latter is shown in Fig. 2. Here the rhodium atom is drawn showing its covalent radius, the ligand atoms their van der Waals radii in order to emphasize the degree of crowding around the metal atom in the molecule. Important calculated bond distances, bond angles and torsional angles are given in Table 1, where they are compared with crystallographic data. As can be seen, PCMODEL reproduces the experimental bond lengths and angles, as well as the $\text{P}(p\text{-tolyl})_3$ torsional angles [3c], of the two diastereoisomers reasonably

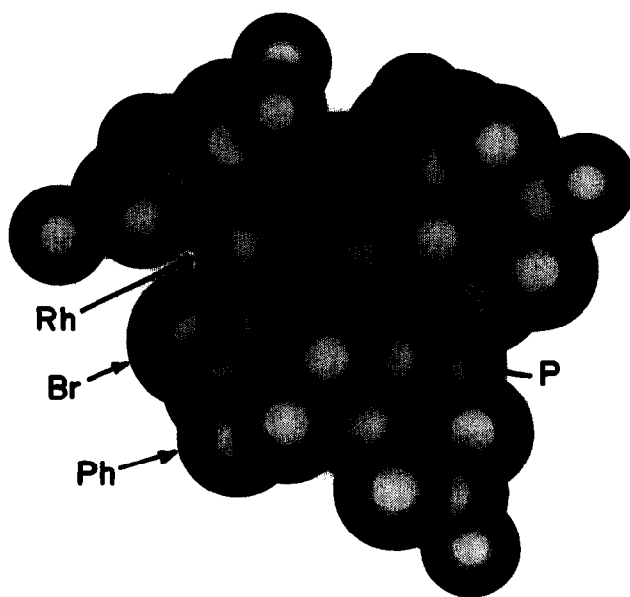


Fig. 2. Space filling molecular model of $\text{Cp}^*\text{RhBr}[\text{P}(p\text{-tolyl})_3]\text{Ph}$.

well, as was observed previously for compounds of the types $\eta^5\text{-CpFe}(\text{CO})\text{LR}$ [3], $(\eta^6\text{-arene})\text{-Cr}(\text{CO})_2(\text{PPh}_3)$ [3c] and $\eta^5\text{-Cp}_2\text{Ti}(\text{SiHRR}')(\text{PMe}_3)$ [3d]. Small differences between experimental and calculated bond angles may be attributable to electronic effects, which PCMODEL cannot assess. In both stereoisomers, the rhodium-bound phenyl group is sandwiched between the Cp^* and a nearby $[\text{P}(p\text{-tolyl})_3]$ ring, and is approximately parallel to both. As can be seen in Table 1, the

TABLE 1(a). Computed and experimental metal–ligand bond lengths

Bond	Bond lengths (Å)			
	<i>S</i> -Enantiomer		<i>R</i> -Enantiomer	
	Experimental	Computed	Experimental	Computed
Average Rh–C(Cp^*)	2.242	2.259	2.237	2.260
Rh–Ph	2.080	2.122	2.065	2.124
Rh–Br	2.525	2.678	2.529	2.677
Rh–P	2.295	2.429	2.317	2.431

TABLE 1(b). Computed and experimental ligand–metal–ligand bond angles

Angle	Bond angles (°)			
	<i>S</i> -Enantiomer		<i>R</i> -Enantiomer	
	Experimental	Computed	Experimental	Computed
Br–Rh–Ph	95.35	94.72	92.15	92.80
P–Rh–Ph	87.61	95.38	92.59	98.09
P–Rh–Br	90.19	88.18	91.98	88.50
Cp^* (centroid)–Rh–P	134.53	136.48	132.51	134.61
Cp^* (centroid)–Rh–Br	117.24	118.16	120.03	119.45
Cp^* (centroid)–Rh–Ph	121.88	114.47	117.81	113.93

TABLE 1(c). Computed and experimental P(*p*-tolyl) torsional angles

Angle	Torsional angles (°)			
	S-Enantiomer		R-Enantiomer	
	Experimental	Computed	Experimental	Computed
C(<i>ipso</i>)-P-Rh-Br	46.99	45.81	55.47	51.40
C(<i>ipso</i>)-P-Rh-Br	165.97	163.54	177.84	170.06
C(<i>ipso</i>)-P-Rh-Br	289.06	285.35	298.23	291.23
C(<i>ortho</i>)-C(<i>ipso</i>)-P-Rh	50.16	43.03	76.90	78.48
C(<i>ortho</i>)-C(<i>ipso</i>)-P-Rh	33.48	39.98	66.35	34.23
C(<i>ortho</i>)-C(<i>ipso</i>)-P-Rh	62.00	71.05	26.95	35.85
C(<i>ortho</i>)-C(<i>ipso</i>)-Rh-Br	95.81	99.51	89.61	91.84

calculated phenyl ring orientation is in both cases very similar to that observed in the solid state.

3.2. Conformational energy profiles for Rh-P(*p*-tolyl)₃ and Rh-Ph rotation in $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(\textit{p}\text{-tolyl})_3]\text{Ph}$

Jones and Feher have determined, on the basis of variable temperature NMR studies, the activation parameters for P(*p*-tolyl)₃ rotation in $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(\textit{p}\text{-tolyl})_3]\text{C}_6\text{D}_5$ ($\Delta H^\ddagger = 15.7 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -2.8 \pm 0.2 \text{ cal deg}^{-1} \text{ mol}^{-1}$) and *p*-tolyl rotation in $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(\text{C}_6\text{D}_5)_3](\textit{p}\text{-tolyl})$ ($\Delta H^\ddagger = 11.0 \pm 0.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -9.8 \pm 0.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$) [4b]. MMX calculations of these barriers were carried out utilizing the compound $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(\textit{p}\text{-tolyl})_3]\text{Ph}$, already discussed above in detail.

The rhodium atom of $\eta^5\text{-Cp}^*\text{RhBr}[\text{P}(\textit{p}\text{-tolyl})_3]\text{Ph}$ is chiral, and thus the three aryl groups of the P(*p*-tolyl)₃ are all non-equivalent, as also are their pairs of P-C(*ortho*) edges. It was therefore anticipated that contributions to the barriers to rotation of the [P(*p*-tolyl)₃] ligand would be complex, and the calculations were carried out while varying the chirality at both the metal and the P(*p*-tolyl)₃, forcing rotation of the latter in both clockwise (cw) and counterclockwise (ccw) [3c] direction. In this way, it was anticipated that a comprehensive understanding of the barriers to [P(*p*-tolyl)₃] rotation would evolve. The calculations were carried out on the the *S,P*- and *S,M*-stereoisomers with all metal-ligand bond lengths fixed to the crystallographic distances with force constants of 50 mdyne Å⁻¹; this approach has been shown previously [3] to be generally useful.

In general, it was found that phosphine rotation settled into a reproducible MMX conformational energy profile within 60–120° and, as anticipated [3c,d], the conformational energy profiles were periodic, exhibiting essentially three-fold barriers with minima and maxima corresponding approximately but not exactly to conformations in which the three aryl substituents are staggered and eclipsed, respectively, with respect to the

three ligands on the rhodium atom. As with other triarylphosphine compounds [3c], distortions away from the perfectly staggered conformational energy minima arise because the propeller-like structure of the [P(*p*-tolyl)₃] results in twisting of the phenyl groups. Since it is the *ortho* hydrogen atoms which dominate the van der Waals interactions of the [P(*p*-tolyl)₃] with the other ligands, eclipsing of the Rh-ligand and P-C bonds does not coincide with the energy maxima.

Although clearly the barriers to rotation (global and local) involved close approaches of the *p*-tolyl groups to all three other ligands, the ligand contributing the most to the barriers appeared to be the bromo group. Detailed examination of the P(*p*-tolyl)₃ torsional angles during P(*p*-tolyl)₃ rotation also showed that the *p*-tolyl groups experienced regular ring flipping, behaviour closely associated with the higher energy barriers. Similar ring flipping has been noted previously with PPh₃ complexes of the type ($\eta^6\text{-arene}$)-Cr(CO)₂(PPh₃) [3c], and results in most instances in changes in chirality of the P(*p*-tolyl)₃ ligand; in the case of the chiral rhodium compound under consideration here, however, the ring flipping appeared to be rather complex and was not investigated exhaustively. In general, there also appeared to be some “gearing” between the Cp* and the P(*p*-tolyl)₃. The former rotated by about 72° for every 120° rotation of the latter, as would be anticipated from meshing of a five-toothed (Cp*) with a three-toothed gear (P(*p*-tolyl)₃).

While P(*p*-tolyl)₃ rotation is thus very complicated, conformational energy profiles for cw and ccw ligand rotation, in all diastereomers, were obtained, including all local and global minima and maxima. Since the rotating ligand would always choose the path of least resistance, it is the lowest barriers which are important here, and these varied between ~17 and ~19 kcal mol⁻¹. The former value is in reasonably good agreement with the literature finding of $15.7 \pm 0.2 \text{ kcal mol}^{-1}$ [4b]. Only a cursory inspection of the potential energy profiles for P(*p*-tolyl)₃ rotation without constraints on

the metal–ligand bond lengths was carried out, the computed barriers being somewhat lower under these conditions.

Calculations on rotation about the Rh–Ph bond were carried out on the *S,P*- and *S,M*-stereoisomers, with all metal–ligand bond lengths either fixed to the crystallographic distances or unconstrained, as above, and starting from the calculated global minimum energy conformation. The conformational energy profiles for cw and ccw rotation were both periodic, exhibiting essentially two-fold barriers with minima and maxima corresponding approximately to conformations in which the rotating phenyl group was approximately parallel to (see above) or eclipsing the Cp* ring, respectively. In the latter case, there appeared also to be repulsive interactions between the *ortho* hydrogen atoms of the phenyl ring and one of the aryl groups of the P(*p*-tolyl). Since the metal atom is chiral, the barriers to rotation varied with the direction of rotation; the minimum barriers calculated for the constrained and unconstrained systems were 12.4 (cw) and 7.6 (ccw) kcal mol⁻¹ respectively, the former being in reasonably good agreement with experiment (11.0 ± 0.2 kcal mol⁻¹).

4. Summary

In summary, PCMODEL, as utilized above, produces a global minimum structure and computed barriers to rotation of the P(*p*-tolyl)₃ and phenyl rotation which agree very well with published experimental data. These results thus confirm our earlier conclusions [3] that PCMODEL can provide useful information concerning conformational energy profiles for ligand rotation in organotransition metal compounds containing π-bonded ligands.

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