

## Fluxionality of [(Ph<sub>3</sub>P)<sub>3</sub>Rh(X)]: The Extreme Case of X = CF<sub>3</sub>

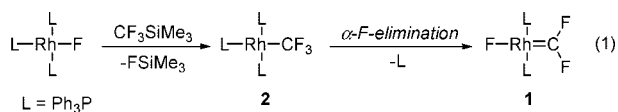
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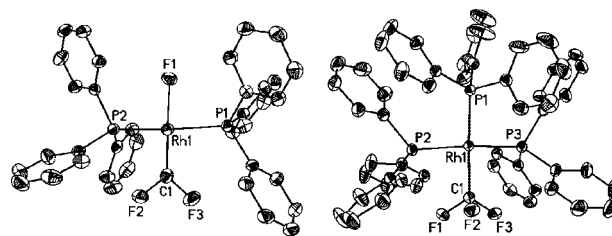
Complexes of the type [(R<sub>3</sub>P)<sub>3</sub>Rh(X)] are ubiquitous in organo-metallic chemistry and catalysis, the most renowned and widely used member of the family being Wilkinson's catalyst, [(Ph<sub>3</sub>P)<sub>3</sub>Rh(Cl)].<sup>1</sup> In the solid state, all of these species are square-planar. While the vast majority retain the same rigid structure in solution, a small number of [(R<sub>3</sub>P)<sub>3</sub>Rh(X)] complexes (X = H, Me, Ph) display equivalency of all three phosphine ligands.<sup>2–5</sup> This unusual phenomenon has received surprisingly little attention in spite of its importance not only for basic science but also for the development of new applications in synthesis and catalysis. In one case, [(Ph<sub>3</sub>P)<sub>3</sub>Rh(H)], the contrast between a square-planar geometry in the solid state and rapid intramolecular exchange in solution has been clearly established.<sup>4</sup> The mechanism of this exchange, however, remains unknown, and it is still unclear how and why certain anionic ligands X promote the rearrangement whereas others confer stereochemical rigidity. Herein we report experimental and computational studies on a novel, uniquely fluxional complex, [(Ph<sub>3</sub>P)<sub>3</sub>Rh(CF<sub>3</sub>)], which maintains phosphine exchange at –100 °C. Our studies on this and related systems not only clarify the mechanism of the peculiar phosphine rearrangement in [(R<sub>3</sub>P)<sub>3</sub>Rh(X)] but also provide new critical insights into the long-puzzling nature of bonding in perfluoroalkyl metal complexes.

Treating [(Ph<sub>3</sub>P)<sub>3</sub>Rh(F)]<sup>6</sup> with CF<sub>3</sub>SiMe<sub>3</sub> in benzene resulted in a dark-red solution, from which uniformly shaped red-orange crystals were isolated upon addition of hexanes. X-ray analysis of the crystals (twice) revealed the structure of the product as *trans*-[(Ph<sub>3</sub>P)<sub>2</sub>Rh(CF<sub>2</sub>)(F)] (**1**; Figure 1), a difluorocarbene fluoride complex. The formation of **1** is likely mediated by [(Ph<sub>3</sub>P)<sub>3</sub>Rh(CF<sub>3</sub>)] (**2**), which undergoes α-F-elimination upon loss of one phosphine (eq 1).<sup>7–9</sup>



While evidence was obtained for the same composition of **1** in the solid state in bulk,<sup>10</sup> upon dissolution in benzene, toluene, or THF, preisolated **1** quickly equilibrated with a number of species, including **2**. A <sup>19</sup>F and <sup>31</sup>P variable-temperature (VT) NMR study indicated a complex system comprising several compounds in equilibrium, with some of the equilibria being fast and some slow on the NMR time scale at 25 °C. The presence of **2** pointed to phosphine dissociation from **1**. As **1** contains only two phosphines per Rh, we propose that isomers of dinuclear complexes [(Ph<sub>3</sub>P)<sub>2</sub>Rh<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>(F)<sub>2</sub>] could be produced.<sup>10</sup> Remarkably, however, addition of excess PPh<sub>3</sub> to this multicomponent solution efficiently shifted all of the equilibria to **2** as the only NMR-detectable species.

This allowed for high-yield (84%) isolation and full characterization of **2**, including X-ray analysis (Figure 1).



**Figure 1.** ORTEP drawings of **1** (left) and **2** (right). Selected bond distances (Å) and angles (deg) for **1**: Rh–C, 1.820(3); Rh–F1, 1.994(2); Rh–P2, 2.335(1); Rh–P1, 2.349(1); C–Rh–F1, 177.0(1); P2–Rh–P1, 169.0(1); F3–C–F2, 100.0(2); F3–C–Rh, 130.8(2); F2–C–Rh, 129.1(2). For **2**: Rh–C, 2.096(2); Rh–P2, 2.310(1); Rh–P1, 2.313(1); Rh–P3, 2.337(1); F1–C, 1.376(2); F2–C, 1.398(2); F3–C, 1.380(2); C–Rh–P1, 163.5(1); P2–Rh–P3, 156.5(1); F1–C–F3, 101.3(1); F1–C–F2, 101.7(1); F3–C–F2, 101.6(1).

Sharp doublets of quartets in the <sup>19</sup>F and <sup>31</sup>P NMR spectra<sup>11</sup> of **2** over the temperature range from 25 to –60 °C indicated fast *intramolecular*<sup>10</sup> ligand exchange. Only at –100 °C (THF-*d*<sub>8</sub>) was the exchange slow enough to observe two broad <sup>31</sup>P doublets at 33.5 (2P, *J*<sub>Rh–P</sub> = 175 Hz) and 30.5 ppm (1P, *J*<sub>Rh–P</sub> = 120 Hz). Although temperatures below –100 °C were not attainable, and hence activation parameters could not be determined, magnetization-transfer experiments allowed for an exchange rate measurement of 12.1 s<sup>–1</sup> at –100 °C.

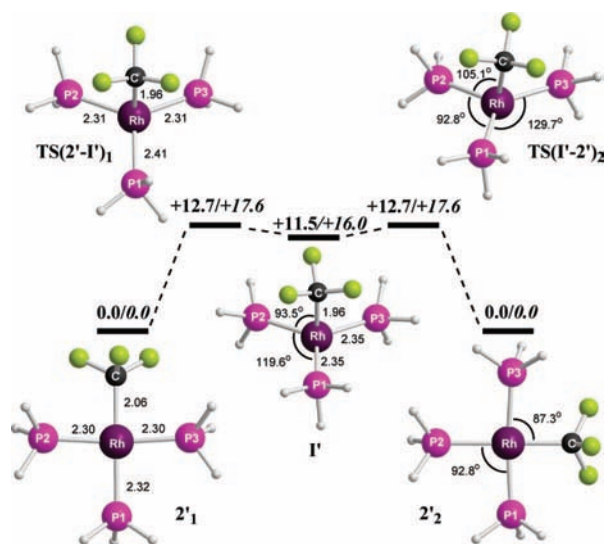
The methyl and phenyl analogues of **2**, [(Ph<sub>3</sub>P)<sub>3</sub>Rh(X)] (X = Me, Ph), were studied by VT <sup>31</sup>P NMR for comparison. The reported<sup>6b</sup> room temperature <sup>31</sup>P NMR “unsymmetrical doublet” from the Ph species became symmetrical at 40 °C (*J*<sub>P–Rh</sub> = 163 Hz), and below the coalescence point (around –20 °C), a complex second-order spectrum was observed, indicating apparent stereochemical rigidity.<sup>12</sup> For [(Ph<sub>3</sub>P)<sub>3</sub>Rh(Me)], the coalescence temperature was ~20 °C, and a well-resolved first-order A<sub>2</sub>BX spectrum could be observed already at –10 °C. Measurements of the exchange rate over the temperature range from –10 to –50 °C allowed for the determination of activation parameters: *E*<sub>a</sub> = 16.5 ± 0.6 kcal mol<sup>–1</sup>, Δ*G*<sup>‡</sup> = 12.9 kcal mol<sup>–1</sup> (calculated at –30 °C), Δ*H*<sup>‡</sup> = 16.0 ± 0.6 kcal mol<sup>–1</sup>, and Δ*S*<sup>‡</sup> = 12.8 ± 2.3 e.u. Using this Δ*S*<sup>‡</sup> value with the exchange rate of 12.1 s<sup>–1</sup> measured for **2** at –100 °C (see above) led to an estimate of Δ*H*<sup>‡</sup> ≈ 11.3 kcal mol<sup>–1</sup> for **2** under the careful assumption of similar entropies of activation for X = Me and CF<sub>3</sub>.

The above results point to the uniquely high fluxionality of **2** among known [(R<sub>3</sub>P)<sub>3</sub>Rh(X)] complexes. For R = Ph and X = Ph, Me, and H, the exchange rates are similar (e.g., 180 s<sup>–1</sup> at –10 °C for X = Me<sup>10</sup> and 230 s<sup>–1</sup> at –13 °C for X = H<sup>4</sup>) and considerably lower than for X = CF<sub>3</sub> (12.1 s<sup>–1</sup> at –100 °C). To account for the

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facile exchange in **2**, we turned to density functional theory calculations<sup>13</sup> to elucidate the mechanism of this process, and initial studies focused on the model system  $[(\text{H}_3\text{P})_3\text{Rh}(\text{CF}_3)]$  (**2'**). Computed bond lengths for **2'** agree well with those for **2**, although the distortion from square-planar geometry seen experimentally is not reproduced because of the use of  $\text{PH}_3$  ligands (see below).



**Figure 2.** Computed reaction profile (kcal mol<sup>-1</sup>) for intramolecular phosphine exchange in **2'** with selected distances (Å) and angles (deg). Structures **2'**<sub>1/2'</sub> and **TS(2'-I)**<sub>1/2'</sub> are structurally equivalent, with the subscript indicating the P center trans to the  $\text{CF}_3$  group. Energies shown in italics were computed at the MP2//BP86 level (see the text for details).

The reaction profile for phosphine exchange was investigated by reducing the trans  $\text{C-Rh-P1}$  angle in **2'**<sub>1</sub> (i.e., with  $\text{CF}_3$  initially trans to P1). This led to transition state **TS(2'-I)**<sub>1</sub> ( $E = +12.7$  kcal mol<sup>-1</sup>), in which  $\text{CF}_3$  lies above the coordination plane ( $\text{P1-Rh-C} = 105^\circ$ ) and the cis phosphines move toward the vacant site ( $\text{P2-Rh-P3} = 130^\circ$ ). **TS(2'-I)**<sub>1</sub> links to intermediate, **I'** ( $E = +11.5$  kcal mol<sup>-1</sup>) which resembles a trigonal bipyramid (TBP) with a vacant axial site trans to  $\text{CF}_3$ . The near- $\text{C}_{3v}$  geometry of **I'** means that three equivalent TS structures can be accessed by increasing the relevant  $\text{C-Rh-P}$  angles: **TS(2'-I)**<sub>1</sub> returns  $\text{CF}_3$  trans to P1, while **TS(2'-I)**<sub>2</sub> and **TS(2'-I)**<sub>3</sub> place  $\text{CF}_3$  trans to P2 (see Figure 2) and P3, respectively. **TS(2'-I)**<sub>1/2/3</sub> are therefore high points on an energy surface that equilibrates all three phosphine ligands in **2'** with (for the BP86 functional)  $\Delta H_{\text{calc}}^\ddagger = 12.7$  kcal mol<sup>-1</sup>.

Calculations on the full  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CF}_3)]$  system indicate a very similar topology for the phosphine-exchange surface. However, a considerable distortion away from square-planar is now computed,<sup>10</sup> which is more in accord with the experimental data (Figure 1). The reactant is thus distorted toward the TS geometry, and a much-reduced barrier of only 4.0 kcal mol<sup>-1</sup> is calculated for the full system. The bulkier  $\text{PPh}_3$  ligands therefore facilitate exchange, but  $\Delta H_{\text{calc}}^\ddagger$  is significantly less than the approximate experimental value of 11.3 kcal mol<sup>-1</sup>. This result was independent of the choice of functional and basis set, but an improved value of 8.7 kcal mol<sup>-1</sup> was obtained when the energies of the BP86-optimized species were recomputed at the MP2 level. The improved performance of the MP2//BP86 method was confirmed for  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{Me})]$  ( $\Delta H_{\text{calc}}^\ddagger = 14.8$  kcal mol<sup>-1</sup> vs  $16.0 \pm 0.6$  kcal mol<sup>-1</sup> from experiment), so this approach was used subsequently.

Table 1 gives  $\Delta H_{\text{calc}}^\ddagger$  for a range of  $[(\text{R}_3\text{P})_3\text{Rh}(\text{X})]$  species, and these show good agreement with observed trends in fluxionality. In particular, the very high value of 48.5 kcal mol<sup>-1</sup> computed for

$[(\text{H}_3\text{P})_3\text{Rh}(\text{Cl})]$  is consistent with the rigidity of Wilkinson's catalyst<sup>1</sup> at ambient temperature.<sup>14</sup> Of the full systems, the TS for  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{Cl})]$  unfortunately could not be located, but low barriers were found for  $\text{X} = \text{CF}_3$ , Me, Ph, and H, mirroring the fluxionality of these experimental systems. An intermediate barrier of 19.4 kcal mol<sup>-1</sup> was computed for  $\text{X} = \text{CN}$ , and experimentally,  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CN})]$  is rigid at room temperature.<sup>15,16</sup>

**Table 1.**  $\Delta H_{\text{calc}}^\ddagger$  (MP2//BP86, kcal mol<sup>-1</sup>) for  $[(\text{R}_3\text{P})_3\text{Rh}(\text{X})]$

X	$\text{CF}_3$	Me	Ph	H	CN	Cl
R = H	17.6	19.9	21.2	12.7	28.2	48.5
R = Ph	8.7	14.8	12.5	9.4	19.4	N/A

The steric factors that facilitate rearrangement in **2** are again evident for all of the  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{X})]$  species in Table 1, with  $\Delta H_{\text{calc}}^\ddagger$  always being less than those for the  $[(\text{H}_3\text{P})_3\text{Rh}(\text{X})]$  congeners. Likewise, while  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{Ph})]$  is fluxional at room temperature, sterically less encumbered  $[(\text{Me}_3\text{P})_3\text{Rh}(\text{Ph})]^{15}$  and *cis*- $[(\text{Ph}_3\text{P})_2(\text{Ph}_2\text{PF})\text{Rh}(\text{Ph})]$  are not.<sup>6b,17</sup> The size of X in  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{X})]$  also plays an important role, with the reduction in barrier height upon introduction of the  $\text{PPh}_3$  ligands being largest for  $\text{X} = \text{CF}_3$  and Ph ( $\sim 9$  kcal mol<sup>-1</sup>), less for Me (5.1 kcal mol<sup>-1</sup>), and smallest for H (3.3 kcal mol<sup>-1</sup>).

Steric effects alone, however, do not account for all of the observations:  $\text{CF}_3$  and Br are approximately the same size, as are Me and Cl, and yet  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{Cl})]$  and  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{Br})]$  are rigid in solution<sup>1</sup> under conditions where  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{Me})]$  and **2** are fluxional. Electronic factors are also important, and it is significant that the previously reported fluxional  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{X})]$  systems ( $\text{X} = \text{Me}$ , H, Ph) all feature ligands with strong trans influence.<sup>18</sup>  $\text{CF}_3$  is also considered to be a strong trans-influence ligand,<sup>19</sup> and this is confirmed by the  $\text{Rh-P1}$  distance of 2.31 Å in **2**, which is as long as that measured in  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{H})]$ .<sup>4,10</sup> Figure 2 shows that as  $\text{CF}_3$  moves into an axial position trans to a developing vacant site, the  $\text{Rh-C}$  bond shortens considerably, implying greater donation to the metal center. Similar changes are seen for all X, but one would expect the greater donor ability characteristic of ligands with the strongest trans influence to offer the greatest stabilization and thus produce lowest barriers. Weaker trans-influence ligands such as  $\text{X} = \text{Cl}$  are unable to stabilize the TS sufficiently, so intramolecular phosphine exchange by this mechanism becomes inaccessible.

Validation of these ideas comes from computed natural atomic charges for the reactant and TS structures (given in Table 2 for the simplified  $[(\text{H}_3\text{P})_3\text{Rh}(\text{X})]$  models). TS formation entails increased donation from the donor atom of X of  $\sim 0.2e$ . Despite this, the electron density on Rh actually diminishes in the TS, and it is the P centers that ultimately receive the extra charge density. This can be understood if the trigonal TS is considered to be a fragment of a TBP. Such a structure has two occupied d orbitals with significant  $\sigma$ -antibonding interactions with the phosphine ligands (consistent with increased  $\text{Rh-P}$  distances in both **TS(2'-I)**<sub>1</sub> and **I'** relative to **2'**, Figure 2). These d orbitals are approximately  $\sigma$ -nonbonding in the square-planar reactant, and thus TS formation entails a delocalization of electron density onto the P centers, each typically receiving  $\sim 0.15e$ .<sup>20</sup> The loss of electron density at Rh can be mitigated by strong donation from X, and the highest charge density at Rh is found when  $\text{X} = \text{CF}_3$ , Me, H, and Ph, consistent with the strong trans influence of these ligands. The smaller charges on Rh in the TS for  $\text{X} = \text{CN}$  (despite its strong trans influence<sup>15,18</sup>) and especially that for  $\text{X} = \text{Cl}$  correlate with the higher barriers computed in these cases. Judging only by the strongest negative charge on Rh (Table 2), one would expect the hydride  $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{H})]$  to be the most fluxional species in the series. This

is not the case, however, possibly because of the steric effect (see above) that is counter-directing and particularly significant for the small H ligand. Entropic effects may also differ in this case.<sup>16</sup>

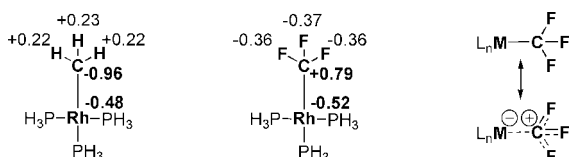
**Table 2.** Selected Computed Natural Atomic Charges ( $q$ ) for [(H<sub>3</sub>P)<sub>3</sub>Rh(X)] Reactants and Transition States<sup>a</sup>

X	reactants			transition states		
	$q(\text{Rh})$	$q(\text{C}^\ominus/\text{X})$	$q(\text{P}_{\text{av}})$	$q(\text{Rh})$	$q(\text{C}^\ominus/\text{X})$	$q(\text{P}_{\text{av}})$
CF <sub>3</sub>	-0.52	+0.79	+0.23	-0.26	+0.93	+0.08
Me	-0.48	-0.96	+0.23	-0.24	-0.73	+0.10
Ph	-0.48	-0.22	+0.24	-0.20	+0.03	+0.08
H	-0.63	-0.09	+0.22	-0.45	+0.14	+0.10
CN	-0.49	-0.02	+0.25	-0.17	+0.14	+0.10
Cl	-0.45	-0.52	+0.25	-0.08	-0.33	+0.10

<sup>a</sup> Other centers display only minor changes in computed charge.<sup>10</sup>

Our computed data also allow us to address the factors underpinning the strong trans influence of the CF<sub>3</sub> ligand.<sup>19,21</sup> Ligand trans influence is thought to be predominantly or exclusively controlled by field effects,<sup>22</sup> so a strong trans influence implies strong electron donation. In complete contrast, the CF<sub>3</sub> group is widely recognized in organic chemistry as a powerful electron acceptor.<sup>23</sup>

The computed charges in Table 2 confirm that the Rh atom in **2'** does indeed bear a large negative charge (-0.52). This actually exceeds that in the CH<sub>3</sub> analogue (-0.48), in spite of the opposite strong charges on the carbon atoms of the CF<sub>3</sub> (+0.79) and the CH<sub>3</sub> (-0.96) ligands (Figure 3). In fact, the charge distribution in **2'** parallels the long-known<sup>24</sup>  $\beta$ -effect in fluorinated organic molecules: substitution of F for H on a carbon atom increases the negative charge on the next C (or H) atom. The explanation of the  $\beta$ -effect in terms of  $\pi$ -donation from the F atoms<sup>24a,c</sup> accounts for the apparent flow of electrons toward the metal center in **2'** (Figure 3). The charge data therefore shed light on the previously perplexing strong trans influence of CF<sub>3</sub> and other perfluoroalkyl ligands.<sup>19,21</sup> Furthermore, an electrostatic attraction resulting from such  $\text{M}^\delta-\delta^+\text{CF}_3$  polarization could contribute to the M-C bond shortening in related polyfluoroalkyl complexes<sup>19,21</sup> compared to their nonfluorinated counterparts.<sup>25</sup> The positive charge on the carbon atom, however, is probably stabilized by the same  $p_\pi$  back-donation mechanism from the fluorines.<sup>24,25b,c</sup>



**Figure 3.** Natural atomic charges computed for [(H<sub>3</sub>P)<sub>3</sub>Rh(CH<sub>3</sub>)] and **2'**<sup>10</sup> and a resonance structure accounting for the  $\beta$ -effect.

In conclusion, the mechanism of the unusual intramolecular ligand exchange in complexes of the type [(R<sub>3</sub>P)<sub>3</sub>Rh(X)] has been elucidated by experimental and computational methods. The rearrangement occurs via a distorted trigonal TS with the anionic ligand X in an axial position trans to a vacant site. Our results explain why certain [(R<sub>3</sub>P)<sub>3</sub>Rh(X)] complexes (X = Cl,<sup>1</sup> Br, I, F,<sup>6</sup> CN,<sup>15</sup> OR,<sup>26</sup> NR<sub>2</sub>)<sup>27</sup> are stereochemically rigid in solution, whereas others (X = Alk,<sup>2,5</sup> Ar,<sup>2,6b</sup> H<sup>3,4</sup>) are fluxional under similar conditions. Exchange is governed by a combination of steric and electronic factors and is facilitated by bulkier ligands on the Rh as well as by strongly donating anionic ligands X that can stabilize the TS.<sup>28</sup> Our studies of the most fluxional new complex **2** (X = CF<sub>3</sub>) have also clarified the previously puzzling strong trans influence and trans effect of R<sub>f</sub> ligands as well as the nature of the bonding in perfluoroalkyl complexes of late transition metals.

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**Supporting Information Available:** Experimental and computational details and X-ray analysis data (CIF) for **1** (two polymorphs), **2**, and [(Ph<sub>3</sub>P)<sub>2</sub>Rh(CO)(F)] and complete ref 13. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The formation of **1** and **2** upon treatment of [(Ph<sub>3</sub>P)<sub>3</sub>RhCl] with [M(CF<sub>3</sub>)<sub>2</sub>] (M = Cd, Hg) has been proposed, but neither complex was detected because of facile hydrolysis leading to Rh carbonyl species. See: Burrell, A. K.; Clark, G. R.; Jeffrey, J. G.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *388*, 391.
- See the Supporting Information for details.
- NMR data for **2** (C<sub>6</sub>D<sub>6</sub>, 20 °C,  $\delta$ ): <sup>19</sup>F: -2.4 (dq,  $J_{\text{F-P}} = 32$  Hz,  $J_{\text{F-Rh}} = 11.5$  Hz). <sup>31</sup>P: 29.4 (dq,  $J_{\text{P-F}} = 32$  Hz,  $J_{\text{P-Rh}} = 158$  Hz).
- Second-order <sup>31</sup>P NMR spectra have been previously observed for similar Rh(I)  $\sigma$ -aryls [(Me<sub>3</sub>P)<sub>3</sub>Rh(Ar)] (Ar = Ph, Tol).<sup>5</sup>
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- Triplet [(H<sub>3</sub>P)<sub>3</sub>Rh(Cl)] ( $E = +22.7$  kcal mol<sup>-1</sup>) is more stable than the singlet TS. This represents the lower limit for the barrier to phosphine exchange via a spin-crossover mechanism but is still too high to be accessed at room temperature. Triplet [(H<sub>3</sub>P)<sub>3</sub>Rh(CF<sub>3</sub>)] ( $E = +27.4$  kcal mol<sup>-1</sup>) is much higher in energy than singlet **TS(2'-I)** and **I'**.
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