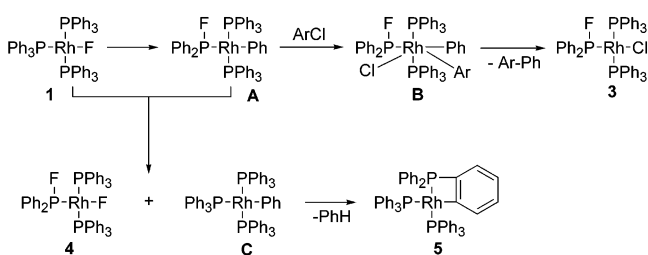


Figure 1. ORTEP drawing of **3** with all H atoms omitted for clarity.

### Scheme 2. Mechanism for Reactions 2 and 3



Stoichiometry considerations suggested that the formation of one molecule of **4** from two molecules of **1** should be accompanied by the production of 1 molecule of  $[(\text{Ph}_3\text{P})_3\text{RhPh}]$ . The latter (like its  $\sigma$ -Me analogue)<sup>15</sup> was found to be unstable under the reaction conditions (80 °C), rapidly decomposing to **5**.

Finally, it was observed that added free  $\text{PPh}_3$  (4 equiv per Rh) did not decelerate reactions 2 and 3, indicating that the rate-determining step of both reactions does not require phosphine pre-dissociation.

Scheme 2 accounts for the above observations. It is believed that the rate-limiting step is the rearrangement of **1** to the electron-rich  $\sigma$ -Ph intermediate **A**, which is fully expected<sup>16</sup> to undergo oxidative addition to give **B**, followed by reductive elimination leading to **3**. In the absence of  $\text{ArCl}$ , **A** and as yet unreacted **1** undergo ligand exchange to produce more stable **4** and **C** that undergoes cyclometalation to **5**. The enhanced stability of **4**, as compared to that of **1**, is manifested by the lack of phosphine dissociation (eq 1) and is likely<sup>3</sup> due to the fluoride ligand being trans to more  $\pi$ -acidic  $\text{Ph}_2\text{PF}$ . The mechanism of the  $\text{Rh-F/P-Ph}$  to  $\text{Rh-Ph/P-F}$  rearrangement remains unknown and may involve a metallophosphorane forming upon F-transfer to the P atom,<sup>17</sup> followed by Ph-transfer to the metal center.

When **1** was treated with much more reactive  $\text{PhI}$  and  $\text{PhBr}$  (excess in benzene; 80 °C, 1–3 h), new  $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{Ph})\text{X}_2]$  ( $\text{X} = \text{I}$  or  $\text{Br}$ ) were produced in high yield, isolated, and fully characterized by NMR and X-ray data. These reactions likely involve the formation of  $[(\text{Ph}_3\text{P})_2(\text{Ph}_2\text{PF})\text{RhX}]$  ( $\text{X} = \text{I}$  or  $\text{Br}$ ; see eq 2 and Scheme 2) which then undergo oxidative addition of the more reactive  $\text{PhX}$  ( $\text{X} = \text{I}$ ,  $\text{Br}$ ) and dissociation of  $\text{Ph}_2\text{PF}$ .<sup>18</sup>

While the reactions of **1** with  $\text{PhX}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) did not result in C–F bond formation, treatment of **1** with excess  $\text{MeI}$  gave rise to  $\text{MeF}$  (ca. 15% yield;  $^{19}\text{F}$  NMR:  $-267.1$ , q,  $J_{\text{F-H}} = 45.9$  Hz), along with other products that were not identified. This C–F bond formation was not due to an oxidative addition–reductive elimination sequence but rather due to the formation of  $[(\text{Ph}_3\text{P})\text{Me}]^+ \text{I}^-$  from the  $\text{MeI}$  and dissociated  $\text{Ph}_3\text{P}$  (eq 1). Halide exchange between the

$\text{I}^-$  produced and **1** would lead to the highly nucleophilic  $\text{F}^-$  that can react<sup>19</sup> ( $\text{S}_{\text{N}}2$ ) with  $\text{MeI}$  to give  $\text{MeF}$ . Indeed, **2** that cannot undergo phosphine dissociation, did not produce  $\text{MeF}$  upon treatment with  $\text{MeI}$ .

In conclusion, the fluoro analogue of Wilkinson's catalyst has been synthesized, fully characterized, and shown to possess exceptional reactivity toward nonactivated chloroarenes due to the novel, facile  $\text{Rh-F/P-Ph} \rightleftharpoons \text{Rh-Ph/P-F}$  exchange.

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**Supporting Information Available:** Experimental procedures and NMR (PDF) and X-ray analysis data for **1**, **2**, **3**, and  $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{Ph})\text{X}_2]$  ( $\text{X} = \text{I}$ ,  $\text{Br}$ ) (CIF and PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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