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## The Fluoro Analogue of Wilkinson's Catalyst and Unexpected Ph–Cl Activation<sup>†</sup>

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Chlorotris(triphenylphosphine)rhodium, [(Ph<sub>3</sub>P)<sub>3</sub>RhCl], often referred to as Wilkinson's catalyst, is one of the most versatile catalysts and a key compound in modern organometallic chemistry.<sup>1</sup> The bromo and iodo analogues, [(Ph<sub>3</sub>P)<sub>3</sub>RhX] (X = Br, I), are also well-characterized complexes that have been known for almost 40 years.<sup>1</sup> In contrast, the fluoride [(Ph<sub>3</sub>P)<sub>3</sub>RhF] (1) has been mentioned in the literature only twice, both times without characterization or systematic studies.<sup>2</sup> Herein we report a simple and efficient synthesis of 1, its full characterization, and most unusual reactivity which might be of considerable interest to the new, promising, and rapidly growing area of late transition metal fluoride complexes.<sup>3</sup>

We found that  $[(Ph_3P)_4Rh_2(\mu-OH)_2]$  reacted with Et<sub>3</sub>N·3HF (TREAT HF; 2/3 equiv) to produce a new dinuclear fluoride  $[(Ph_3P)_4Rh_2(\mu-F)_2]$  (2; for X-ray and NMR data, see Supporting Information). Treatment of 2 with PPh<sub>3</sub> led to 1<sup>4</sup> as an orange-yellow solid, which can also be prepared in up to >90% yield, and more conveniently, by reacting  $[(COD)_2Rh_2(\mu-OH)_2]$  with TREAT HF in the presence of excess PPh<sub>3</sub> (Scheme 1).<sup>5</sup>

The formation and stability of **1** is somewhat peculiar. The *i*-Pr<sub>3</sub>P analogue of **2** has been shown<sup>6</sup> to react only with strongly  $\pi$ -acidic ligands L (CO, RNC, Ph<sub>2</sub>C<sub>2</sub>, and CH<sub>2</sub>==CH<sub>2</sub>) to give stable *trans*-[(*i*-Pr<sub>3</sub>P)<sub>2</sub>Rh(F)L], but not with weak  $\pi$ -acids such as Py or MeCN. This trend has been rationalized<sup>6</sup> in terms of the favorable transarrangement of the  $\pi$ -acid and fluoride which may be viewed as a powerful  $\pi$ -base<sup>3a,d,7</sup> or as a poorly polarizable, "hard" base bearing a localized negative charge.<sup>3c</sup> In either case, a  $\pi$ -acid trans to the F ligand is expected to alleviate  $d_{\pi}$ -p<sub> $\pi$ </sub> filled/filled repulsion.<sup>7</sup> Since PPh<sub>3</sub> is very weakly  $\pi$ -acidic, **1** was expected to be less stable than Wilkinson's catalyst.

To our surprise however, the Rh–P bond distances and coordination angles that we found in the X-ray structure of **1** (Scheme 1) were remarkably similar to those of  $[(Ph_3P)_3RhCl]$ , both the orange and red forms (Table 1).<sup>1</sup> Furthermore, the degree of phosphine dissociation from **1** (eq 1) in benzene under rigorously anhydrous conditions was measured by <sup>31</sup>P NMR and calculated at 30% for  $[1] = 5 \times 10^{-4}$  mol dm<sup>-3</sup>. Under identical conditions, the same degree of dissociation (30%) was determined for Wilkinson's catalyst (eq 1). Thus, both the solid state and solution data for **1** and  $[(Ph_3P)_3RhCl]$  are remarkably similar. This result is unusual, as most often late transition metal fluorides are distinct, differing considerably from their iodo, bromo, and chloro counterparts.<sup>3</sup>

$$2[(Ph_{3}P)_{3}RhF] \rightleftharpoons [(Ph_{3}P)_{4}Rh_{2}(\mu - F)_{2}] + 2PPh_{3} \quad (1)$$

$$1 \quad 2$$

Also, like [(Ph<sub>3</sub>P)<sub>3</sub>RhCl],<sup>1</sup> **1** readily reacted with CO and decarbonylated DMF (90 °C) to produce the well-known complex *trans*-[(Ph<sub>3</sub>P)<sub>2</sub>Rh(F)(CO)] which was identified by its <sup>31</sup>P NMR and IR ( $\nu_{CO} = 1957 \text{ cm}^{-1}$  in Nujol) data.<sup>3a</sup>

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**Scheme 1.** Synthesis and an ORTEP Drawing of 1  $[(Ph_3P)_4Rh_2(\mu-OH)_2]$ 



Table 1. Geometry Parameters for 1 and [(Ph<sub>3</sub>P)<sub>3</sub>RhCl]

parameter,	[(Ph <sub>3</sub> P) <sub>3</sub> RhF], 1	[(Ph <sub>3</sub> P) <sub>3</sub> RhCl] (ref 1)	
Å or deg	(this work)	orange	red
Rh-X	2.070 (2)	2.404 (4)	2.376 (4)
Rh-P trans to X	2.193 (1)	2.225 (4)	2.214 (4)
Rh-P trans to P	2.325 (1)	2.304 (4)	2.322 (4)
Rh-P trans to P	2.325 (1)	2.338 (4)	2.334 (4)
X-Rh-P	166.9 (1)	166.7 (2)	156.2 (2)
P-Rh-P	159.7 (1)	159.1 (2)	152.8 (1)

In sharp contrast with all of the above similarities was the unusual reactivity that **1** exhibited toward haloarenes. Oxidative addition of most reactive iodoarenes to  $[(Ph_3P)_3RhX]$  (X = Cl, I) is known<sup>8,9</sup> to occur only at elevated temperatures (>100 °C), in the presence of a large excess of ArI. Incomparably more inert<sup>10</sup> PhCl did not react with  $[(Ph_3P)_3RhCl]$  under such conditions.<sup>11</sup>

To our surprise, the fluoro complex **1** was found to easily cleave the most unreactive C–Cl bond of chlorobenzene (eq 2). Both the mild conditions required for reaction 2 (1–3 h at 80–100 °C) and the formation of **3** were totally unexpected.

$$\begin{array}{c|c} PPh_3 \\ Ph_3P-Rh-F \\ PPh_3 \\ PPh_3 \\ 1 \end{array} \xrightarrow{PhCl} Ph \begin{array}{c} Ph \\ Ph \\ F-P-Rh-Cl \\ Ph \\ PPh_3 \\ Ph \end{array} + Ph-Ph (2)$$

The new fluorophosphine complex  $3^{12}$  (Figure 1) was formed in ca. 70% <sup>31</sup>P NMR yield (isolated yield: 50%), along with [(Ph<sub>3</sub>P)<sub>3</sub>RhCl] (ca. 30%) which possibly formed from **3** via phosphine ligand exchange. Several experiments were carried out in order to gain insight into the mechanism of reaction 2.

First, it was shown that the reaction of **1** with *p*-chlorotoluene led to 4-MeC<sub>6</sub>H<sub>4</sub>Ph and only traces of Ph<sub>2</sub> (<1%, GC-MS).

Second, it was found that the thermal decomposition of **1** in benzene at 80 °C occurred readily and selectively to produce two Rh complexes  $4^{13}$  and  $5^{14}$  in a 1:1 ratio (eq 3).



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



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 [(Ph<sub>3</sub>P)<sub>3</sub>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 PPh<sub>3</sub> (4 equiv per Rh) did not decelerate reactions 2 and 3, indicating that the ratedetermining step of both reactions does not require phosphine predissociation.

Scheme 2 accounts for the above observations. It is believed that the rate-limiting step is the rearrangement of 1 to the electronrich  $\sigma$ -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 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 Ph<sub>2</sub>PF. The mechanism of the Rh-F/P-Ph to 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 PhI and PhBr (excess in benzene; 80 °C, 1–3 h), new  $[(Ph_3P)_2Rh(Ph)X_2]$  (X = I or Br) were produced in high yield, isolated, and fully characterized by NMR and X-ray data. These reactions likely involve the formation of  $[(Ph_3P)_2(Ph_2PF)RhX]$  (X = I or Br; see eq 2 and Scheme 2) which then undergo oxidative addition of the more reactive PhX (X = I, Br) and dissociation of  $Ph_2PF$ .<sup>18</sup>

While the reactions of 1 with PhX (X = Cl, Br, I) did not result in C-F bond formation, treatment of 1 with excess MeI gave rise to MeF (ca. 15% yield; <sup>19</sup>F NMR: -267.1, q,  $J_{F-H} = 45.9$  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 [Ph<sub>3</sub>PMe]<sup>+</sup> I<sup>-</sup> from the MeI and dissociated Ph<sub>3</sub>P (eq 1). Halide exchange between the I<sup>-</sup> produced and **1** would lead to the highly nucleophilic F<sup>-</sup> that can react<sup>19</sup> (S<sub>N</sub>2) with MeI to give MeF. Indeed, 2 that cannot undergo phosphine dissociation, did not produce MeF upon treatment with 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 Rh-F/P-Ph - 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 [(Ph<sub>3</sub>P)<sub>2</sub>Rh(Ph)- $X_2$  (X = I, Br) (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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  (4) NMR data for 1 (C<sub>6</sub>D<sub>6</sub>, 20 °C), δ. <sup>1</sup>H: 7.0 (m, 3H, m, p-Ph); 7.9 (m, 2H, o-Ph). <sup>19</sup>F: -286.3 (ddt, coupling observable in the presence of excess PPh<sub>3</sub>, J<sub>F-Rh</sub> = 77.6 Hz, J<sub>F-P(trans)</sub> = 172.4 Hz, J<sub>F-P(cis)</sub> = 28.5 Hz). <sup>31</sup>P: 32.4 (ddd, 2P, J<sub>P-Rh</sub> = 154.3 Hz, J<sub>P-P</sub> = 39.0 Hz, J<sub>P-F</sub> = 28.5 Hz); 57.4 (ddt, 1P, J<sub>P-Rh</sub> = 181.4 Hz, J<sub>P-P</sub> = 39.0 Hz, J<sub>P-F</sub> = 172.4 Hz).
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  $$\label{eq:loss} \begin{split} & [(Ph_3P)_2Rh(Ph)Cl(I)]^{8a} \text{ and also } [(Ph_3P)_2Rh(Ph)Cl_3] \text{ and } [(Ph_3P)_2Rh(Ph)-I_2] \text{ in a } 2:1:1 \text{ ratio } (^{31}P \text{ NMR}), \text{ due to halide exchange.} \end{split}$$
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- (12) NMR data for 3 (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), δ. <sup>1</sup>H: 7.0−7.7 (m, Ph). <sup>10</sup>F: −110.7 (ddt, J<sub>F−P</sub> = 856 Hz, J<sub>F−P</sub> = 20.0 Hz, J<sub>F−Rh</sub> = 14.1 Hz). <sup>31</sup>P: 35.5 (ddd, 2P, J<sub>P−Rh</sub> = 139.0 Hz, J<sub>P−P</sub> = 40.7 Hz, J<sub>P−F</sub> = 20.0 Hz); 181.4 (ddt, 1P, J<sub>P−F</sub> = 856 Hz, J<sub>P−Rh</sub> = 222.1 Hz, J<sub>P−P</sub> = 40.7 Hz).
  (13) NMR data for 4 (C<sub>2</sub>D<sub>6</sub>, 20 °C), δ. <sup>10</sup>F: −109.7 (ddt, 1F, J<sub>F−P</sub> = 848 Hz, J<sub>F−P</sub> = 30 Hz, J<sub>F−Rh</sub> = 15 Hz, P−F); −267.9 (ddt, J<sub>F−Rh</sub> = 58.5 Hz, J<sub>F−P</sub>(trans) = 217 Hz, J<sub>F−P</sub>(si) = 27 Hz, Rh−F). <sup>31</sup>P: 32.3 (dddd, 2P, J<sub>P−Rh</sub> = 150 Hz, J<sub>P−P</sub> = 41.5 Hz, J<sub>P−F</sub> = 27 Hz; J<sub>P−F</sub> = 15 Hz); 188.8 (dddt, 1P, J<sub>P−F</sub> = 848 Hz, J<sub>P−F</sub> = 217 Hz, J<sub>P−F</sub> = 27 Hz; J<sub>P−F</sub> = 15 Hz); 188.8 (dddt, 1P, J<sub>P−F</sub> = 848 Hz, J<sub>P−F</sub> = 217 Hz, J<sub>P−Rh</sub> = 207.4 Hz, J<sub>P−P</sub> = 41.5 Hz).
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