

## $(\eta^6\text{-Benzene})(\eta^5\text{-ethyltetramethylcyclopentadienyl})\text{rhodium (III)}$ **Hexafluorophosphate: a Reagent for Catalytic Phenol Oxidative Coupling**

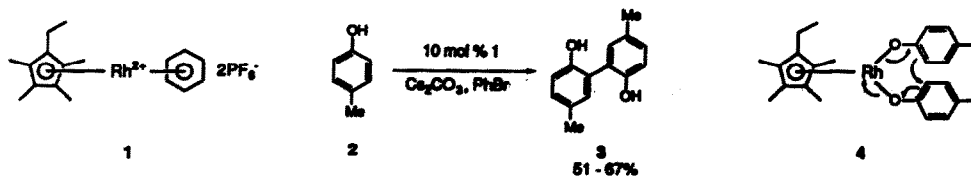
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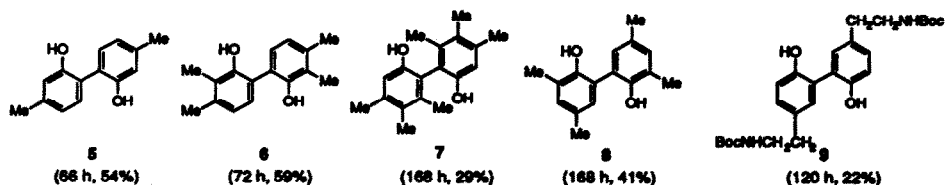
**Abstract:** Reaction of p-cresol with the title catalyst (10 mol %), cesium carbonate, and bromobenzene at 90 °C gave 2,2'-dihydroxybiphenyl (51-67%). The reaction was extended to other phenols to provide the corresponding o,o'-dimers (15-56%).

Phenol oxidative coupling is a transformation of fundamental importance in the biosynthesis and biomimetic synthesis of diverse natural products.<sup>1,2</sup> Many different oxidants including alkaline potassium ferricyanide, copper(II)amine complexes, manganese(III)acetylacetonate, silver carbonate-celite, triphenylbismuth carbonate, etc. have been used stoichiometrically to effect such transformations.<sup>2</sup> Recently, we had occasion to examine the chemistry of  $(\eta^6\text{-benzene})(\eta^5\text{-ethyltetramethylcyclopentadienyl})\text{rhodium(III)}$  hexafluorophosphate (1). This complex has been shown to catalyze the reaction of fluorobenzene with sodium methoxide to produce anisole.<sup>3</sup> The catalytic cycle was proposed to involve rapid arene exchange and nucleophilic substitution of the  $\eta^6$ -complexed fluorobenzene.<sup>4</sup> In principle, such aromatic nucleophilic substitution chemistry should be of use in other systems.

Since we are particularly interested in devising new methods for diaryl ether synthesis,<sup>5</sup> we further examined the chemistry of complex 1. Thus, p-cresol (2) was allowed to react with the rhodium(III) complex (1; 10 mol %) and cesium carbonate in bromobenzene at 90 °C. Under these conditions, no 4-methylphenyl phenyl ether was observed but 2,2'-dihydroxybiphenyl (3) was isolated as the major product. In a representative, optimized procedure, bromobenzene (0.5 mL) was added to a mixture of p-cresol (2) (54 mg, 0.5 mmol), 1 (29 mg, 0.05 mmol) and cesium carbonate (0.18 g, 0.55 mmol) at 25 °C under argon. The reaction mixture was stirred and heated at 90 °C for 24 h under argon and cooled to room temperature. Hydrochloric acid (1 M, ca. 10 mL) was added and the mixture extracted with dichloromethane. The combined extracts were dried ( $\text{MgSO}_4$ ), evaporated, and chromatographed on silica (eluant hexanes:EtOAc 5:1) to give 2,2'-dihydroxybiphenyl (3) (27 mg, 51%). Several features about this reaction need further comment. Firstly, the yields of 3 were lower using other bases [  $\text{Li}_2\text{CO}_3$  (1%),  $\text{Na}_2\text{CO}_3$  (8%),  $\text{K}_2\text{CO}_3$  (22%) ] even on prolonged reaction. Secondly, p-anisole was not oxidatively coupled under the reaction conditions. Thirdly, the yield of 3 was increased to 67% when water (2.2 equiv.) was present in the reaction mixture.



The rhodium catalyzed phenol oxidative coupling reaction was extended to other phenols to provide the corresponding *o-o'*-dimers 5-9. In each of these examples the reaction times and yields are given in parenthesis. These products 6,7 were all obtained in modest to good yields, although the efficiency of the reaction was diminished by steric congestion (dimers 7 and 8). It is apparent from these results that the yields of dimers were in excess of the stoichiometry of 1. However, the nature of the catalytic cycle is not clear. Possibly, bromobenzene, which is essential for the reaction, is functioning as a reoxidant. Mechanistically it is reasonable to speculate that bond reorganization (see arrows) in the intermediate 4 should lead to the product 3. It is possible that other rhodium complexes may function more efficiently in catalytic phenol oxidative coupling reactions.



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