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Hydrogenolysis of C(sp^3)–O bonds Catalyzed by Acidic Group 9 Hydride Complexes

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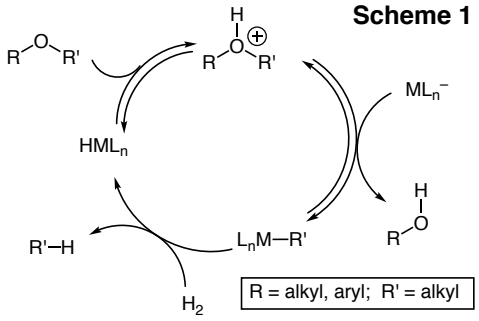
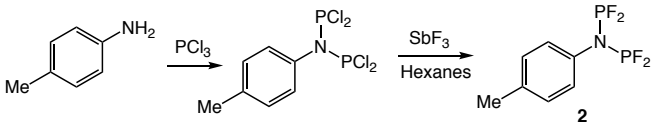
Introduction. The overarching objective of this project is the synthesis of group 9 hydride complexes bearing π-acceptor phosphine ligands to be employed as catalysts for the hydrogenolysis and silyative hydrogenolysis of C(sp^3)–O bond of dialkyl and alkyl aryl ethers. The targeted and mechanistically distinct catalytic cycle involves 1) proton transfer from the acidic catalyst to the ether oxygen atom, 2) nucleophilic displacement of the protonated carbinol with the resulting transition metal anion, and 3) hydrogenolysis of the resulting metal alkyl complex with H_2 to regenerate the metal hydride catalyst (Scheme 1).

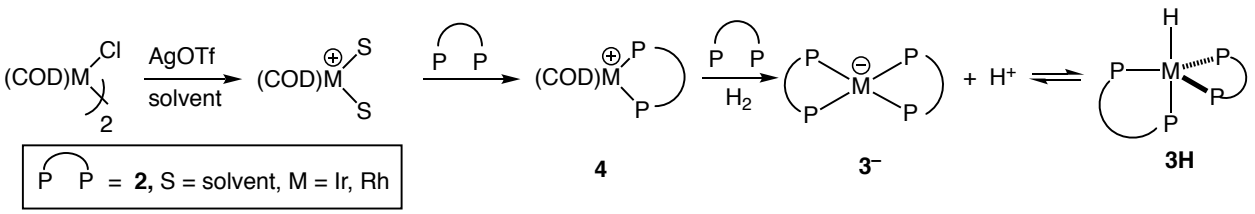
Scheme 1



Progress toward objectives. Our efforts in the previous funding period focused on the synthesis of the rhodium tetrakis(flourinated phosphite) hydride complex HRh[P(OCH_2CF_3)$_3$]$_4$ (**1**) and its reactivity toward the C–O bond cleavage reaction of styrene oxide. Unfortunately, catalysis was inefficient and produced only ~2 turnovers to form 2-phenylacetaldehyde after 5 days at 55 °C. Equilibrium deprotonation experiments indicated that complex **1** lacked the acidity required to efficiently effect C–O bond cleavage by the mechanism depicted in Scheme 1 and, for this reason, we focused our efforts on identifying more acidic group 9 hydride complexes. In the current funding period, we targeted the bis(diflurophosphino)amine ligand **2**, which is highly π-acidic owing to the combined effect of the two fluorine atoms and amine group on each phosphine, but which possesses a low steric profile. We have synthesized ligand **2** in two steps from *p*-toluidine and PCl_3.



Toward the synthesis of anionic group 9 tetrakis(phosphine) complexes (P–P)$_2$M$^-$ (P–P = **2**; M = Ir, Rh; **3**$^-$) containing ligand **2** and/or the corresponding five-coordinate hydride complexes (P–P)$_2$MH (**3H**), we were inspired by the synthetic approaches developed by Roddick for the synthesis of tetrakis(phosphine) iridium complexes containing the electron-deficient bidentate phosphine ligand (C_6F_5)$_2$PCH_2C_2P(C_6F_5)$_2$, which is outlined in Scheme 2. Unfortunately, despite this precedent and the investigation of a number of variations of this general synthetic approach as a function of solvent, temperature, reducing agent, and metal, no conclusive evidence for the formation of the desired tetrakis(phosphine) complexes **3**$^-$ or **3H** was obtained. Our initial experiments focused on the synthesis of iridium phosphine complexes and in the most encouraging iteration of this procedure, the iridium cyclooctadiene chloride dimer [(COD)Ir(μ-Cl)]$_2$ was ionized with AgOTf in acetonitrile to form a yellow solution of the known bis(acetonitrile) complex [(COD)Ir(NCMe)$_2$]$^+$ OTf$^-$. This latter solution was treated with 2.1 equiv. of **2** at room temperature to form a bright red solution, presumably containing the cationic bis(phosphine) complex **4**, although the ^{1}H and ^{31}P NMR spectra were broad and uninformative. Exposure of this red solution to hydrogen (1 atm) rapidly generated a yellow solution, but again, the NMR spectra were broad and uninformative.



P P = **2,** S = solvent, M = Ir, Rh

Scheme 2

Having failed to make headway in the synthesis of iridium complexes containing ligand **2**, we turned our attention to the synthesis of the analogous rhodium complexes owing to our successful synthesis of the rhodium tetrakis(phosphine) complex **1**. Toward this objective, we investigated the reactions of ligand **2** with a number of rhodium(I) precursors including $[(COD)Rh(\mu\text{-}Cl)]_2$, $[(NBD)Rh(\mu\text{-}Cl)]_2$, $Rh(H)(CO)_2PPh_3$, $[Rh(CO)_2(\mu\text{-}Cl)]_2$, and $Rh(acac)(H_2C{=}CH_2)_2$. Of these, a series of experiments employing the rhodium chloride-bridged dimer $[(COD)Rh(\mu\text{-}Cl)]_2$ were most encouraging although the outcomes generally paralleled that of the corresponding iridium complexes. For example, addition of **2** to a colorless solution of $[(COD)Rh(acetone)_2][BF_4]$ (generated *in situ* via ionization of $[(COD)Rh(\mu\text{-}Cl)]_2$ with $AgBF_4$ in acetone-d_6) led to immediate formation of a bright orange solution (**A**). ^{19}F NMR analysis of **A** displayed multiplets at –9.7, –13.1, –34.5, and –37.5 that were distinct from those of the free ligand, which established the coordination of **2** to rhodium. Exposure of this orange solution to H_2 (1 atm) at room temperature led to graduate darkening with the appearance of new resonances in the ^{19}F NMR spectrum at –8.5, –12.2, and –34.8, which increased in intensity at the expense of the resonances for **A** and then disappeared over the course of ~2 h, presumably due to decomposition of the reduced product. ^{31}P NMR analysis of both **A** and **B** displayed a broad resonance at δ ~140.

Impact of the research and future directions. Despite the problems encountered in the attempted synthesis of group 9 complexes containing ligand **2**, these activities provided valuable experience for graduate student participant Nana Kim who has gained experience in the areas of ligand synthesis and group 9 organometallic chemistry that are distinct from the other areas of inquiry she has explored in her graduate career. Furthermore, we have gained valuable insight into the behavior of ligand **2** that guide our future investigations in this area. Firstly, we have found that the P–F bonds of **2** are sensitive to hydrolysis in alcoholic solvents, which suggests that ligands containing P–F bonds will be unsuitable toward our broader objectives (Scheme 1). Secondly, we hypothesize that the low solubility and largely unintelligable NMR spectra of complexes containing **2** maybe due to disproportionation of the desired tetrakis(phosphine) complexes to form dimers and even oligomers with bridging phosphine ligands, which we attribute to the narrow bite angle of ligand **2**. Therefore, moving forward, we will target wider bite angle bidentate ligands containing hydrolytically stable $P(CF_3)_2$ groups in these investigations.