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A High-Yield Conversion of *trans*-Rh(Cl)(CO)(PPh$_3$)$_2$ to Rh(Cl)(PPh$_3$)$_3$

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Introduction

Chlorotris(triphenylphosphine)rhodium (**1**) is a potentially useful reagent for the decarbonylation of organic carbonyls such as aldehydes,[1] acyl halides,[2] thioesters,[3] and acyl cyanides,[4] as well as metal carbonyls.[5,6]

Both the organic and organometallic decarbonylation reactions are stoichiometric in rhodium with complex **1** being converted to *trans*-Rh(Cl)(CO)(PPh$_3$)$_2$ (**2**). The expense of rhodium metal coupled with the stoichiometric nature of these transformations has limited the applications of this potentially useful chemistry for 25 years. Prior attempts to recycle the rhodium metal by reconversion of **2** to **1** have been frustrated by the stability of the rhodium carbonyl complex. We now report the first high-yield procedure for conversion of **2** to **1**.

Experimental Section

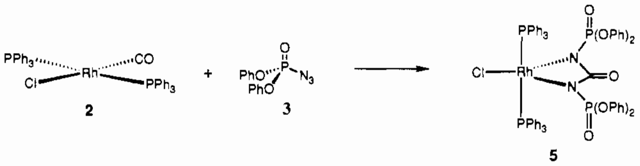
Synthesis of Rh(Cl)(PPh$_3$)$_3$ (1) from *trans*-Rh(Cl)(CO)(PPh$_3$)$_2$ (2). A 25-mL round bottom flask containing a stir bar was charged with **2** (50 mg, 0.072 mmol), degassed THF (2.5 mL), and DPPA (**3**, 22 μL, 0.11 mmol). The solution was stirred under nitrogen for 1 h, during which time a salmon pink precipitate formed. Triphenylphosphine (57 mg, 0.22 mmol) was then added, and the precipitate slowly dissolved with a concomittant change in the solution color from faint yellow to dark red. After 1 h the THF was removed under vacuum and 5 mL of absolute ethanol was added to the residue. The mixture was refluxed under nitrogen for 1 h, and the red precipitate was then collected by filtration, washed with 2 × 1 mL of ethanol, and dried under vacuum to give **1** as a red solid in 97% yield (64.4 mg): mp 156–157 °C (lit. mp 157 °C);[7] ^{31}P{^{1}H} NMR (CDCl$_3$)[8] δ 46.8 (dt, $J_{\mathrm{Rh-P}} = 192.1$ Hz, $J_{\mathrm{P-P'}} = 37.0$ Hz), 29.8 (dd, $J_{\mathrm{Rh-P'}} = 143.8$ Hz, $J_{\mathrm{P-P'}} = 37.0$ Hz). In addition to resonances attributed to **1**, a small amount (<5%) of rhodium dimer,[9] [Rh(PPh$_3$)$_2$Cl]$_2$, and free PPh$_3$ was attributed to resonances at δ 51.0 (d, $J_{\mathrm{Rh-P}} = 195.8$ Hz) and −6.1 (s), respectively. In solution complex **1** is known to exist in equilibrium with a minor amount of [Rh(PPh$_3$)$_2$Cl]$_2$ dimer.[10]

In a separate experiment, a 25-mL round bottom flask containing a stir bar was charged with **2** (50 mg, 0.072 mmol), degassed THF (2.5 mL), and DPPA (22 μL, 0.11 mmol). The solution was stirred under N$_2$ for 1 h, during which time a salmon pink precipitate formed. The solvent was removed under vacuum, and the precipitate was washed with 3 × 1 mL of absolute ethanol (degassed) and dried under vacuum to give a solid with mp 259–260 °C (lit. mp 260 °C for [Rh(PPh$_3$)$_2$Cl]$_2$). In the ^{31}P{^{1}H}NMR (THF-d_8) spectrum of this solid two doublets are observed in a 4.4:1 ratio at δ 51.2 (d, $J = 194.7$ Hz) and 28.3 ($J = 126$ Hz), respectively. The doublet at 51.2 ppm corresponds to [Rh(PPh$_3$)$_2$Cl]$_2$.

Results and Discussion

We recently reported the use of diphenylphosphoryl azide (DPPA, **3**) as a stoichiometric reagent for in situ carbon monoxide abstraction from **2**, in the decarbonylation of primary aldehydes catalyzed by **1** (5 mol %; Scheme I).[11] In this system DPPA abstracts carbon monoxide from **2** with liberation of dinitrogen and formation of diphenylphosphoranyl isocyanate, **4**. The in situ use of azides such as DPPA in metal-catalyzed decarbonylation systems will be problematic for those cases where substrate functionality is incompatible with the azide reagent or isocyanate byproduct. In addition, many metal complexes catalytically decompose azides, thereby limiting the in situ use of DPPA for catalytic decarbonylation of metal carbonyl complexes by **1**. The reconversion of **2** to **1** is therefore critical to the widespread use of **1** as a decarbonylation reagent.

On the basis of our success with **1**/DPPA as an efficient system for metal-catalyzed decarbonylation of primary aldehydes, we set out to investigate the use of DPPA (**3**) for the stoichiometric conversion of **2** to **1**. Diphenylphosphoryl azide, **3**, was previously reported by Beck to undergo reaction with **2** in benzene to give the urylene complex RhCl(PPh$_3$)$_2$(RNCONR) [**5**, R = P(O)(OPh)$_2$].[12] Formation of complex **5** presumably arises from reaction of isocyanate **4**, or a rhodium complex of **4**, with H$_2$NP(O)(OPh)$_2$, the hydrolysis product of **4**.



We have found no evidence for formation of **5** in the reaction of **2** and **3** under the conditions reported herein. Thus, when **2** (0.07 mmol, 28 mM) and DPPA (0.11 mmol) were dissolved in dry THF (under N$_2$, at room temperature), a large amount of a salmon pink precipitate formed over the course of 1 h. Addition of 3 equiv (0.22 mmol) of triphenylphosphine to the slurry resulted in a dark red homogeneous solution. The sequential addition of DPPA and PPh$_3$ avoids potential complications from formation of *N*-(diphenylphosphinyl)iminophosphorane Ph$_3$P=NP(=O)(OPh)$_2$.[13] After 1 h the solvent was removed, the residue dissolved in ethanol, and the solution refluxed for 1 h, whereupon a red precipitate formed. The precipitate was filtered out, washed with ethanol, and dried under vacuum to give **1** in 97% yield.

In the procedure described above, simple addition of ethanol, without reflux, results in a sticky red solid which proved difficult to manipulate. The ethanol also plays a beneficial role in the conversion of isocyanate byproduct, **4**, to the more soluble ethyl carbamate, (PhO)$_2$(P=O)N(C=O)OEt.[14]

In theory, other azides should prove equally useful for conversion of **2** to **1**. However, we have found that substitution of furoyl azide for DPPA in the above procedure leads to a mixture of rhodium-containing products, with no formation of **1** and only

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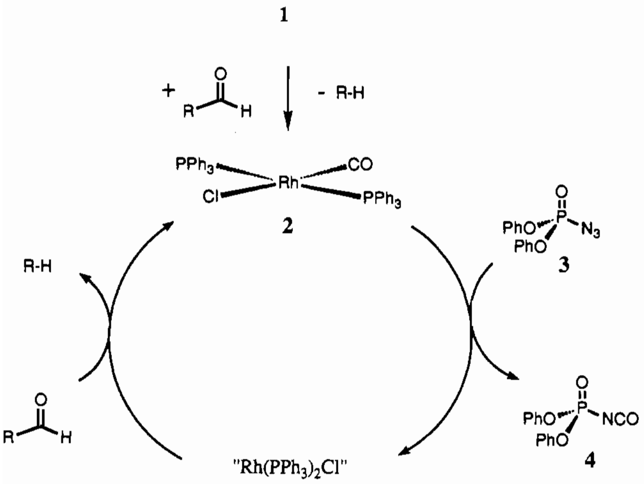
Scheme I



a small amount of dimer. The major product was unreacted starting material, **2**. When 10 equiv of furoyl azide was employed, all of the starting material was consumed, with no formation of dimer or **1**. Finally, when the reaction **2** and furoyl azide (1.5 equiv) was run in the presence of ethanol (5 equiv), followed by addition of PPh$_3$, only a trace of **1** was observed by ^{31}P{^{1}H} NMR spectroscopy.

For comparison to this new azide procedure, there have been at least three published approaches for conversion of **2** to **1**. Shortly after Tsuji first described the use of **1** as a decarbonylation reagent, Wilkinson reported that thermolysis of **2** in molten triphenylphosphine at 100 °C failed to displace the carbon monoxide ligand.[9a] Stille and Fries later reported[15] a procedure in which **2** was refluxed in α-chlorotoluene for 36 h, and the solvent removed by distillation to give an oily residue of Rh(Cl)$_2$(PPh$_3$)(η^3-CH$_2$-Ph), **6**. Benzyl complex **6** was taken up in anhydrous benzene, followed by addition of absolute ethanol and a 10-fold excess of triphenylphosphine. The mixture was then refluxed for 45 min to give a 74% isolated yield of **1**. In still other work, Geoffroy examined the photochemistry of **2** and found that simple photoelimination (254 or 366 nm) of CO does not occur in oxygen-free solutions.[16] Ultraviolet irradiation of air-saturated solutions of **2** resulted in oxidation of CO to CO$_2$ and PPh$_3$ to P(O)Ph$_3$, with formation of oligomeric [RhCl(O$_2$)(Ph$_3$PO)$_{0.67}$]$_x$ (**7**). When **7** and 15 equiv of PPh$_3$ were refluxed in ethanol for 2 h a 61% yield of **1** resulted.

Summary

The first high-yield procedure for conversion of *trans*-Rh(Cl)(CO)(PPh$_3$)$_2$ to Rh(Cl)(PPh$_3$)$_3$ has been achieved by utilization of the commercially available[17] DPPA as a carbonyl ligand abstraction reagent.

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(17) Diphenylphosphoryl azide, DPPA (**5**), is a nonexplosive, high-boiling azide available in kilogram quantities from Aldrich Chemical Co.