Convenient Synthesis of Ruthenium(II) Dihydride Phosphine Complexes $Ru(H)_2(PP)_2$ and $Ru(H)_2(PR_3)_x$ (x = 3 and 4)

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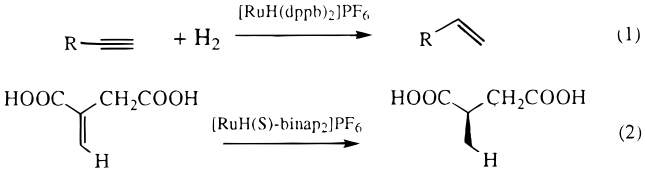
A novel and convenient one-pot synthesis of ruthenium(II) dihydride phosphine complexes from the air-stable $[RuCl_2(COD)]_x$, the appropriate phosphine, and NaOH in sec-butyl alcohol under argon at 80 °C is reported. A series of chelating (dcpm, dcpe, dppe, dppb, dppp, dppf, and depe) and monodentate phosphine (PEt_3 and PPh_3) complexes have been synthesized using this methodology. The crystalline products are isolated in high yield. These dihydride complexes have been shown to be useful precursors to cationic dihydrogen hydride complexes, some of which exhibit significant activity as hydrogenation catalysts.

Introduction

The use of metal hydride complexes is prevalent throughout organometallic chemistry and homogeneous catalysis since these complexes play a prominent role as active catalysts in the isomerization, polymerization, and hydrogenation of olefins.[2−5] In most cases, the ancillary ligation associated with these metal hydride moieties is comprised of tertiary phosphine ligands. These ligands have been shown to possess a wide range of tunable steric and electronic properties.[6] Bidentate phosphine ligands[7] of the type $R_2PCH_2CH_2PR_2$ (R = alkyl and aryl) have also proven the be a useful class of supporting ligands in organometallic complexes and catalysis.[2,4] Significant research efforts have been devoted to the investigation of ruthenium hydrides bearing bidentate phosphines.[8,9] This interest stems from the catalytic activity displayed by these complexes in hydrogenation processes. Chiral biphosphines such as BINAP[10] and DuPhos[11] have recently been included to the list of chelating diphosphines capable of supporting mononuclear hydrides of ruthenium. The displayed reactivity of these $RuH(PP)_2^+$ (PP = chelating diphosphine) complexes extends from hydrogenation of alkynes[12] (eq 1) to asymmetric transfer hydrogenation of prochiral olefins bearing carboxylic acids[13] (eq 2).



Multistep synthetic routes to these complexes have been described in the literature (*vide infra*). In the present contribution, we report a straightforward synthetic methodology leading to gram quantities of a variety of $Ru(H)_2(PP)_2$ (PP = chelating diphosphine) complexes, from an air-stable precursor. These complexes are immediate synthetic precursors to the cationic complexes displaying catalytic behavior.

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk-tube techniques or in a Vacuum Atmospheres glovebox containing less than 1 ppm of oxygen and water. Ligands were purchased from Strem Chemicals and used as received. Sec-butyl alcohol was purchased from Aldrich as anhydrous grade (99.5%) and purged with Ar prior to use. NMR spectra were recorded using a GE 400 MHz spectrometer. Solvents were purified using procedures previously reported.[14]

Synthesis. The identity of $Ru(H)_2(dppe)_2$ (**1**),[15] $Ru(H)_2(dppf)_2$ (**4**),[16] $Ru(H)_2(dcpe)_2$ (**5**),[17] $Ru(H)_2(depe)_2$ (**7**),[15] $Ru(H)_2$-

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(7) Abbreviations used in the text for chelating phosphines: $PPh_2CH_2CH_2PPh_2$ (dppe), $PPh_2(CH_2)_3PPh_2$ (dppp), $PPh_2(CH_2)_4PPh_2$ (dppb), $(PPh_2C_5H_4)_2Fe$ (dppf), $PCy_2CH_2PCy_2$ (dcpm), $PCy_2CH_2CH_2PCy_2$ (dcpe), $PEt_2CH_2CH_2PEt_2$ (depe).

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$(PEt_3)_4$ (**8**),[18] $Ru(H)_2(PPh_3)_3$ (**9**),[19] and $[RuH(dcpe)_2]BF_4$ (**10**)[17] was confirmed by comparing experimental to reported spectroscopic information. $[RuCl_2(COD)]_x$ was synthesized according to the literature procedure.[20] Experimental synthetic procedures, leading to isolation of crystalline materials, for all complexes are reported below.

$Ru(H)_2(dppe)_2$ (1). A 250 mL Schlenk flask containing a Teflon-coated magnetic stirring bar was charged with NaOH (1.0 g, 25 mmol). The flask was then taken into the glovebox where $[RuCl_2(COD)]_x$ (0.352 g, 1.25 mmol) and $PPh_2CH_2CH_2PPh_2$ (dppe) (1.0 g, 2.5 mmol) were added to the reaction vessel. The vessel was removed from the glovebox and connected to a Schlenk line where degassed sec-butyl alcohol (80 mL) was added using a cannula. The reaction vessel was then sealed and heated to 80 °C for 3 h. The system was then allowed to cool to room temperature, and degassed water (100 mL) was added to dissolve the excess NaOH. The suspension was then transferred using a cannula onto a medium porosity collection frit where the yellow solid was further washed with 3 × 20 mL portions of degassed methanol and finally dried in vacuo to yield 0.95 g (85%) of $Ru(H)_2(dppe)_2$.

$Ru(H)_2(dppp)_2$ (2). In an identical fashion as for the synthesis of **1**, but using $PPh_2(CH_2)_3PPh_2$ (dppp), **2** was isolated as a yellow microcrystalline solid in 84% yield. ^1H NMR (400 MHz, C_6D_6, 25 °C): −7.60 (m). ^{31}P NMR (161.9 MHz, C_6D_6, 25 °C): 29.12 (t, J_{P-P} = 28 Hz), 33.92 (t, J_{P-P} = 27 Hz). Anal. Calcd for $C_{54}H_{54}P_4Ru$: C, 69.89; H, 5.87. Found: C, 69.92; H, 5.99.

$Ru(H)_2(dppb)_2$ (3). In an identical fashion as for the synthesis of **1**, but using $PPh_2(CH_2)_4PPh_2$ (dppb), **3** was isolated as a yellow microcrystalline solid in 88% yield. ^1H NMR (400 MHz, C_6D_6, 25 °C): −9.54 (m). ^{31}P NMR (161.9 MHz, C_6D_6, 25 °C): 35.81 (m), 50.27 (m). Anal. Calcd for $C_{55}H_{56}P_4Ru$: C, 70.13; H, 5.99. Found: C, 69.78; H, 6.17.

$Ru(H)_2(dppf)_2$ (4). In an identical fashion as for the synthesis of **1**, but using $(PPh_2C_5H_4)_2Fe$ (dppf), **4** was isolated as an orange microcrystalline solid in 85% yield.

$Ru(H)_2(dcpe)_2$ (5). In an identical fashion as for the synthesis of **1**, but using $PCy_2CH_2CH_2PCy_2$ (dcpe), **5** was isolated as a white microcrystalline solid in 80% yield.

$Ru(H)_2(dcpm)_2$ (6). In an identical fashion as for the synthesis of **1**, but using $PCy_2CH_2PCy_2$ (dcpm), **6** was isolated as an off-white microcrystalline solid in 54% yield. ^1H NMR (400 MHz, C_6H_6, 25 °C): −11.49 (m). ^{31}P NMR (161.9 MHz, C_6D_6, 25 °C): 66.10 (s). Anal. Calcd for $C_{50}H_{94}P_4Ru$: C, 65.26; H, 10.29. Found: C, 65.10; H, 10.32. Exact mass (HRMS) calcd for $C_{50}H_{94}P_4Ru$ (M^+), 919.5271, found 919.5254.

$Ru(H)_2(depe)_2$ (7). A 250 mL Schlenk flask containing a Teflon-coated magnetic stirring bar was charged with NaOH (1.0 g, 25 mmol). The flask was then taken into the glovebox where $[RuCl_2(COD)]_x$ (0.340 g, 1.20 mmol) and $PEt_2CH_2CH_2PEt_2$ (depe) (0.500 g, 2.40 mmol) were charged into the reaction vessel. The vessel was removed from the glovebox and connected to a Schlenk line where degassed sec-butyl alcohol (80 mL) was added by cannula. The reaction vessel was sealed and heated to 80 °C for 2 h. The system was allowed to cool to room temperature, and degassed water (100 mL) was added to dissolve the excess NaOH. The orange organic layer was decanted by cannula into a 200 mL Schlenk, where the volatiles were removed in vacuo. The product was recrystallized from methanol to yield 0.87 g (70%) of $Ru(H)_2(depe)_2$.

$Ru(H)_2(PEt_3)_4$ (8). In a manner analogous to the procedure leading to the isolation of **7**, **8** was obtained in 60% yield after recrystallization from methanol.

$Ru(H)_2(PPh_3)_3$ (9). In an identical fashion as for the synthesis of **1**, but using 3 equiv of PPh_3, **9** was isolated as an orange-brown microcrystalline solid in 88% yield.

$[RuH(dcpe)_2]BF_4$ (10). A 50 mL Schlenk flask containing a Teflon-coated magnetic stirring bar was charged with **5** (0.250g, 0.264 mmol) and tetrahydrofuran (20 mL). To this solution was added HBF_4 (40 μL of a 54% solution, Aldrich). After 10 min, the volatiles were removed in vacuo and the residue washed with Et_2O (2 × 20 mL) and dried in vacuo. This procedure yields 220 mg (80%) of the product as a yellow solid. NMR data are the same as those reported for PF_6 salt.

$[RuH(dppp)_2]BF_4$ (11). In the glovebox, an NMR tube was charged with **2**, C_6D_6, and 1 equiv of HBF_4 and was then fitted with a septum cap. The ^1H and ^{31}P both provide spectroscopic evidence of the complete conversion to **11** (see Discussion).

$[RuH(dppb)_2]BF_4$ (12). A similar procedure as for the synthesis of **11** was used for **12** but using **3**. Complete conversion was observed by ^1H and ^{31}P NMR spectroscopy (see Discussion).

Results and Discussion

Researchers at Du Pont have recently reported the use of $[RuCl_2(COD)]_x$ and NaOH in the isolation of ruthenium hydride (dihydrogen) complexes, eq 3.[21] The

$$[RuCl_2(COD)]_x + 2PCy_3 + \text{xs NaOH} \xrightarrow[H_2]{\text{toluene}} [Ru(H)_2(H_2)_2(PCy_3)_2] + 2NaCl + C_8H_{16} \quad (3)$$

reported experimental conditions required elevated pressures of hydrogen (69 atm) and prolonged heating of the toluene/water solution in the presence of a phase-transfer agent. The use of a strong base was necessary for complete conversion of Ru−Cl into Ru−H. This point was recently illustrated in the synthesis of ruthenium hydrido chloride complexes, eq 4.[22] This approach

$$[RuCl_2(COD)]_x + 2PCy_3 + NEt_3 \xrightarrow[H_2]{\text{sec-BuOH}} [Ru(H)(Cl)(H_2)_2(PCy_3)_2] + HNEt_3Cl + C_8H_{16} \quad (4)$$

suggested that the synthesis of $Ru(H)_2(PP)_2$ complexes might also be possible in this fashion. Initially, reactions were conducted under a hydrogen atmosphere, but the use of hydrogen sometimes led to the over-reduction of the ruthenium center. This problem was circumvented by the use of alcohols as the hydrogen source in ruthenium chemistry.[8,23] Reactions involving $[RuCl_2(COD)]_x$, NaOH, and 2 equiv of a chelating phosphine in sec-butyl alcohol were carried out in the absence of hydrogen and led to high yields of $Ru(H)_2(PP)_2$ complexes, eq 5. This simple process represents a marked

$$^1/_x[RuCl_2(COD)]_x + 2PP \xrightarrow[\text{sec-BuOH}]{\text{xs NaOH}} Ru(H)_2(PP)_2 + C_8H_{16} + 2NaCl$$

$$PP = \text{Chelating Phosphine} \quad (5)$$

improvement on the reported synthetic routes to these complexes.

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The $Ru(H)_2(PP)_2$ complexes themselves have demonstrated catalytic activity, but their cationic derivatives display greater reactivities.[24] Two major routes to the cationic complexes have been employed. The first series of reactions leads to the $Ru(H)_2(PP)_2$ in three steps, eqs 6−8.[15] A number of dihydrides have been isolated by a

$$RuCl_3 + \text{xs DMSO} \rightarrow RuCl_2(DMSO)_4 \quad (6)$$

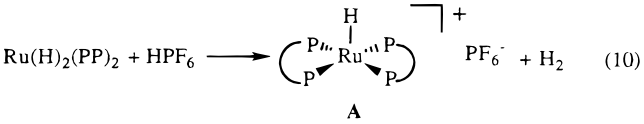
$$RuCl_2(DMSO)_4 + 2\text{dppe} \rightarrow RuCl_2(\text{dppe})_2 + 4\text{DMSO} \quad (7)$$

$$RuCl_2(\text{dppe})_2 + 2\text{NaOEt} \rightarrow Ru(H)_2(\text{dppe})_2 + 2\text{NaCl} \quad (8)$$

simple substitution reaction with the $Ru(H)_2(PPh_3)_4$ synthon.[25] The example given in eq 9 affords the product in 61% yield.[17] Once the dihydride compounds

$$Ru(H)_2(PPh_3)_4 + 2\text{dcpe} \rightarrow Ru(H)_2(\text{dcpe})_2 + 4PPh_3 \quad (9)$$

have been isolated, simple protonation with acids affords the cationic monohydride complexes, eq 10.[17,26]



A (10)

The second pathway to complexes of type **A** is also a multistep process, eqs 11−13, the last of which involves direct phosphine substitution from a cationic ruthenium hydrazine complex.[12,27]

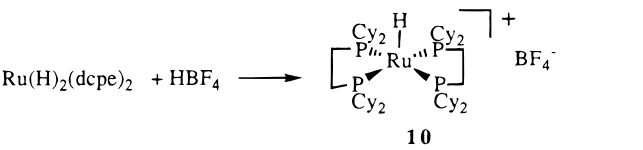
$$RuCl_3 \cdot xH_2O + \text{COD} \rightarrow {}^1/_x[RuCl_2(\text{COD})]_x \quad (11)$$

$$[RuCl_2(\text{COD})]_x + 3NH_2NMe_2 \xrightarrow{NH_4PF_6} [(\text{COD})RuH(NH_2NMe_2)_3]PF_6 \quad (12)$$

$$[(\text{COD})RuH(NH_2NMe_2)_3]PF_6 + 2\text{dppb} \rightarrow [RuH(\text{dppb})_2]\,PF_6 + 3NH_2NMe_2 + \text{COD} \quad (13)$$

The usefulness of the reported methodology should now become apparent. An air-stable complex, synthesized in air with yields of >85% (eq 11), can be directly used with sodium hydroxide, the appropriate phosphine, and sec-butyl alcohol. Reaction times were usually kept constant at 3 h.[28] Addition of degassed water, filtration of the reaction mixture, a methanol rinse of the collected solid, and drying affords the products in high yields and in high enough purity that NMR analysis does not detect the presence of any side products.

The protonation step of one $Ru(H)_2(PP)_2$ product was carried out with HBF_4 and afforded the desired cationic complex in 80% yield, eq 14.[29] All NMR data for **10**



10 + H_2 (14)

proved identical to that reported for the PF_6^- salt. Confirmation of the composition of complexes **2** and **3** was further obtained by identification of their protonation product by NMR.[24a,29]

In view of the important catalytic behavior of ruthenium complexes bearing monodentate phosphines[1] and in order to test the generality of the methodology, reactions were carried out in an analogous manner with monodentate phosphines, eq 15. It should be noted that

$${}^1/_x[RuCl_2(\text{COD})]_x + nPR_3 \xrightarrow[\text{sec-BuOH}]{\text{NaOH}} Ru(H)_2(PR_3)_n + C_8H_{16} + 2\text{NaCl}$$

$n = 3$; R = Ph; 88% yield

$n = 4$; R = Et; 60% yield (15)

the new methodology possesses significant advantages over reported routes where metal hydrides[30] (PPh_3 case) and excess phosphine[18] (PEt_3 case) had to be used, eq 16.

$$RuCl_3 \cdot nH_2O + \text{xs } PEt_3 \xrightarrow{[NBu_4]BH_4} Ru(H)_2(PEt_3)_4 \quad (16)$$

Conclusion

A simple synthetic procedure that produces a high yield of high-purity $Ru(H)_2(PP)_2$ complexes has been developed. These complexes can be readily converted into an important class of hydrogenation catalysts. The ease of preparation of the $[RuCl_2(\text{COD})]_x$ starting complex, the low cost of the solvent and base, and the ease of workup make this methodology quite attractive for the synthesis of ruthenium hydride complexes. The generality of the methodology is presently being tested for other ruthenium and late transition metal complexes.

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(28) Reactions often are completed in shorter times, as is apparent by the dramatic color changes associated with reaction completion.

(29) Protonation following this protocol was performed for $Ru(H)_2(dppp)_2$ (**2**) and $Ru(H)_2(dppb)_2$ (**3**). Spectroscopic data for both cationic species **11** and **12**, respectively, match those reported in ref 24a. These syntheses were performed using evacuation of volatiles in a last isolation step; H_2 is also removed in this step, as in the synthesis of **10**.

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