Articles

Use of an Iodide-Modified Merrifield Resin in the Synthesis of Ruthenium Hydride Complexes. The Structure of RuHI((*R*)-binap)(PPh_3)

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Transition metal complexes that function as catalysts or precatalysts are sometimes synthesized by the displacement of phosphine ligands from precursor complexes. A common problem in the synthesis is the separation of the desired complex from the phosphine contaminants that have similar solubility properties. This is the case in the synthesis of the coordinatively unsaturated ruthenium complexes RuHX((*R*)-binap)(PPh_3) (X = Cl, **2**; X = I, **3**) from $RuHCl(PPh_3)_3$ (**1**). The new iodo ruthenium complex RuHI((*R*)-binap)(PPh_3) (**3**) is prepared in good yield and purity by treatment of the chloro derivative **2**, which is contaminated with triphenylphosphine, triphenylphosphine oxide, binap, binap monoxide, and binap dioxide, with an iodide-modified Merrifield resin. The resin was prepared following a modification of a procedure described by Lipshutz and Blomgren. The structure determination of **3** by single-crystal X-ray diffraction is reported. Complex **3** reacts with the alkoxides $KOCR_2$-2-py (R = Me, potassium dimethyl-2-pyridylmethoxide; R = Ph, potassium diphenyl-2-pyridylmethoxide) to produce the coordinatively unsaturated hydrido alkoxide complexes $RuH(OCR_2$-2-py)((*R*)-binap) (R = Me **4**, R = Ph **5**). Complexes **4** and **5** are poor catalysts for asymmetric hydrogenation and are not catalysts for Michael addition reactions at room temperature, conditions where certain ruthenium complexes with diamine and phosphine ligands are known to be very active. The modified resin is demonstrated to be an effective phosphine scavenger in the synthesis of the known complex *trans*-$RuH(I)(dppe)_2$ (**6**) and the new complex *trans*-$RuH(I)(dppb)_2$ (**7**).

Introduction

The synthesis of a transition metal complex with phosphine ligands is often complicated by the separation of the product from phosphine in solution when their solubilities are similar and the complex cannot survive conventional chromatography. Dioumaev et al. overcame this problem in synthesizing trimethylphosphine ruthenium complexes by using BPh_3 to remove a PMe_3 contaminant as the less soluble borane-phosphine adduct.[1] They provide a useful list of "phosphine sponge" reagents mentioned in the literature, which are used in syntheses or to promote phosphine dissociation in catalysis. These reagents, along with more recent examples, include MeI,[2–4] boranes,[1,5,6] sulfur,[3] CS_2,[7] $ONMe_3$,[8] cuprous halides,[9–11] and a variety of metal complexes.[1]

Most of these sponge reagents are oxidizing or reactive toward transition metal hydride complexes such as the 16-electron complex RuHCl(binap)(PPh_3), binap = (*R*)- or (*S*)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl (**2**).[12,13] This latter complex is prepared by the reaction of $RuHCl(PPh_3)_3$ (**1**) with binap, but is very difficult to separate from excess binap and PPh_3, released as the byproduct (eq 1).

$$\underset{\mathbf{1}}{RuHCl(PPh_3)_3} + \text{binap} \rightarrow \underset{\mathbf{2}}{RuHCl(PPh_3)(\text{binap})} + 2PPh_3 \quad (1)$$

Complex **1** has been used to prepare a variety of RuHCl(binap)(L-NH_2) complexes where L-NH_2 are enantiopure bidentate

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ligands such as diamines[12–14] and β-aminophosphines (eq 2).[15–17] These are precatalysts for the asymmetric hydrogenation of the polar bonds of ketones and imines where the amino group plays a crucial role in the outer-sphere H^+/H^- transfer from a ruthenium hydridoamine H−RuN−H grouping to the polar bond.[18]

$$\mathbf{2} + \text{L-NH}_2 \rightarrow \text{RuHCl(L-NH}_2\text{)(binap)} + \text{PPh}_3 \quad (2)$$

The amine complexes of eq 2 are usually less soluble than PPh_3 and can be separated and purified in acceptable yields.

We wondered whether alcohol ligands, such as L-OH, could be used instead of L-NH_2 to produce complexes of the type RuHX(binap)(L-OH) and lead to active catalysts. These might utilize a H−RuO−H motif in ketone hydrogenation. Complexes with the $HRu(C_5R_4OH)$ substructure are already known to catalyze the outer-sphere hydrogenation of ketones.[19–24] For such an approach to succeed, it is important to remove traces of free PPh_3, which would compete with the weakly coordinating alcohol donor for ruthenium. However the sponge reagents mentioned seem too reactive. We therefore investigated the approach described by Lipshutz and Blomgren,[25] where PPh_3 and $OPPh_3$ can be scavenged by using an iodide-modified Merrifield resin (chloromethylpolystyrene-divinylbenzene). This allowed them to efficiently purify the C−C coupled products of Pd-catalyzed Stille reactions and Ni-catalyzed Negishi, Suzuki, and Kumada reactions. This report describes the successful use of this purification method and the synthesis of new hydrido alkoxo complexes of ruthenium. Other complexes of this class have been identified as important species in the catalytic hydrogenation of ketones.[26,27]

Experimental Section

General Information. All syntheses and manipulations except for the preparation of iodide-modified Merrifield resin were carried out under Ar or N_2 atmosphere using conventional Schlenk line and glovebox techniques. Dry, oxygen-free solvents were always used. Tetrahydrofuran, diethyl ether, and hexane were distilled from sodium benzophenone under argon. Deuterated solvents were degassed and dried over activated molecular sieves. NMR spectra were recorded on Mercury and Varian NMR System 400 MHz spectrometers, which were 400 MHz for ^1H, 100.4 MHz for ^{13}C, and 161.8 MHz for ^{31}P. The ^1H and $^{13}C\{^1H\}$ resonances of the partially deuterated solvents were used as the internal reference, but the chemical shifts are reported with respect to TMS. All ^{31}P chemical shifts are reported relative to 85% H_3PO_4 as an external reference. The infrared spectrum was recorded on a Spectrum One FT-IR spectrometer (Perkin-Elmer). Elemental analysis was done on a sample handled under Ar in the Department of Chemistry, University of Toronto. Merrifield resin (4.3 mmol/g Cl loading; 2% cross-linked with divinylbenzene; 200–400 mesh particle size) was purchased from Fluka. $RuHCl(PPh_3)_3$ was prepared according to the literature procedure.[28]

The catalytic hydrogenation experiments and the kinetic measurements were performed under constant pressures of H_2 gas in a 50 mL Parr high-pressure reactor. A constant temperature for these experiments was maintained using a Fisher Scientific IsoTemp 1016D water bath. The samples were analyzed by chiral GC on a Perkin-Elmer Autosystem XL with a Chrompack capillary column (ChirasilDEX CB 25 m × 0.25 mm). Hydrogen was used as a carrier gas at 5 psi in the column at 130 °C. The injector and FID temperatures were 250 and 275 °C, respectively. The retention times were as follows: acetophenone, 5.20 min; (*R*)-1-phenylethanol, 8.95 min; (*S*)-1-phenylethanol, 9.50 min.

Preparation of Potassium Dimethyl-2-pyridylmethoxide ($KOCMe_2$-2-py). Dimethyl-2-pyridylmethanol[29] as well as the corresponding lithium alkoxide[30] have been described in the literature. In this experiment, the precursor alcohol was prepared by a modified literature method.[31] A solution of 2-acetylpyridine (10.0 g, 83 mmol) in 70 mL of THF was added to a THF solution of methyl lithium (1.6 M, 56.2 mL, 90 mmol) and was reacted for 1 h at −95 °C (toluene/N_2(l)) under Ar. After stirring overnight at 20 °C, the addition of aqueous NH_4Cl solution (40.0 g NH_4Cl, 100 mL of H_2O) was followed by the addition of $CHCl_3$ (200 mL) and subsequent separation of the two layers. The solvents in the organic phase were evaporated. Precipitation from diethyl ether/hexane yielded a reddish-orange oil. Yield of dimethyl-2-pyridylmethanol: 4.40 g, 32 mmol (39%). Potassium hydride (0.300 g, 7.5 mmol) was suspended in ca. 10 mL of THF and this was added dropwise to a solution of the reddish-orange oil (1.02 g, 7.4 mmol) in ca. 10 mL of THF at –78 °C under N_2. After stirring for 30 min, the solvent was evaporated from the filtrate to yield a reddish solid, which was redissolved in diethyl ether. The mixture was then filtered through Celite, and the filtrate was concentrated. Addition of hexane yielded an orange product that was isolated by filtration and dried in vacuo. Yield of potassium dimethyl-2-pyridylmethoxide: 1.20 g (92%). Overall yield: 36%. ^1H NMR (DMSO-d_6, δ): 8.66 (d, $^3J_{HH}$ = 4.48 Hz, py), 8.26 (d, $^3J_{HH}$ = 7.89 Hz, py), 7.85 (t, $^3J_{HH}$ = 7.59 Hz, py), 7.31 (t, $^3J_{HH}$ = 5.73 Hz, py), 1.64 (s, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 176.6, 146.6, 134.9, 119.25, 119.2 (py), 72.49 (quarternary C), 34.21 (CH_3).

Preparation of Potassium Diphenyl-2-pyridylmethoxide ($KOCPh_2$-2-py). Diphenyl-2-pyridylmethanol[32,33] as well as the corresponding lithium alkoxide[30] have been described in the literature. A THF (44 mL) solution of 2-bromopyridine (6.17 mL, 65 mmol) was slowly added to another THF (44 mL) solution of butyl lithium (1.6 M, 43.5 mL, 70 mmol). Stirring at −95 °C (toluene/liq. N_2) for 45 min under Ar resulted in a deep red solution. Benzophenone (12.7 g, 70 mmol) was then added, followed by

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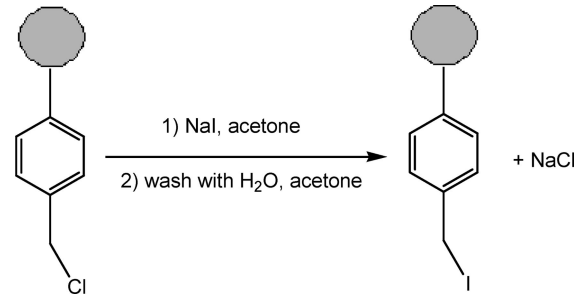
another portion of THF (40 mL), yielding a deep green mixture. After stirring overnight at room temperature, the mixture turned blue. The subsequent addition of H_2O (50 mL) gave a yellow mixture, which was separated into two layers. The aqueous phase was washed with $CHCl_3$ (15 mL), and the combined extracts were dried over $MgSO_4$ overnight. Evaporation of the solvents then yielded a white solid product. Yield of diphenyl-2-pyridylmethanol: 10.3 g, 62%. When the alcohol (1.00 g, 3.8 mmol) was reacted with potassium hydride (0.153 g, 3.8 mmol) in THF (20 mL) under N_2, H_2 gas evolved and a yellow solution with white precipitate resulted. The mixture was filtered through Celite and washed extensively with THF in order to remove residual potassium hydride. The solvent was evaporated from the filtrate *in vacuo*. Hexane was then added to the concentrated solution in order to precipitate the white product. The product was filtered, washed with hexane, and dried *in vacuo*. Yield: 0.906 g, 3.0 mmol (79%). Overall yield: 49%. ^{1}H NMR (DMSO-d_6, δ): 8.33, 7.97 (m, py), 7.52, 7.39, 7.09–6.97 (m, phenyl, pyridyl). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 172.9 (py), 154.1 (Ph), 146.3 (py), 135.0 (py), 128.3 (Ph), 126.1 (Ph), 124.2 (Ph), 122.2 (py), 119.7 (py), 83.49 (quarternary C).

Preparation of Iodide-Modified Merrifield Resin. High-loading 4.3 mmol Cl/g Merrifield resin (1.92 g) was stirred with sodium iodide (1.24 g) in acetone (10 mL). The resultant solid was filtered and washed extensively with water in order to eliminate the NaCl byproduct and any unreacted NaI. The resin was then washed with acetone and dried *in vacuo* to give 2.56 g of the product.

Preparation of RuHI((*R*)-binap)(PPh$_3$) (3). $RuHCl(PPh_3)_3$ (638 mg, contains 1 equiv of free PPh_3, 0.54 mmol) was reacted with (*R*)-binap (430 mg, 0.69 mmol) for 16 h in refluxing THF (15 mL) under N_2. The ^{31}P NMR spectrum recorded at this time on the reaction mixture with an insert (C_6D_6/trimethyl phosphite) as an internal reference indicated the presence of RuHCl((*R*)-binap)(PPh_3) as well as substantial amounts of free PPh_3 and binap and minor amounts of phosphine oxides. Iodide-modified Merrifield resin (900 mg) was added to the mixture and was left stirring overnight. The solvent was evaporated, diethyl ether (7 mL) was added to the concentrated solution, and Celite was used to filter out the phosphine-bound resin. The filtrate was concentrated to 3 mL, and hexane (4 mL) was added to precipitate the product. The red solid was filtered out, washed with hexane, and dried *in vacuo*. The ^{31}P NMR spectrum of the isolated product showed no evidence for the presence of free phosphines and phosphine oxides. After the product was isolated, dark red crystals were collected from the filtrate. Yield: 494 mg, 83%. ^{1}H NMR (CD_2Cl_2, δ): 8.2–6.1 (m, phenyl, binaphthyl), −22.87 (dt, $^2J_{HP}$ = 23.54, 33.16 Hz, RuH). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 138.2–124.3 (binaphthyl, phenyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 81.91 (X part of ABX, $^2J_{PP}$ = 20.4, 38.3 Hz, binap), 45.09 (B part of ABX, $^2J_{PP}$ = 38.3, 290.7 Hz, binap), 37.65 (A part of ABX, $^2J_{PP}$ = 20.4, 290.7 Hz, PPh_3). IR (CH_2Cl_2, cm^{-1}): 1967 (ν(RuH)). Anal. Calcd for $RuIP_3C_{62}H_{48}$: C, 66.85; H, 4.34. Found: C, 66.62, H, 4.24. ESI-MS (*m*/*z*) of complex in methanol: 1015.2 $[RuH(binap)(PPh_3)(OHCH_3)]^+$.

Preparation of RuH(OCMe$_2$-2-py)((*R*)-binap) (4). RuHI((*R*)-binap)(PPh_3) (170 mg, 0.16 mmol) and $KOCMe_2$-2-py (70 mg, 0.40 mmol) were stirred in THF (15 mL) overnight under Ar. The solution was filtered through Celite to eliminate potassium iodide. The solution was concentrated under vacuum, and then diethyl ether (6 mL) was added. The solution was again concentrated to 2 mL, and hexane (3 mL) was added to precipitate the product. The reddish-brown precipitate was filtered out, washed with hexane, and dried *in vacuo*. Yield: 32 mg, 0.037 mmol (24%). ^{1}H NMR (CD_2Cl_2, δ): 8.42–6.21 (m, Ph, py), 1.66 (s, CH_3), −19.79 (dd, $^2J_{HP}$ = 27.05, 42.14 Hz, RuH). ^{2}C{^{1}H} NMR (CD_2Cl_2, δ): 138.0–124.0 (binaphthyl, py), 65.86 (quarternary C), 31.79 (CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 90.45 (d, $^2J_{PP}$ = 36.5 Hz, binap), 62.99 (d, $^2J_{PP}$ = 36.5 Hz, binap). The spectra also revealed the presence of about 5% free PPh_3. This complex does not withstand the conditions used for the resin method of purification or for ESI-MS or EI-MS characterization.

Scheme 1



Preparation of RuH(OCPh$_2$-2-py)((*R*)-binap) (5). The procedure for synthesizing **4** was followed to react RuHI((*R*)-binap)(PPh_3) (120 mg, 0.11 mmol) with $KOCPh_2$-2-py (61 mg, 0.2 mmol). Yield: 25 mg, 0.024 mmol (23%). ^{1}H NMR (CD_2Cl_2, δ): 8.59 – 6.17(m, Ph, py), −20.36 (dd, $^2J_{HP}$ = 26.74, 42.71 Hz, RuH). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 137.9–123.2 (binaphthyl, py), 65.83 (quarternary C). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 90.07 (d, $^2J_{PP}$ = 39.4 Hz, binap), 63.20 (d,$^2J_{PP}$ = 39.4 Hz, binap). The spectra also revealed the presence of about 7% free PPh_3. This complex does not tolerate the conditions used for ESI-MS or EI-MS.

Catalytic H$_2$-Hydrogenation. The alkoxide complex **4** or **5** (5 mg, ca. 5 μmol) and acetophenone (305 mg, 2.5 mmol) were dissolved in 2-propanol or benzene (4 mL) and stirred under 10 atm of H_2 at 22 °C. The conversion to 1-phenylethanol was monitored by chiral gas chromatography. Complex **4** contaminated with 5% PPh_3 in ^{i}PrOH gave only 14% conversion to 1-phenylethanol (13% ee (*R*)) after 3 days. Complex **5** was not active in ^{i}PrOH. Using **5** contaminated with 12% PPh_3 in benzene gave 22% conversion to 1-phenylethanol (49% ee (*R*)) after 23 h. With 7% contamination by PPh_3 of **5**, the conversion after 23 h was only 6% (33% ee (*R*)).

Attempted Michael Addition Reactions. The alkoxide complex **4** or **5** (5 mg, ca. 5 μmol), dimethyl malonate (66 mg, 0.5 mmol), and 2-cylcohexen-1-one (48 mg, 0.5 mmol) were stirred in THF under Ar. There was no conversion after 24 h.

Preparation of *trans*-RuHI(dppe)$_2$ (6). $RuHCl(PPh_3)_3$ (150 mg, 0.12 mmol contaminated with PPh_3) was stirred with dppe (100 mg, 0.25 mmol added in two portions with monitoring by ^{31}P NMR to ensure complete conversion) in THF (10 mL) under N_2 for 2 h, during which time the color changed from purple to brownish orange. The mixture was filtered through Celite. Iodide-modified Merrifield resin (570 mg) was added to the filtrate, and the resulting mixture was stirred overnight. The resin was filtered out with Celite, and the filtrate was concentrated to approximately 1 mL, from which a yellow precipitate formed. The product was filtered and dried *in vacuo* and shown to be spectroscopically pure. Elemental analyses were acceptable for H and N but low for C probably due to a combustion problem. Yield: 65 mg, 53%. ^{1}H NMR ($CDCl_3$, δ): 7.2–6.6 (m, phenyl), 2.48 (m, $P(CH_2)_2$), 1.72 (m, $P(CH_2)_2$), −15.86 (qnt, $^2J_{HP}$ = 19.45 Hz, RuH). ^{31}P{^{2}H} NMR ($CDCl_3$, δ): 61.98 (s, dppe). These NMR data agree with those reported by Hirano et al.[34] and Gandhi et al.[35]

Preparation of *trans*-RuHI(dppb)$_2$ (7). The procedure for the preparation of **6** was followed. Reaction of $RuHCl(PPh_3)_3$ (135 mg, 0.09 mmol contaminated with PPh_3) with dppb (75 mg, 0.18 mmol) in THF (10 mL) yielded a yellow solution. Treatment with iodide-modified Merrifield resin (700 mg) removed the free PPh_3 and dppb

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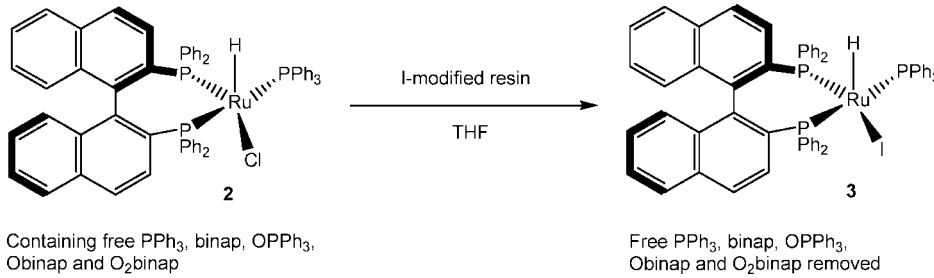
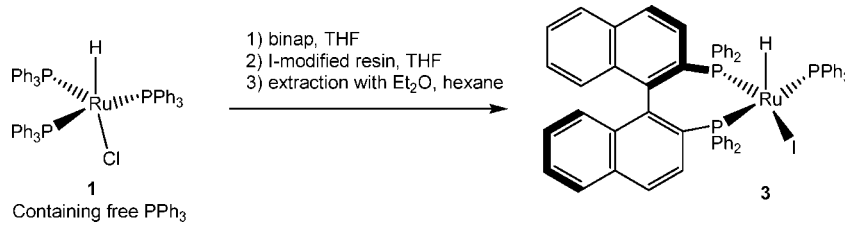
Scheme 2



Scheme 3



from the reaction mixture. The sample was spectroscopically pure and gave acceptable elemental analyses for N and H but low in C. Yield: 63 mg, 65%. ^{1}H NMR ($CDCl_3$, δ): 7.6–6.7 (m, phenyl), 0.91 (m, $P(CH_2)_4$), 0.52 (m, $P(CH_2)_4$), −16.42 (tt, $^2J_{HP}$ = 15.75, 23.56 Hz, RuH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 133.5–126.7 (phenyl), 30.6 (CH_2), 29.6 (CH_2), 21.6 (CH_2), 12.9 (CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 71.37 (t, $^2J_{PP}$ = 31.2 Hz, dppb), 54.76 (t, $^2J_{PP}$ = 31.2 Hz, dppb). ESI-MS (*m*/*z*) of complex in methanol: 955.3 [RuH(dppb)$_2$]$^+$.

Results and Discussion

While Lipshutz and Blomgren directly added Merrifield resin and NaI to solutions contaminated with PPh_3,[25] we found it advantageous to first isolate the iodo-substituted resin (Scheme 1). The white Merrifield resin was converted into a yellow iodo-substituted resin by reaction with NaI in acetone. This was then washed with water and acetone and dried *in vacuo*.

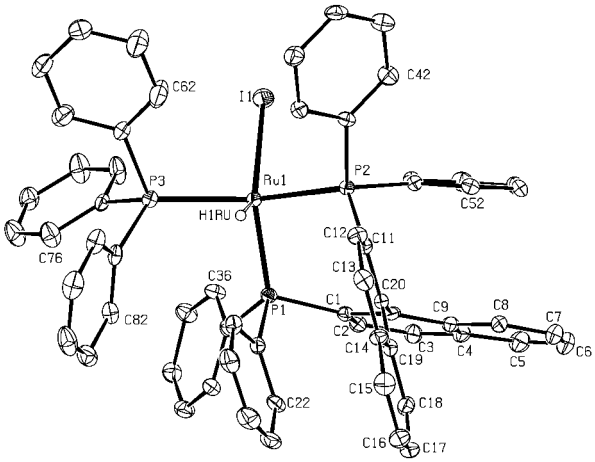


Figure 1. Structure of RuHI((*R*)-binap)(PPh_3) (**3**). Selected bond distances (Å) and angles (deg): I(1)−Ru(1) 2.7332(4), Ru(1)−H(1RU) 1.59(5), Ru(1)−P(1) 2.214(1), Ru(1)−P(2) 2.313(1), Ru(1)−P(3) 2.376(1); H(1RU)−Ru(1)−P(1) 83(2), H(1RU)−Ru(1)−P(2) 80(2), P(1)−Ru(1)−P(2) 90.37(4), H(1RU)−Ru(1)−P(3) 79(2), P(1)−Ru(1)−P(3) 98.85(4), P(2)−Ru(1)−P(3) 156.45(4), H(1RU)−Ru(1)−I(1) 136(2), P(1)−Ru(1)−I(1) 141.27(3), P(2)−Ru(1)−I(1) 92.08(3), P(3)−Ru(1)−I(1) 94.04(3).

A mixture produced via eq 1, which contained complex **2**, free PPh_3, $OPPh_3$, binap, and binap oxides, was treated with iodide-modified resin (Scheme 2) for 2 h in THF and then filtered. The iodo resin (1 g containing ≤ 3.1 mmol/g I) was determined to react with up to approximately 2.1 mmol of phosphine. The ^{31}P NMR spectrum of the filtrate showed that the isolated product was free of phosphorus-containing contaminants. However complex **2** was converted quantitatively into the new, red iodo complex, RuHI(PPh_3)((*R*)-binap) (**3**), which was recovered in 89% yield.

Complex **3** can also be prepared in 83% yield directly from $RuHCl(PPh_3)_3$ (contaminated with 1 equiv of PPh_3) with the use of the resin (Scheme 3).

Complex **3** in CD_2Cl_2 has a characteristic hydride resonance as a doublet of triplets at −22.87 ppm in the ^{1}H NMR spectrum and a diagnostic ABX pattern in the ^{31}P{^{1}H} NMR spectrum. RuHI(PPh_3)((*R*)-binap) readily crystallizes out of THF, diethyl ether, and hexane as long as the solution contains no impurities, and the complex is fully converted to the iodo product. This is significant because we have not been able to obtain crystals of the useful synthon RuHCl(PPh_3)((*R*)-binap).

The structure of a red crystal **3** is shown in Figure 1. The metal coordination geometry in **3** is distorted trigonal bipyramidal with P(2) and P(3) approximately axial (P(2)−Ru(1)−P(3) 156.45(4)°). The equatorial angles involving iodide (H(1RU)−Ru(1)−I(1) 136(2)°, P(1)−Ru(1)−I(1) 141.27(3)°) are large, while all of the P−Ru−H angles are small, falling in the range 79–83°. This contrasts with the angles in the equatorial plane of the related five-coordinate complexes $RuHCl(PPh_2NHC_6H_{10}NHPPh_2)(PPh_3)$ (H−Ru−Cl 158.7(12)°, P−Ru−Cl 108.92 (3)°)[12] and RuHCl(bpap)(PPh_3) (H−Ru−Cl 168.8(8)°, P−Ru−Cl 110.54(2)°),[36] where the smaller chloride ligand takes up a position that defines a distorted square pyramid. The Ru−I bond distance of 2.7332(4) Å is similar to the ones found in $Ru(P(CH_2)_6N_3)_3I_2(OH_2)$, 2.710(1) and 2.717(1) Å,[37] $[Ru(CO)_2I(P(O^iPr)_2CH_2CH_2CH_2PPhCH_2CH_2CH_2P(O^iPr)_2)]I$, 2.7582(7)

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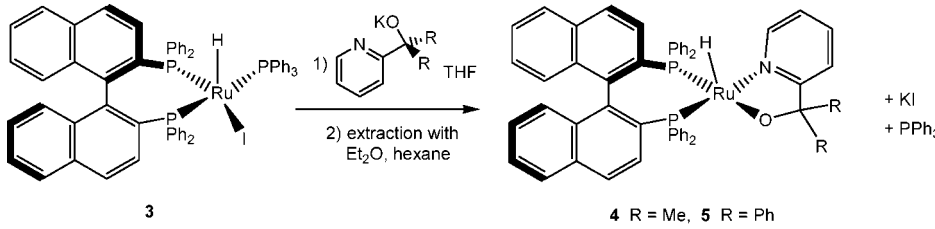
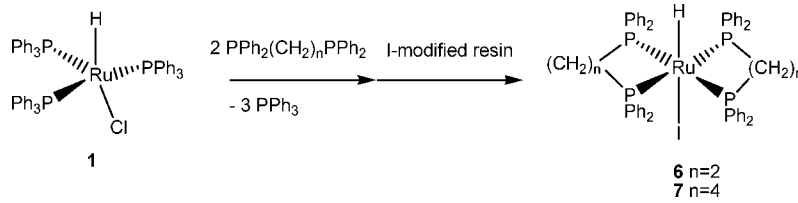
Scheme 4



Scheme 5



Å,[38] $[RuI(dppp)_2]PF_6$, 2.705(1) Å,[39] and $[RuI(dppe)_2]PF_6$, 2.6856(8) Å.[39]

With the pure complex **3** in hand, a variety of new hydride complexes can be prepared including the new hydrido alkoxide complexes $RuH(OCMe_2\text{-}2\text{-}py)((R)\text{-}binap)$ (**4**) and $RuH(OCPh_2\text{-}2\text{-}py)((R)\text{-}binap)$ (**5**) (Scheme 4).

The reddish-brown products **4** and **5** are rare, reactive five-coordinate hydrido alkoxide complexes. They are soluble in most common solvents to give solutions that immediately turn green upon exposure to air. A characteristic doublet of doublets at −19.79 ppm for **4** and −20.36 ppm for **5** was observed for the hydride in the ^1H NMR spectra of the hydrido alkoxide complexes in CD_2Cl_2. An AB pattern was seen in the $^{31}P\{^1H\}$ NMR spectrum of each of **4** and **5**, indicating complete dissociation of PPh_3 from the complexes. The isolated complexes were still contaminated with 5–7% of PPh_3. An attempt at using the resin treatment failed; instead it destroyed these very reactive hydrido alkoxide complexes. Complexes **4** and **5** do not react with 1 atm of H_2 in C_6D_6, unlike the related amido complex $RuH(PPh_3)_2(NHCMe_2CMe_2NH_2)$, which produces a *trans* dihydride diamine complex.[14]

Complexes **4** and **5** were tested as catalysts for the hydrogenation of acetophenone using H_2 or ^{i}PrOH as the source of the hydrogen. No evidence for transfer hydrogenation from ^{i}PrOH was observed in either highly phosphine-contaminated hydrido alkoxide complexes or those with only 5–7% PPh_3. The H_2 hydrogenation activity of complex **5** increased with the amount of the PPh_3 contamination. In general these alkoxide complexes were not active catalysts compared to the amido complexes $RuH(PPh_3)_2(NHCMe_2CMe_2NH_2)$ and $RuH(binap)(NHCMe_2CMe_2NH_2)$.[14] Complexes **4** and **5** were inactive as catalysts for the Michael addition reaction of dimethyl malonate with 2-cyclohexen-1-one. In contrast, $RuH(PPh_3)_2(NHCMe_2CMe_2NH_2)$ is an excellent catalyst under similar conditions.[40] These results imply that the alkoxide oxygen is not basic enough to effect the heterolytic splitting of dihydrogen or the deprotonation of dimethyl malonate, steps that are thought to be essential to the mechanism of action of the related amido catalysts.[40]

The utility of the resin to facilitate the synthesis of ruthenium complexes was further explored in the reactions of $RuHCl(PPh_3)_3$ with diphosphine ligands. The diphosphines 1,2-diphenylphosphinoethane and 1,4-diphenylphosphine butane were used to prepare the known complex *trans*-$RuH(I)(dppe)_2$ (**6**) and the new complex *trans*-$RuH(I)(dppb)_2$ (**7**) from $RuHCl(PPh_3)_3$ that was contaminated with PPh_3 in excellent yield (Scheme 5).

While the NMR spectra of complex **6** are simple, consisting of a quintet in the hydride region of the ^1H spectrum and a singlet in the $^{31}P\{^1H\}$ spectrum, those of complex **7** are somewhat unexpected for a *trans* complex. The hydride resonance is a triplet of triplets, while the $^{31}P\{^1H\}$ NMR spectrum has two triplets. These spin patterns have been observed before, for example, for the complexes *trans*-$[RuH(\eta^2\text{-}H_2)((R)\text{-}binap)_2]^+$,[41] *trans*-$[RuHL((R,R)\text{-}Me\text{-}duphos)_2]^+$, L = H_2, N_2,[42] and *trans*-$RuHCl((R,R)\text{-}diop)_2$.[43] The steric demands of these diphosphine ligands force the phosphorus donors of the chelate to alternate in position above and below the equatorial plane of complex. For the dppb ligands of **7**, one set of PPh_2 groups that are *trans* to each other are closer to the hydride, while the other set is closer to the iodide, thus producing the features observed in the NMR spectra.

Conclusions

We have reported the use of the iodide-modified Merrifield resin as a scavenger of byproduct in the synthesis of a useful new complex $RuHI((R)\text{-}binap)(PPh_3)$ (**3**). It was also used effectively in the synthesis of the known complex *trans*-$RuH(I)(dppe)_2$ and the new complex *trans*-$RuH(I)(dppb)_2$. Complex **3** was used to prepare the novel hydrido alkoxide complexes $RuH(OCMe_2\text{-}2\text{-}py)((R)\text{-}binap)$ (**4**) and $RuH(OCPh_2\text{-}2\text{-}py)((R)\text{-}binap)$ (**5**). These are poor catalysts for asymmetric hydrogenation, transfer hydrogenation, and Michael addition reactions, presumably because of the weak basicity of the alkoxide in these complexes.

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Supporting Information Available: X-ray crystallographic data in CIF format for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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