Amphiphilic Resin-Supported Ruthenium(II) Complexes as Recyclable Catalysts for the Hydrogenation of Supercritical Carbon Dioxide

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Abstract: Dichloro- and dihydridoruthenium(II) catalysts attached to an amphiphilic resin (PS – PEG) were prepared and tested for hydrogenation of supercritical carbon dioxide ($scCO_2$) in the presence of dimethylamine leading to *N*,*N*-dimethylformamide (DMF). The supported catalysts were successfully recyclable with only moderate loss of activity.

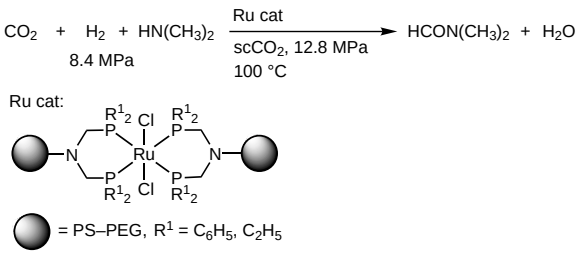
Keywords: amphiphilic resins; hydrogenation; immobilization; P ligands; ruthenium; supercritical carbon dioxide

Catalytic CO_2 hydrogenation to formic acid derivatives is one of the most promising approaches for utilizing the abundant C_1 feedstock.[1] Supercritical CO_2 ($scCO_2$) has been proven to act as an advantageous reaction medium and as a reactant for Ru-catalyzed hydrogenation in the presence of dimethylamine to give *N*,*N*-dimethylformamide (DMF) with very high efficiency and selectivity.[2,3] However, at a later stage of the CO_2 hydrogenation, the rate of the DMF formation drastically dropped possibly because of precipitation of the coproduct water in the $scCO_2$ phase resulting in phase separation between the catalyst and dimethylamine. The use of water-soluble Ru complexes with OH-substituted alkylphosphine ligands has been found to minimize the negative effect of water resulting in a significant improvement in the outcome of the reaction.[4] This finding of a highly effective water-soluble Ru catalyst for the CO_2 hydrogenation prompted us to investigate the separation and recovery of active Ru catalysts from such a complicated phase system including water and $scCO_2$.

The immobilization of molecular catalysts on an insoluble matrix has been emerging as a major option for easy isolation of the reaction product and recycling the catalyst. Baiker's group has prepared a series of sol-gel derived heterogeneous catalysts containing Ru complexes with bidentate phosphine ligands.[5] The structure of these hybrid materials considerably affected the outcome of the DMF synthesis, indicating that a suitable choice of the supporting compounds for immobilization of Ru complexes is likely important. We now describe the preparation and characterization of Ru complexes attached to an amphiphilic resin and the application of the recyclable resin-bound catalysts to the formation of DMF in $scCO_2$ as shown in Scheme 1.

We examined tertiary phosphines attached to cross-linked polystyrene-poly(ethylene glycol) graft copolymers (PS-PEG resin) as amphiphilic supporting materials for Ru complexes. This PS-PEG resin can give a clue to the catalyst recovery and may overcome the limited mass transfer of the reaction components involving the gaseous reactants (H_2 and CO_2), the hydrophilic amines, and water.[6] While a number of phosphine ligands have been tested for the CO_2 hydrogenation,[7] bidentate chelating diphosphines, which potentially have higher coordinating ability than the monodentate phosphines, should be appropriate supporting ligands for the octahedral Ru system.[5]

Attachment of diphosphine to the terminal of the polymer chains was performed by treatment of a commercially available ArgoGel-NH_2® resin with paraformaldehyde and secondary phosphines (HPR_2; R = C_6H_5 and C_2H_5) according to the Reetz's method as shown in Scheme 2.[8,9] The $^{31}P\{^1H\}$ NMR spectra of the resulting resin-supported phosphine ligand **1a** or **1b** in the gel-phase showed only a singlet at -28 or -33 ppm, respectively. Ligand displacement of the



Scheme 1. Hydrogenation of $scCO_2$ catalyzed by PS-PEG-bound Ru complexes.

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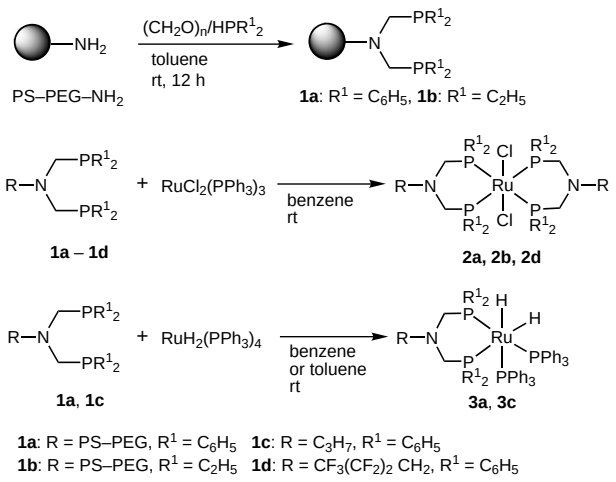

Scheme 2. Preparation of Ru-phosphine complexes **1 – 3**.

dichlororuthenium(II) complex, $[RuCl_2\{P(C_6H_5)_3\}_3]$ with ligand **1** in benzene yielded the immobilized Ru complex **2** as brown beads (Scheme 2). Incorporation of the Ru moiety into the resins was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. The phosphorus signals of the complexes **2a** and **2b** were observed as a singlet at -3.9 and -1.8 ppm, respectively, i.e., shifted to lower field compared with the those of the ligands **1a** and **1b**, indicating that these complexes have a symmetrical structure around the Ru metal center.

In order to obtain further information on the structure of the Ru complexes attached to the resin, non-supported diphosphine analogues **1c**[8] and **1d** were synthesized from *n*-propylamine or 2,2,3,3,4,4,4-heptafluorobutylamine in a similar manner to **1a** and **1b**. The ligand substitution of the triphenylphosphine on the $[RuCl_2\{P(C_6H_5)_3\}_3]$ with **1d** successfully occurred to yield a yellow complex **2d**, whereas the reaction with **1c** gave a pale yellow complex **2c** that was not identified due to its poor solubility in organic solvents. The $^{31}P\{^1H\}$ NMR of **2d** in acetone-d_6 exhibited a singlet at -5.5 ppm, indicating that four triphenylphosphine ligands were replaced by two diphosphine ligands to give a *trans*-configurated dichloro complex. The single-crystal X-ray crystallographic analysis of the complex **2d**,[10] as illustrated in Figure 1, confirms that it has an octahedral coordination environment with two bidentate phosphine ligands and two chloro ligands at the *trans*-positions. A similarity in the $^{31}P\{^1H\}$ NMR spectra between **2a**, **2b**, and **2d** indicates that the Ru center of **2a** or **2b** is fixed on the resin by two diphosphine units with a *trans*-configuration. These NMR studies as well as elemental analysis of the resins **2a** and **2b** allowed us to determine the Ru loading to be 0.23 mmol per gram of the resin.

A dihydridoruthenium(II) complex, *cis*-$[RuH_2\{P(C_6H_5)_3\}_4]$, can be immobilized into the amphiphilic resin **1a** in the same way (Scheme 2). The

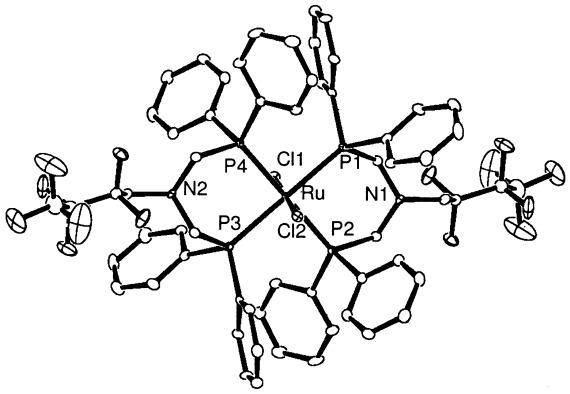

Figure 1. Thermal ellipsoid representation of complex **2d**.

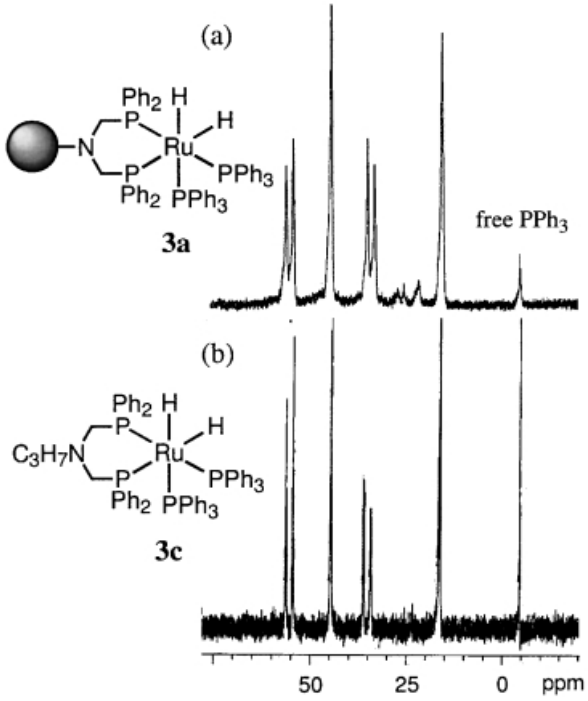

Figure 2. $^{31}P\{^1H\}$ NMR spectra of **3a** and **3c**.

^1H NMR spectrum of the resulting yellow beads **3a** showed two broad signals due to the hydride around -10 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **3a** gave four broad peaks in the range of 16 to 55 ppm as shown in Figure 2 (a). The triphenylphosphine ligands in *cis*-$[RuH_2\{P(C_6H_5)_3\}_4]$ were also exchanged with the non-supported diphosphine analogue **1c** in toluene at ambient temperature to give the dihydridoruthenium complex **3c**. The structure of **3c** was determined to be an all-*cis*-configuration by the $^{31}P\{^1H\}$ NMR spectrum, which showed four signals each with three $^2J_{P,P}$ couplings [Figure 2 (b)]. The similarity of the spectra between **3a** and the resin-free complex **3c** indicates that the Ru center on **3a** has analogous geometry in the complex **3c**. Noticeably, only two triphenylphosphine ligands in *cis*-$[RuH_2\{P(C_6H_5)_3\}_4]$ were exchanged with **1a** or **1c** to give

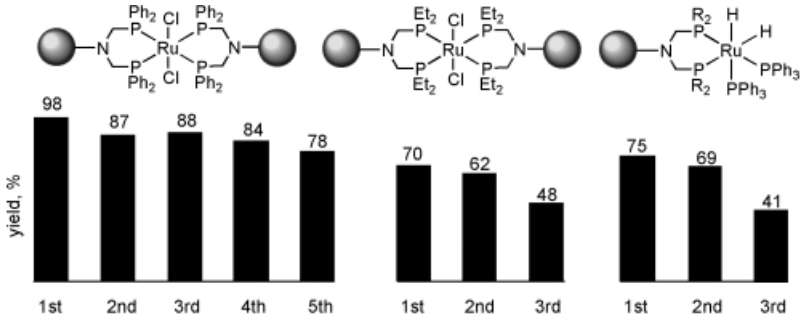

Figure 3. Catalytic activities of **2a**, **2b**, and **3a** in recycle runs.

the dihydridoruthenium complex **3a** or **3c**, even if an excess amount of chelate phosphine was used. The Ru loading was determined to be 0.37 mmol per gram of the resin by elemental analysis and was close to the theoretical loading.

The synthesis of DMF *via* CO_2 hydrogenation was performed under H_2 (8.4 – 8.6 MPa) and CO_2 (12.8 – 13.0 MPa) at 100 °C with an amine/catalyst molar ratio of 2,000:1. The isolated complex **2c** exhibited high catalytic activity, a turnover number (TON) = 1,620, in 15 h.[11] Comparable catalytic activities were observed for the resin-supported catalysts, **2a**, **2b**, and **3a** in the reaction. The color of the resin beads **2a** and **2b** was found to change from brown to yellow within the initial 4 h of the reaction. The ^{1}H NMR spectrum of the yellow beads from **2a** showed a broad signal around -7.5 ppm, possibly due to the Ru-bound hydrogen atoms. It should be noted that the yields of DMF were increased remarkably with the formation of the yellow resins, in which hydridoruthenium was possibly generated as a catalytically active species under the reaction conditions.

The catalyst resins can be successfully separated by decantation and reused after drying under vacuum. In fact, as shown in Figure 3, the catalyst **2a** could be reused four times with high TONs in the range of 1,560 – 1,960. However, the catalysts **2b** and **3a** were not able to maintain the activities in the repeated experiments. According to the ^{31}P{^{1}H} NMR of the recovered catalyst beads, the trialkylphosphine ligands on the catalyst **2b** were partially oxidized during the reaction in $scCO_2$ to give phosphine oxides. A significant loss of the catalytic activity of **3a** during the recycling may have resulted from the metal leaching. A strong *trans* effect of the hydrido ligands of **3a** may promote the dissociation of the phosphine ligands to provide unstable Ru species.

In summary, the amphiphilic polymer (PS-PEG) supported catalysts were successfully applied to DMF synthesis in $scCO_2$ and amphiphilic properties can combine the advantages of both hydrophilic homogeneous systems and recyclable heterogeneous catalysts. The NMR observation of the resins provided important information on the structure of the metal fragments, which strongly affects catalyst performance.

Experimental Section

Preparation of PS-PEG Resin-Supported Diphosphines 1a and 1b

Commercially available PS-PEG-NH_2 resin (ArgoGel NH_2®) was first washed several times with acetonitrile and then dichloromethane before being dried under vacuum. A mixture of methanol (5.0 mL), paraformaldehyde (3.2×10^{-2} g, 1.0 mmol), and diethylphosphine in 10 wt % in hexane (1.37 mL, 1.0 mmol) was heated at 65 °C for 20 min under an argon atmosphere. The mixture was cooled to room temperature and treated with PS-PEG-NH_2 resin (1.0 g, 0.4 – 0.5 mmol N/g · resin). After 30 min stirring at room temperature, toluene (15 mL) was added, and the mixture was heated again at 65 °C for 30 min. The reaction mixture was filtered and the resin was washed with methanol (15 mL × 4), acetonitrile (15 mL × 4), and dichloromethane (15 mL × 2). The resin was dried under vacuum to give the pale yellow beads of **1b**. ^{31}P{^{1}H} NMR (acetone-d_6): $\delta = -32.8$.

The diphosphine-bound resin **1a** was prepared in a similar way. ^{31}P{^{1}H} NMR (acetone-d_6): $\delta = -27.6$.

Preparation of Resin-Free Diphosphine 1d

A mixture of paraformaldehyde (0.32 g, 10.2 mmol) and diphenylphosphine (2.0 g, 10.8 mmol) in methanol (5.0 mL) was heated at 65 °C for 20 min under an argon atmosphere. The mixture was cooled to room temperature and treated with 2,2,3,3,4,4,4-heptafluorobutylamine (1.0 g, 5.3 mmol). After 30 min stirring at room temperature, toluene (15 mL) was added, and the mixture was heated at 65 °C for 30 min. The reaction mixture was evaporated under reduced pressure. The residue was extracted with *n*-pentane (5 mL), and the product was obtained as viscous oil. ^{1}H NMR (acetone-d_6): $\delta = 7.33 - 7.47$ (m, 20H), 3.84 (d, $J = 2.9$ Hz, 4H), 3.73 (t, $J = 17.2$ Hz, 2H); ^{19}F NMR (acetone-d_6): $\delta = -40.0$, -51.8, -82.5; ^{31}P{^{1}H} NMR (acetone-d_6): $\delta = -27.6$.

Preparation of PS-PEG Resin-Supported Ru Complexes 2a, 2b, and 3a

To a benzene suspension (10 mL) of resin-supported diphosphine ligand **1a** (0.4 g) was added $[RuCl_2\{P(C_6H_5)_3\}_3]$ (0.19 g, 0.2 mmol) at room temperature and the mixture was stirred slowly for 18 h. After filtration, the resin was washed with

benzene (10 mL × 3) and dried under vacuum to give brown beads of **2a**. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ = – 3.9; chlorine content: 1.66%; loading: 0.23 mmol g^{-1}.

The dichloro complex **2b** was prepared in a similar way. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ = – 1.8; chlorine content: 1.56%; loading: 0.23 mmol g^{-1}.

The dihydrido complex **3a** was synthesized by treatment of **1a** with $[RuH_2\{P(C_6H_5)_3\}_4]$ under similar conditions. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ = 54.9 (d, J = 219.0 Hz), 44.2, 33.7 (d, J = 219.0 Hz), 15.1; nitrogen content: 0.52%; loading: 0.37 mmol g^{-1}.

Preparation of Dichloro-Ru Complex 2d

A solution of diphosphine **1d** (937 mg, 1.57 mmol) in benzene (5 mL) was added dropwise to benzene (10 mL) solution of $[RuCl_2\{P(C_6H_5)_3\}_3]$ (725 mg, 0.756 mmol). The mixture was stirred at room temperature for 17 h. A light yellow solid precipitated and was washed with ether. After recrystallization from acetone, yellow blocks were obtained; yield: 0.184 g (18%). ^1H NMR (acetone-d_6): δ = 7.96 – 7.52 (m, 40H), 4.29 (br, 8H), 3.67 (t, J = 17.6 Hz, 4H); ^{19}F NMR (acetone-d_6): δ = – 39.0, – 51.9, – 82.5; $^{31}P\{^1H\}$ NMR (acetone-d_6): δ = – 5.5; anal. calcd. for $C_{60}H_{52}Cl_2F_{14}N_2P_4Ru \cdot C_2H_6O$: C 53.25, H 4.11, N 1.97, Cl 4.99%; found: C 52.88, H 4.32, N 2.01, Cl 4.84%.

Formation of Dihydrido-Ru Complex 3c

A solution of diphosphine **1c** (0.45 g, 0.98 mmol) in toluene (5 mL) was added dropwise to a toluene (40 mL) solution of $[RuH_2\{P(C_6H_5)_3\}_4]$ (1.04 g, 0.90 mmol). The mixture was stirred at room temperature for 30 min. The resulting solution was filtered through active carbon to remove metallic particles and evaporated to dryness. The residue was washed with *n*-pentane (15 mL) and dried under vacuum. Formation of **3c** was confirmed by $^{31}P\{^1H\}$ NMR. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ = 54.7 (ddd, J = 21.1, 21.5, 222.2 Hz), 44.2 (ddd, J = 14.2, 21.5, 21.5 Hz), 34.1 (ddd, J = 14.2, 25.6, 222.2 Hz), 15.9 (ddd, J = 21.1, 21.5, 25.6 Hz).

Standard Procedure for the Hydrogenation

The reactor was charged with argon gas and was placed in the oven at 100 °C before the introduction of reagents. A mixture of $[(CH_3)_2NH_2]^+[OCON(CH_3)_2]^-$[3] (46.0 mmol) and Ru catalyst (4.6 μmol) was transferred into the reactor with a syringe through an opening against the flow of CO_2. CO_2 (12.8 – 13 MPa) was introduced, and the mixture was stirred for 30 min. After reaching a steady state, H_2 (8.4 – 8.6 MPa) was added with a syringe pump. After stirring for 15 h, the reactor was cooled in a bath of methanol with dry ice. CO_2 was vented, and the reactor was slowly warmed to the room temperature. The yields of products were determined by NMR analyses.

***Safety warning*:** Operators of high-pressure equipment should take proper precautions to minimize the risk of personal injury.

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[10] X-ray crystal structure analysis of **2d**: crystallized from chloroform, formula: $C_{62.5}H_{55}Cl_{11}F_{14}N_2P_4Ru$, M = 1715.0, yellow crystal 0.20 × 0.20 × 0.10 mm, a = 28.825(9) Å, b = 10.011(3) Å, c = 25.300(8) Å, β = 107.225(4)°, V = 6973.2 Å^3, ρ_{calc} = 1.634 g · cm^{-3}, μ = 8.17 cm^{-1}, F(000) = 3444.00, Z = 4, monoclinic, space group $C2/c$ (#15), MoK_α radiation (λ = 0.71070 Å, graphite monochromator), T = 123 K. 18417 reflections collected, 7677 independent reflections, 7669 observed reflections (I >

0.00σ(I)), 456 refined parameters. $R1 = 0.066$, w$R2 = 0.171$. Data collection was performed with a Rigaku Mercury Detector. The structure was solved by direct methods (SIR92; A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435) and expanded using Fourier techniques (DIRDIF99; P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. deGelder, R. Israel, J. M. M. Smits, **1999**; *The DIRDIF99 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands). Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as deposition No. CCDC-190840.

[11] The catalyst activity of **2c** was as high as that of the previously reported PMe_3- and DPPE-coordinated Ru complexes.