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Rhodium amine complexes tethered on silica-supported gold–palladium bimetal catalysts. Arene hydrogenation

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Abstract

Arene hydrogenation activities of catalysts prepared by tethering $Rh(COD)[H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3](X)$ on the silica support of the bimetal catalyst Au:Pd–SiO_2 were studied under the mild conditions of 40°C and 1 atm H_2 pressure. The most active catalyst PF_6–Rh(N–N)/Au:Pd–SiO_2, with the weakly coordinating PF_6^- anion, remains highly active for toluene hydrogenation through at least three catalytic cycles involving 2900 mol H_2/mol Rh turnovers over a 19-h period. As compared with the activity of the Pd-supported catalyst PF_6–Rh(N–N)/Pd–SiO_2, the catalysts with added Au are less active only by a factor of two. But the activity depends strongly on the Pd and Rh complex loadings. Although the detailed functioning of these TCSM catalysts (tethered complex on a supported metal) is not known, a mechanism that is consistent with the results involves dissociative adsorption of H_2 on the supported Pd. The hydrogen spills over onto the silica surface where the Rh complex uses it to hydrogenate the arene substrate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: TCSM; Tethered complex catalysts; Bimetallic catalysts; Toluene hydrogenation; Palladium; Gold

1. Introduction

The heterogenization of metal complex catalysts on solid supports generates catalysts that have the advantage over their homogeneous counterparts that they may be easily separated from the reaction products [1–3]. Several materials including organic polymers as well as inorganic solids such as silica, zeolites, glass, clay and metal oxides have been used as supports [4]. Among these, silica is widely used to tether homogeneous transition metal complexes that contain siloxy groups that can bind to the silica surface [5,6]. Supported bimetallic heterogeneous catalysts have been studied extensively [7] and show improved characteristics such as high activity and stability over those of monometallic supported catalysts [8]. In this research group, a new type of heterogeneous catalyst has been developed by tethering homogeneous complexes to the silica of supported metal catalysts such as Pd–SiO_2 [9]. These TCSM catalysts (tethered complex on supported metal) function by the synergistic effects of both the tethered

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complex and supported metal. TCSM catalysts consisting of tethered rhodium amine complexes on Pd–SiO_2, Pt–SiO_2 and Au–SiO_2 have been used for the hydrogenation of arenes [10]. Their activities are much higher than those of the tethered complex or the supported metal separately. A possible explanation for the high activities of these catalysts is that the supported metal, e.g., Pd, is the site at which H_2 is activated to produce spillover hydrogen which moves onto the SiO_2 surface where the tethered complex uses it for the hydrogenation of the arene substrates [9]. In order to explore the effect of *two* supported metals on the catalytic activities of TCSM catalysts consisting of a rhodium amine complex tethered on silica-supported Au and Pd, we performed the studies described in this paper.

Although several rhodium diamine complexes have been prepared, few have been used as catalysts [11,12]. Gokak et al. [13] studied polymer-supported $Rh(N \sim N)Cl_3$, where $N \sim N$ = 1,2-diaminoethane, for the hydrogenation of 1-octene at atmospheric pressure and in the temperature range 30–55°C; the polymer was styrene-divinylbenzene. The rhodium complex $Rh(COD)(N \sim N)^+$ ($N \sim N$ = pyridyl-imine ligand) was used by Brunner et al. to catalyze the hydrosilylation of ketones [14]. Câpka et al. [15] studied the silica-anchored rhodium carbonyl complex prepared from $(CH_3O)_3Si(CH_2)_2$-py (py = 2-pyridyl) and $Rh_2Cl_2(CO)_4$ in the hydrogenation of 1-octene under the conditions of 65°C and 1 atm H_2 pressure. They observed that the immobilized rhodium complex was three times more active than the analogous homogeneous catalyst. Corma et al. [16] recently reported a zeolite-supported rhodium complex $Rh(COD)(N \sim N)PF_6$, where COD = 1,5-cyclooctadiene, $N \sim N$ = 2-(3-triethoxysilyl-propyl-aminocarbonyl)pyrrolidine, that catalyzes the hydrogenation of arenes under 6 atm of H_2 pressure and 80°C. As noted above, a rhodium complex with the diamine ligand $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$ tethered on Pd–SiO_2 is a highly active TCSM catalyst for arene hydrogenation under the mild conditions of 40°C and 1 atm H_2 pressure [10]. Only a few homogeneous catalysts are active under the low pressure of 1 atm H_2, but their activities are low [17–19]. Otherwise, such catalysts require high pressures for the hydrogenation of arenes [20–22]. On the other hand, TCSM catalysts are active for the hydrogenation of arenes under mild conditions such as 40°C and 1 atm H_2 pressure [9,10].

In the present study of toluene hydrogenation reactions, we examine the effects of various loadings of Pd and Au supported on silica to which rhodium complexes of the type $Rh(COD)[H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3](X)$ are tethered. We also describe the influence of the X^- anion in the complex on the activities of the TCSM catalysts.

2. Experimental

2.1. General procedures

Syntheses of the rhodium complex catalysts were performed using standard Schlenk techniques under a nitrogen atmosphere. Rhodium trichloride ($RhCl_3 \cdot 3H_2O$) was purchased from Pressure Chemicals. $PdCl_2$ and $HAuCl_4 \cdot xH_2O$ (Au, 49%) were purchased from D.F. Goldsmith Chemical and Stevens Metallurgical, respectively. The rhodium dimer $[Rh(COD)Cl]_2$ was prepared according to the literature method [23]. The $[Rh_2(\mu\text{-}S(CH_2)_3Si(OCH_3)_3)_2(CO)_4]$ complex (Rh–S) was prepared by the published procedure [24]. Silica gel 100 (B.E.T. surface area, 400 m^2/g) and 3(2-amino ethylamino)-propyltrimethoxysilane $[H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3]$ were obtained from Fluka. The 1,5-cyclooctadiene (COD) was purchased from Aldrich. Solvents were dried by refluxing over CaH_2 under nitrogen before use. All other reagents and chemicals were commercial samples and were used as received, unless otherwise mentioned.

^{1}H NMR spectra were obtained on samples in $CDCl_3$ solvent using a Varian VXR 300-MHz NMR spectrometer with TMS as the internal reference ($\delta = 0.00$ ppm). FTIR and DRIFT spectra were recorded on a Nicolet 560 spectrophotometer equipped with TGS and MCT detectors in the main compartment and in the auxiliary experiment module (AEM), respectively. The AEM housed a Harrick diffuse reflectance accessory. The solution IR spectra were measured in the main compartment in a cell with NaCl salt plates. The DRIFT spectra were recorded with the samples in the Harrick microsampling cup. A Varian 3400 GC interfaced to a Finnigan TSG 700 high-resolution magnetic sector mass spectrometer with electron ionization (70 eV) was used for all GC–MS measurements. Gas chromatographic analyses were performed with a Hewlett Packard HP 6890 GC system with an FID detector using a 25 m HP-1 capillary column. Elemental microanalyses were performed on a Perkin-Elmer 2400 Series 11 CHNS/O analyzer. The rhodium contents of the TCSM catalysts were determined using atomic emission spectroscopy. The analytical samples were prepared by first treating the catalysts (50.0 mg) with 5.00 ml of aqua regia at room temperature for 5–10 min with shaking. Then 5.00 ml of aqueous HF (5%) was added and the mixture was heated until all of the solid dissolved. The resulting solution was diluted to 25.0 ml with distilled water.

2.2. Preparation of the catalysts

2.2.1. Preparation of the silica-supported heterogeneous metal and bimetal catalysts

2.2.1.1. Pd–SiO_2. This was prepared according to the general procedure described in Ref. [25]. An aqueous solution of $H_2PdCl_4 \cdot xH_2O$ (prepared by dissolving 1.20 g of $PdCl_2$ in 80.0 ml of aqueous HCl (0.200 M)) was added to a flask containing 7.00 g of SiO_2. After the mixture was stirred at room temperature overnight, the water was removed by slow evaporation in a rotary evaporator at 80°C. The resulting sample was dried at 110°C for 5 h in an oven and then calcined at 500°C in an air flow for 4 h in a tube furnace. The calcined material was subsequently reduced in a H_2 flow for 4 h at 380°C and then passivated under a flow of air at room temperature for 1 h to give black Pd/SiO_2 (Pd 9.9 wt.%) powder.

2.2.1.2. Au–SiO_2. Following the procedure in Ref. [26], a mixture of 5.00 g of SiO_2 and 1.0 g of $HAuCl_4 \cdot xH_2O$ (Au, 49%) in an aqueous HCl solution (0.200 M, 75.0 ml) was stirred at room temperature overnight. After the water was removed by rotary evaporation at ca. 80°C, the solid was dried in an oven at 110°C for 5 h. Then the solid was reduced by a flow of H_2 at 250°C for 4 h to give a red-brown powder Au/SiO_2 (Au 10 wt.%).

2.2.1.3. Au:Pd–SiO_2. A series of Au:Pd/SiO_2 catalysts with different wt.% of Pd and Au were prepared by incipient wetness coimpregnation [27] of silica with appropriate amounts of the metal chlorides. Both $HAuCl_4 \cdot xH_2O$ (0.085–0.861 g) and H_2PdCl_4 (0.201–0.833 g) (H_2PdCl_4 was prepared by dissolving $PdCl_2$ in 0.200 M HCl) in solution were stirred with silica overnight at room temperature in order to achieve the desired Au and Pd wt.% mentioned at the end of this paragraph. Since about 2.20 ml of impregnation solution per gram of SiO_2 (> 400 m^2/g) was sufficient to bring about incipient wetness [28], the amount of water added was determined by the amount of SiO_2. The slurries obtained after impregnation were dried on a hot plate at 80°C. Then they were calcined at 500°C in a stream of air for 5 h and finally reduced in a H_2 flow for 18 h at 380°C to give black Au:Pd–SiO_2 powder. Two series of bimetallic catalysts were prepared by this procedure. Series 1: The Pd wt.% was a constant 9.9%. Au wt.% increased as follows: 0.80, 2.1, 4.2%. Series 2: The Au wt.% was a constant 4.2%. Pd wt.% increased as follows: 1.0, 4.1, 9.9%.

2.2.2. Preparation of the rhodium complexes

2.2.2.1. Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3$-$Si(OCH_3)_3$](Cl) (Cl–Rh(N–N)). A mixture of $[Rh(COD)Cl]_2$ (0.090 g, 0.181 mmol) and $(NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3)$ (0.120 ml, 0.501 mmol) in CH_2Cl_2 (10.0 ml) was stirred under nitrogen at room temperature for 1 h. The solution became yellow, and the solvent was removed under vacuum at room temperature. The yellow solid was washed with hexanes (5.00 ml × 2) and dried under vacuum to give a yellow powder of Cl–Rh(N–N) in 91% yield. The ^1H-NMR assignments are based on the reported values [29] for the free ligands COD and $[NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3]$. ^1H NMR/$CDCl_3$ δ (ppm): 5.00 (br, 1H, CH_2NHCH_2), 4.39 (br, 2H, H_2NCH_2) 4.22 (s, br, 4H, CH=CH), 3.61 (s, 9H, OCH_3), 2.97 (m, 2H, $H_2NCH_2CH_2$), 2.73 (m, 2H, $H_2NCH_2CH_2NH$), 2.51 (m, 2H, $CH_2HNCH_2CH_2$), 2.36 (m, 4H, $CH_2CH{=}CH$), 1.76–1.82 (m, 6H, CH_2CH_2Si and $CH_2CH{=}CH$), 0.57 (t, 2H, CH_2Si). ($C_{16}H_{34}ClN_2O_3RhSi$): Found (calc.): % C, 40.98 (40.53), % H 7.31 (7.02), % N 5.97 (6.03).

2.2.2.2. Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3$-$Si(OCH_3)_3$](PF_6) (PF_6–Rh(N–N)). Following a previously reported method [30], a solution of Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3$] Cl (0.171 g, 0.360 mmol) dissolved in 20.0 ml of MeOH was treated with the slow addition of 0.121 g (0.650 mmol) of KPF_6 dissolved in 5.00 ml of distilled water. This mixture was stirred at room temperature under nitrogen for 30 min. After most of the MeOH was removed under vacuum, the solid was filtered off and dissolved in CH_2Cl_2. After the KCl was separated by filtration, the CH_2Cl_2 was removed from the filtrate under vacuum to leave a dark yellow solid which was washed with hexanes (5.00 ml × 2) and dried under vacuum to give PF_6–Rh(N–N) in 85% yield. ^1H NMR/$CDCl_3$ δ (ppm): 5.00 (br, 1H, CH_2NHCH_2), 4.39 (br, 2H, H_2NCH_2) 4.21 (s, br, 4H, CH=CH), 3.56 (s, 9H, OCH_3), 2.97 (m, 2H, $H_2NCH_2CH_2$), 2.72 (m, 2H, $H_2NCH_2CH_2NH$), 2.49 (m, 2H, $CH_2HNCH_2CH_2$), 2.33 (m, 4H, $CH_2CH{=}CH$), 1.70–1.80 (m, 6H, CH_2CH_2Si and CH_2-CH=CH), 0.56 (t, 2H, CH_2Si). ($C_{16}H_{34}F_6$-N_2O_3 PRhSi): Found (calc.): % C 32.91 (33.22), % H 5.59 (5.55), % N 5.12 (4.84).

2.2.2.3. Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3$-$Si(OCH_3)_3$](CF_3SO_3) (CF_3SO_3–Rh(N–N)). Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3$]-(Cl)(0.171 g, 0.360 mmol) was dissolved in 20.0 ml of MeOH. To this solution, NaO_3SCF_3 (0.080 g, 0.460 mmol) dissolved in 4.00 ml of MeOH was added. After the solution was stirred for 30 min at room temperature, MeOH was removed under vacuum, and the resulting solid was dissolved in CH_2Cl_2 (10.0 ml). This solution was filtered to remove the NaCl; then the CH_2Cl_2 was removed under vacuum. The resulting pale yellow solid was recrystallized from CH_2Cl_2/diethyl ether to give CF_3SO_3–Rh(N–N) in 61% yield. ^1H NMR/$CDCl_3$ δ (ppm): 5.00 (br, 1H, CH_2NHCH_2), 4.39 (br, 2H, H_2N-CH_2),4.02 (s, br, 4H, HC=CH), 3.56 (s, 9H, OCH_3),2.83 (m, 2H, $NH_2CH_2CH_2$), 2.63 (m, 2H, $H_2NCH_2CH_2NH$), 2.49 (m,4H, $CH_2CH{=}CH$), 2.36 (m, 2H, CH_2NHCH_2-CH_2), 1.82 (m, 4H, $CH_2CH{=}CH$), 1.66 (m,2H, CH_2CH_2Si), 0.57 (t, 2H, CH_2Si). ($C_{17}H_{34}$-$F_3N_2O_6RhSSi$): Found (calc.): % C35.44-(35.17), % H 5.76 (5.55), % N 5.06 (4.82), % S 5.80 (5.52).

2.2.2.4. Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3$-$Si(OCH_3)_3$]](I) (I–Rh(N–N)). To a solution of Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3$] (Cl) (0.172 g, 0.360 m mol) in 20.0 ml of dry acetone, NaI (0.060 g, 0.401 mmol) in 5.00 ml of toluene was added. The solution was stirred under nitrogen for 20 min at room temperature as it became brown in color. The solution was filtered and the acetone was evaporated under vacuum. The resulting brown solid was washed with diethyl ether and dried under vacuum to obtain the complex I–Rh(N–N) in 70% yield.

^{1}H NMR/CDCl$_3$ δ (ppm): 5.00 (br, 1H, $\mathrm{CH_2N}H\mathrm{CH_2}$), 4.39 (br, 2H, $H_2\mathrm{NCH_2}$), 4.14 (s, br, 4H, $H\mathrm{C{=}C}H$), 3.53 (s, 9H, $\mathrm{OC}H_3$), 2.94 (m, 2H, $\mathrm{NH_2C}H_2\mathrm{CH_2}$), 2.75 (m, 2H, $\mathrm{H_2NCH_2C}H_2\mathrm{NH}$), 2.40 (m, 2H, $\mathrm{CH_2NHC}H_2\mathrm{CH_2}$), 2.50 (m, 4H, $\mathrm{C}H_2\mathrm{CH{=}CH}$), 1.60–1.79 (m, 6H, $\mathrm{C}H_2\mathrm{CH_2Si}$ and $\mathrm{C}H_2\mathrm{CH{=}CH}$), 0.57 (t, 2H, $\mathrm{C}H_2\mathrm{Si}$). ($\mathrm{C_{16}H_{34}IN_2O_3RhSi}$): Found (calc.): % C 34.46 (34.30), % H 5.84 (5.73), % N 5.36 (5.10).

2.2.2.5. $Rh(COD)[NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3](BPh_4)$ (BPh_4–Rh(N–N)). To $\mathrm{Rh(COD)[NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3](Cl)}$(0.172 g, 0.360 mmol) dissolved in 20.0 ml of MeOH, $\mathrm{NaBPh_4}$ (0.121 g, 0.420 mmol) dissolved in 5.00 ml of distilled water was added. This mixture was stirred under nitrogen for 30 min at room temperature. A yellow solid was filtered off and washed with a mixture of MeOH and $\mathrm{H_2O}$ (1:1) and dried under vacuum. The resulting pale yellow solid was washed with hexanes (5.00 ml × 2) to give $\mathrm{BPh_4}$–Rh(N–N) in 73% yield. ^{1}H NMR/CDCl$_3$ δ (ppm): 6.75–7.15 (m, 20H, Ph), 5.00 (br, 1H, $\mathrm{CH_2N}H\mathrm{CH_2}$), 4.39 (br, 2H, $H_2\mathrm{NCH_2}$), 3.75 (s, br, 4H, $H\mathrm{C{=}C}H$), 3.47 (s, 9H, $\mathrm{OC}H_3$), 2.38 (m, 2H, $\mathrm{NH_2C}H_2\mathrm{CH_2}$), 2.09 (m, 2H, $\mathrm{H_2NCH_2C}H_2\mathrm{NH}$), 1.50 (m, 2H, $\mathrm{CH_2NHC}H_2\mathrm{CH_2}$), 1.95 (m, 4H, $\mathrm{C}H_2\mathrm{CH{=}CH}$), 1.34 (m, 4H, $\mathrm{C}H_2\mathrm{CH{=}CH}$), 1.22 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2Si}$), 0.89 (m, 2H, $\mathrm{C}H_2\mathrm{Si}$). ($\mathrm{C_{40}H_{54}BN_2O_3RhSi}$): Found (calc.): % C 64.27 (64.00), % H 7.08 (6.93), % N 3.97 (3.73).

2.3. Preparation of the tethered rhodium complex TCSM catalysts

2.3.1. X–Rh(N–N)/Pd–SiO$_2$ ($X = Cl^-$, I^-, PF_6^-, BPh_4^-, $CF_3SO_3^-$)

A solution of X–Rh(N–N) ($\mathrm{X = Cl^-}$, $\mathrm{I^-}$, $\mathrm{PF_6^-}$, $\mathrm{BPh_4^-}$, $\mathrm{CF_3SO_3^-}$) dissolved in 15 ml of $\mathrm{CH_2Cl_2}$ was added to previously degassed Pd–SiO$_2$ (1.00 g) under vacuum. This mixture was refluxed (while stirring) for 4 h under nitrogen. The solid was filtered and washed with $\mathrm{CH_2Cl_2}$ (10.0 ml × 3). The tethered rhodium-amine complex catalyst X–Rh(N–N)/Pd–SiO$_2$ was obtained after drying in vacuum.

2.3.2. X–Rh(N–N)/Au:Pd–SiO$_2$ ($X = Cl^-$, I^-, PF_6^-, BPh_4^-, $CF_3SO_3^-$)

These bimetallic catalysts were prepared in the same manner as X–Rh(N–N)/Pd–SiO$_2$ by using Au:Pd–SiO$_2$ (prepared in two series as mentioned in Section 2.2.1.3) instead of Pd–SiO$_2$. The X–Rh(N–N)/Au:Pd–SiO$_2$ ($\mathrm{X = PF_6^-}$ and $\mathrm{Cl^-}$) catalysts were characterized by stirring them (0.102 g) in 4.0 ml of toluene under a CO atmosphere for 5 h at room temperature. After filtration, the solid catalyst was washed with toluene (10 ml × 2) and dried under vacuum. The resulting X–Rh(N–N)/Au:Pd/SiO$_2$ catalysts (Au:Pd wt.% 4.2:1.0) gave IR spectra (DRIFT) with two ν(CO) absorptions: $\mathrm{X = Cl^-}$, 2085(s), 2037(vs) cm^{-1} and $\mathrm{X = PF_6^-}$, 2093(s), 2047(vs) cm^{-1}.

2.3.3. [$Rh_2(\mu\text{-}S(CH_2)_3Si(OCH_3)_3)_2(CO)_4$]/Au:Pd–SiO$_2$ (Rh–S/Au:Pd–SiO$_2$)

The $\mathrm{Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4}$ complex (0.049 g, 0.065 mmol) in 15.0 ml of toluene was added to 1.00 g of previously degassed Au:Pd–SiO$_2$ (Au:Pd wt.% 4.2:1.0) and refluxed for 4 h under nitrogen. The solid catalyst was separated by filtration and washed with toluene (15 ml × 3). After drying under vacuum, the Rh–S/Au:Pd–SiO$_2$ catalyst analyzed for 1.53 wt.% Rh. The IR spectrum (DRIFT) of this catalyst gave ν(CO) values of 2072(s), 2051(s), 2002(s) cm^{-1}. These wavenumbers and intensities are similar to those (2070(m), 2050(s) and 2002(s)) of the free $\mathrm{[Rh_2(\mu\text{-}S(CH_2)_3Si(OCH_3)_3)_2(CO)_4]}$ complex in toluene and to those (2081(m), 2064 (s) and 2020 (s) cm^{-1}) previously reported for this complex tethered on just SiO$_2$ [24].

2.4. Hydrogenation reactions

The hydrogenation reactions were carried out in a three necked, jacketed vessel (about 100 ml) closed with a self-sealing silicon rubber cap and containing a stirring bar; the vessel was connected to a vacuum/H_2 line and a constant pressure 1 atm gas burette. The temperature of the circulating ethylene glycol passing through the jacket was maintained by a thermostated bath (Haake B3-DC1). After the catalyst was added and the air in the vessel was replaced with H_2, the substrate was injected into the vessel. While being constantly stirred at a speed of 550 rpm, H_2 uptake was followed with the constant pressure gas burette. The rates of the reactions measured by the rate of H_2 uptake, were reproducible within ±3% for typical reactions. The products were identified by GC and GC–MS.

3. Results and discussion

3.1. Hydrogenation of toluene with the TCSM catalysts

The TCSM catalysts $Rh(COD)[NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3](X)$ / Pd–SiO_2,Rh(COD) $[NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3](X)$/Au:Pd–$SiO_2$, ($X = Cl^-$, I^-, PF_6^-, BPh_4^-, $CF_3SO_3^-$) and $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4$/Au:Pd–$SiO_2$, were used to catalyze the hydrogenation of toluene to methylcyclohexane under the conditions of 40°C and 1 atm of H_2 pressure. No hydrogenolysis products were detected during the reactions. Table 1 gives the hydrogenation activities of the Au:Pd–SiO_2 catalyst, the PF_6–Rh(N–N) complex tethered on just SiO_2 [PF_6–Rh/SiO_2] and three TCSM catalysts; these activities are expressed in terms of TOF (turnover frequency), TO (turnover number) or mmol of H_2 uptake as defined in the table.

The first two TCSM catalysts, Cl–Rh(N–N)/Au:Pd–SiO_2 and PF_6–Rh(N–N)/Au:Pd–SiO_2 are much more active than either the tethered rhodium complex on just silica (PF_6–Rh(N–N)/SiO_2) or just the supported bimetallic Au:Pd–SiO_2 (Au:Pd wt.% 4.2:1.0) catalyst. Of these two TCSM catalysts, PF_6–Rh(N–N)/Au:Pd–SiO_2 shows the higher activity. However, the TCSM catalyst Rh–S/Au:Pd–SiO_2, containing the rhodium carbonyl thiolate complex (Rh–S), had no activity and is therefore less active than just Au:Pd–SiO_2. Dirhodium complexes of the general formula $Rh_2(\mu\text{-}SR)_2(CO)_4$ were previously demonstrated to be active olefin hydroformylation catalysts [31]. When tethered on phosphine-modified silica, P–(Pd–SiO_2), where P = ($Ph_2P(CH_2)_3Si(OC_2H_5)_3$, it was an active TCSM catalyst for the hydrogenation of toluene [32].

Since PF_6–Rh(N–N)/Au:Pd–SiO_2 showed good activity for the hydrogenation of toluene, it was studied in other arene hydrogenations under the same mild conditions to give the corresponding cyclohexane products (Table 2). The percent conversions increase in the follow-

Table 1
Hydrogenation of toluene with TCSM catalysts[a]

Catalyst	Rh (%)	TOF (mol H_2/ mol Rh min)	TO[b] (mol H_2/ mol Rh)	H_2 uptake[b] (mmol)
Cl–Rh(N–N)/Au:Pd–SiO_2^c	3.6	0.239	155 (10 h)	2.69 (10 h)
PF_6–Rh(N–N)/Au:Pd–SiO_2^c	0.61	3.73	1655 (7 h)	4.49 (7 h)
Rh–S/Au:Pd–SiO_2^c	1.5	0.00	0.00 (5 h)	0.00 (5 h)
PF_6–Rh(N–N)/SiO_2	1.4	0.00	0.00 (5 h)	0.00 (5 h)
Au:Pd–SiO_2^c	0.00	–	–	1.56 (19 h)

[a] Reaction conditions: 50 mg solid catalyst, 5.00 ml toluene, 40°C, 1 atm H_2.
[b] TO and H_2 uptake values correspond to the reaction times (in hours) in parentheses.
[c] Au:Pd wt.% is 4.2:1.0%.

Table 2
Arene hydrogenation using the PF_6–Rh(N–N)/Au:Pd–SiO_2 catalyst[a]

Substrate	TOF (mol H_2/ mol Rh min)	TO[b] (mol H_2/ mol Rh)	H_2 uptake[b] (mmol)
anisole	0.294	488 (26 h)	4.74 (26 h)
toluene	0.124	198 (23 h)	1.91 (23 h)
benzene	0.176	165 (26 h)	1.56 (26 h)
ethyl benzene	0.055	138 (23 h)	1.33 (23 h)

[a] Reaction conditions: 1 ml substrate, 4 ml heptane (spectroscopic grade), 50 mg solid catalyst (Au:Pd 4.2:1.0 wt.% and Rh 2.0 wt.%), 40°C, 1 atm H_2 pressure.
[b] Footnote is the same as in Table 1.

ing order: ethylbenzene (4.6%, 23 h) < benzene (4.8%, 26 h) < toluene (6.6%, 23 h) < anisole (13.3%, 26 h). Anisole reacts fastest of the studied arenes, indicating that electron donating substituents on the arene ring accelerate the rate. A comparison of the rate of hydrogenation of toluene with that of ethylbenzene indicates the size of the alkyl substituent affects the rate little. Similar substituent effects on arene hydrogenation rates were observed with other TCSM catalysts such as Rh–CNR_2/Pd–SiO_2 and Rh–CNR_3/Pd–SiO_2 [9,33].

The durability of the PF_6–Rh(N–N)/Au:Pd–SiO_2 catalyst (Rh 1.2%, Au:Pd wt.% 4.2: 1.0) was tested by running three successive hydrogenation reactions of toluene using the conditions in Table 1. In the first cycle, the maximum TOF was 1.52 and TO was 696 for a 7-h run. Then, the catalyst was filtered from the reaction mixture, washed with fresh toluene (5 ml × 2) in air, dried under vacuum at room temperature and then used for the second run. The second hydrogenation cycle gave a maximum TOF of 3.20 and TO of 1227 after 6 h. After the catalyst was treated as described after the first cycle, the third run gave a maximum TOF of 2.47 and a TO of 971 for 6 h. Thus, the catalyst was more active in the second and third cycles than in the first, and after the three runs (19 h), the total TO was 2900 mol H_2/mol Rh. The DRIFT spectrum of the catalyst after three cycles, followed by treatment with 1 atm CO, contained bands at 2092(s) and 2049(vs) cm^{-1}, which are the same as those (2093(s), 2047(vs) cm^{-1}) observed for the CO-treated catalyst before use in the hydrogenation reactions. When the untethered PF_6–Rh(N–N) complex was treated with CO (1 atm) in toluene, it gave a similar spectrum (2094(s), 2025(s) cm^{-1}) also indicating the formation of a Rh(diamine)$(CO)_2^+$ complex. These results are consistent with the formation of a Rh(diamine)$(CO)_2^+$ complex even after three hydrogenation cycles.

In order to test for the possibility that the Rh complexes leach from the catalyst and homogeneously catalyze the toluene hydrogenation, the *solution* after each of the three runs was treated with more toluene (5 ml) and tested for H_2 uptake, but there was none after 7 h. Atomic emission spectroscopic analyses of the used solutions gave no detectable Rh, which suggests that Rh did not leach from the catalyst.

3.2. Effect of counter anion (X^-) on toluene hydrogenation

Since the Cl–Rh(N–N)/Au:Pd–SiO_2 and PF_6–Rh(N–N)/Au:Pd–SiO_2 TCSM catalysts had significantly different toluene hydrogenation activities (Table 1), we decided to examine the X–Rh(N–N)/Au:Pd–SiO_2 TCSM catalysts with other counter anions, PF_6^-, BPh_4^-, $CF_3SO_3^-$, I^- and Cl^-, in the tethered complex (Table 3). For the series of catalysts in which the X–Rh(N–N) complexes were tethered on Au:Pd–SiO_2 (Au:Pd wt.%, 4.2: 1.0%), the rates of toluene hydrogenation as a function of the anion (X^-) are given in Table 3 and Fig. 1. The plots of TO vs. time (Fig. 1) show the rates of hydrogenation to decrease in the order: PF_6^- >

Table 3
Comparison of rates of toluene hydrogenation with different counter anions in X–Rh(N–N)/Au:Pd–SiO_2 and X–Rh(N–N)/Pd–SiO_2 catalysts[a]

X^-	Rh (%)	TOF (mol H_2/ mol Rh min)	TO[b] (mol H_2/ mol Rh)	H_2 uptake[b] (mmol)
X–Rh(N–N)/Au:Pd–SiO_2 catalysts[c]				
PF_6^-	0.47	9.3	3160 (6 h)	6.95 (6 h)
BPh_4^-	0.94	3.3	1211 (6 h)	5.45 (6 h)
$CF_3SO_3^-$	1.3	1.2	504 (6 h)	3.17 (6 h)
I^-	0.26	7.4	786 (23 h)	0.91 (23 h)
Cl^-	3.6	0.18	91 (6 h)	1.58 (6 h)
X–Rh(N–N)/Pd–SiO_2 catalysts[d]				
BPh_4^-	0.70	12	5738 (7 h)	19.4 (7 h)
PF_6^-	0.82	6.9	2931 (6.5 h)	11.7 (6.5 h)
I^-	1.1	3.2	1389 (7 h)	7.6 (7 h)
$CF_3SO_3^-$	1.7	2.6	1336 (7.25 h)	10.9 (7.25 h)
Cl^-	2.3	1.4	576 (7 h)	6.34 (7 h)

[a] Reaction conditions: 5 ml toluene, 50 mg solid catalyst, 40°C, 1 atm H_2 pressure.
[b] Footnote is the same as in Table 1.
[c] Au:Pd 4.2:1.0 wt%.
[d] Pd 9.8 wt%.

$BPh_4^- > CF_3SO_3^- > Cl^-$. The I–Rh(N–N)/Au:Pd SiO_2 catalyst showed a comparatively high rate at the beginning of the reaction but became inactive after about 2 h as indicated in Fig. 1. The rates of toluene hydrogenation as a function of the anion for the X–Rh(N–N)/Pd–SiO_2 catalysts, in which Pd–SiO_2 is the supported metal, follow a similar, but not identical, trend (Table 3 and Fig. 2): $BPh_4^- > PF_6^- > I^- \approx CF_3SO_3^- > Cl^-$. In general, the most weakly coordinating anions, PF_6^- and BPh_4^-, gave the most active catalysts.

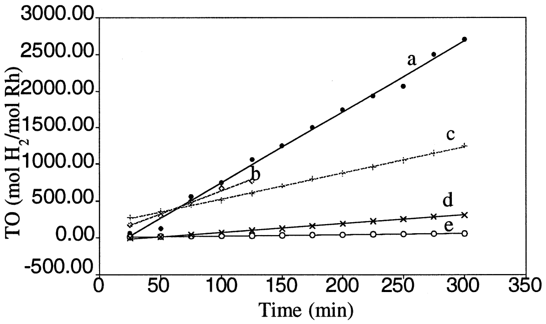

Fig. 1. Kinetic plots for the hydrogenation of toluene over the X–Rh(N–N)/Au:Pd–SiO_2 catalysts: X^- = (a) PF_6^-, (b) I^-, (c) BPh_4^-, (d) $CF_3SO_3^-$, (e) Cl^-. Reaction conditions are the same as those in Table 3.

Studies of the effects of anions on catalyst activity have been performed in relatively few other systems. Burckhardt et al. [34] investigated anion effects on the enantioselectivity of asymmetric allylic amination of 1,3-diphenylprop-2-enylethylcarbonate with benzyl amine using a homogeneous Pd-catalyst with ferrocenyl phosphine ligands. They observed enhancement of ee (to > 99.5%) with small hard anions such as F^- and BH_4^- while very low ee

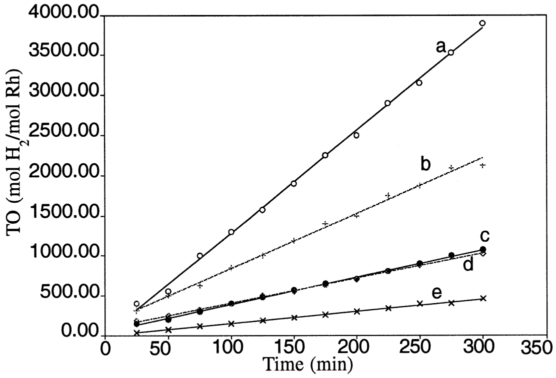

Fig. 2. Kinetic plots for the hydrogenation of toluene over the X–Rh(N–N)/Pd–SiO_2 catalysts: X^- = (a) BPh_4^-, (b) PF_6^-, (c) I^-, (d) $CF_3SO_3^-$, (e) Cl^-. Reaction conditions are the same as those in Table 3.

($< 10\%$ ee) were obtained with non-coordinating anions such as PF_6^-. Studies of the hydrogenation of imines [35] such as [ArMeC=NCH$_2$Ph] using Rh[(−)-dbpp](NBD) (ClO_4) as a catalyst and a sulfonate (RSO_3^-) co-catalyst showed high enantioselectivity. On the other hand, the Rh complex together with halide co-catalysts gave an almost complete reversal of enantioselectivity. The authors proposed that the hydrogenations proceed via a monohydride pathway in the presence of RSO_3^- in non-polar solvents, but in the presence of halides it occurs by a dihydride pathway [35]. Thus, anions in other catalytic systems also have a marked effect on the course of reactions.

3.3. *Effect of temperature on toluene hydrogenation rates*

The effects of temperature on the catalytic activities of the X–Rh(N–N) complexes ($X = PF_6^-$ and BPh_4^-), when tethered on Au:Pd–SiO_2 (Au:Pd wt.%, 4.2:1.0) and Pd–SiO_2, were studied. The results (Table 4) show that for the Au:Pd–SiO_2-supported catalysts, the rates increase as the temperature increases from 24 to 70°C for $X^- = BPh_4^-$, but the rates for $X^- = PF_6^-$ increase from 24 to 40°C then decrease at 70°C. For the Pd-supported TCSM catalysts, the activity of the $X^- = BPh_4^-$ catalyst increases from 24 to 40°C but decreases upon further heating to 70°C. However, for $X^- = PF_6^-$, the rates increase from 24° through to 70°C. The increase in rate with increasing temperature is expected for most reactions and is observed for the BPh_4–Rh(N–N)/Au:Pd–SiO_2 and PF_6–Rh(N–N)/Pd–SiO_2 catalysts. On the other hand, the rates for the PF_6–Rh(N–N)/Au:Pd–SiO_2 and BPh_4–Rh(N–N)/Pd–SiO_2 catalysts go through a maximum at 40°C. Although rate maxima for the latter two catalysts are surprising, such behavior has been observed previously with simple heterogeneous catalysts. For example, Joice and Rooney [36] observed that the rates of hydrogenation of 1-butene on catalysts composed of Au:Pd (Au mol% 0–65) supported on pumice increase up to 90°C but then decrease at higher temperatures. On the other hand, the rate of neopentane conversion to methane, ethane, propane, isobutane, isopentane, and *n*-pentane on 2 wt.% (total metal) Au:Pd–SiO_2 increases with an increase in temperature: $240 < 260$°C [27]. For the TCSM catalysts, PF_6–Rh(N–N)/Au:Pd–SiO_2 and BPh_4–Rh(N–N)/Pd–SiO_2,

Table 4
Study of the temperature effect on toluene hydrogenation[a]

Catalyst	Temperature (°C)	TOF (mol H_2/ mol Rh min)	TO[b] (mol H_2/ mol Rh)	H_2 uptake[b] (mmol)
BPh_4–Rh(N–N)/Au:Pd–SiO_2^c	70	3.8	1500 (6 h)	6.75 (6 h)
(Rh wt.% 0.94)	40	3.3	1211 (6 h)	5.45 (6 h)
	24	1.0	516 (6 h)	2.32 (6 h)
PF_6–Rh(N–N)/Au:Pd–SiO_2^c	70	5.2	1414 (6 h)	4.19 (6 h)
(Rh wt.% 0.61)	40	3.7	1655 (7 h)	4.49 (7 h)
	24	0.55	124.0 (6 h)	0.36 (6 h)
BPh_4–Rh(N–N)/Pd–SiO_2^d	70	6.3	2432 (6 h)	8.27 (6 h)
(Rh wt.% 0.70)	40	13.1	4980 (6 h)	16.9 (6 h)
	24	5.3	2679 (6 h)	9.11 (6 h)
PF_6–Rh(N–N)/Pd–SiO_2^d	70	29	10 572 (6 h)	42.2 (6 h)
(Rh wt.% 0.82)	40	6.9	2931 (6.5 h)	11.7 (6.5 h)
	24	6.3	2522 (6 h)	10.0 (6 h)

[a] Reaction conditions: 5 ml toluene, 50 mg catalyst, 1 atm H_2 pressure.
[b] Footnote is the same as in Table 1.
[c] Au:Pd wt.% is 4.2:1.0%.
[d] Pd wt.% is 9.8.

Table 5
Hydrogenation of toluene using Au:Pd–SiO_2 catalysts[a]

Mol% (wt.%)		H_2 uptake[b] (mmol)	Initial time[c] period (h)
Au	Pd		
0.0 (0.0)	100 (9.9)	1.77 (24.0 h)	3.0
18.6 (5.0)	81.3 (11.6)	1.59 (22.5 h)	2.5
38.4 (4.2)	61.5 (4.07)	1.57 (19.0 h)	4.0
69.3 (4.2)	30.6 (1.0)	1.39 (22.5 h)	2.0
89.8 (6.6)	10.1 (0.41)	1.56 (22.5 h)	2.5

[a] Reaction conditions: 50 mg of Au:Pd–SiO_2, 5.0 ml of toluene, 40°C, 1 atm pressure.
[b] Total reaction period in parentheses.
[c] Time period required to consume 1 ml of H_2 at the beginning of the reaction.

the maxima in rates are presumably related to the behavior of the X^- anion in the complex.

3.4. Effects of Au and Pd loadings on the catalytic activity of Cl–Rh(N–N)/Au:Pd–SiO_2 catalysts

The purpose of these investigations was to understand the effects of the Au and Pd loadings on the TCSM catalyst activities.

3.4.1. Activity of Au:Pd–SiO_2 supported catalysts

Prior to examining the TCSM catalysts, we studied the Au:Pd–SiO_2 catalysts in toluene hydrogenation under the conditions of 40°C and 1 atm pressure. The activities of all of these catalysts are much lower than those of the TCSM catalysts (Table 1). In Table 5 are shown the amounts of H_2 (mmol) consumed in 19–24 h for Au:Pd–SiO_2 catalysts with Pd metal mole percentages ranging from 10.1 to 100%. Surprisingly, these rates are all very similar. As another measure of catalytic activity, we determined the time that it took for 1.0 ml of H_2 to be consumed at the beginning of the reaction. Again, the times are all very similar (2.0–4.0 h) for the different Au and Pd loadings. It should be emphasized that these rates are all slow as indicated by the observation that it takes only 35 min to consume 1.0 ml of H_2 when using PF_6–Rh(N–N)/Au:Pd–SiO_2 (0.47% Rh, Au:Pd wt.% 4.2:1.0) catalyst.

3.4.2. Effect of various gold loadings with constant palladium loading on Cl–Rh(N–N)/Au:Pd–SiO_2 catalytic activity

The catalyst Cl–Rh/Au:Pd–SiO_2 that contains no Au is more active than any of the catalysts that contain some Au (Table 6). For the series of catalysts in which the Pd loading is kept constant at 9.8%, the rate (in parentheses) as measured by the TO/h for the total reaction time changes with increasing Au content (% Au) in the order: 0.8% Au (35 TO/h), 2.1% (48 TO/h), 4.2% (43 TO/h). The variation in rate is rather small with increasing Au loading, and the irregular trend in rates may be due to changes in the morphology of the supported bimetal catalysts. Studies of Au:Pd–SiO_2 performed by Juszczyk et al. [27] showed that in all catalysts that they prepared with different Au:Pd mole

Table 6
Effect of Au and Pd loadings on the activities of Cl–Rh(N–N)/Au:Pd–SiO_2 catalysts in toluene hydrogenation[a]

Au:Pd	Rh (%)	TOF (mol H_2/mol Rh min)	TO[b] (mol H_2/mol Rh)	TO/h[c] (mol H_2/mol Rh h)
0.0:9.8	2.3	1.3	707 (9.5 h)	74
0.8:9.8	1.2	0.48	266 (7.5 h)	35
2.1:9.8	0.82	0.74	481 (10 h)	48
4.2:9.8	1.5	0.79	304 (7.0 h)	43
4.2:4.1	2.5	0.63	455 (18 h)	25
4.2:1.0	3.6	0.23	155 (10 h)	16

[a] Reaction conditions: toluene 5 ml, catalyst 50 mg, 1 atm H_2 pressure.
[b] Footnote is the same as in Table 1.
[c] TO/h for the total reaction time.

ratios, there are two types of particles on the surface: Pd-rich and Au-rich particles. At low Au loadings (e.g., 4 mol% Au and 96 mol% Pd), the Pd-rich islands dominate and the metal dispersion is 0.80. At higher Au loadings (e.g., 30 mol% Au and 70 mol% Pd), both Pd-rich and Au-rich particles are present; and the Au-rich islands are composed of 91% Au. The metal dispersion of the 30:70 Au:Pd catalyst is only 0.53. These results suggest that there are also probably substantial structural changes in the Au:Pd–SiO_2 portion of the Cl–Rh(N–N)/Au:Pd–SiO_2 catalyst. These changes may account for the irregularly changing activities as the Au loading is increased.

On the other hand the % Rh is also changing in these catalysts even though the tethering process is the same for all of the catalysts. If TO were to change with the Rh complex loading, this would also affect the activities of these catalysts. In fact, for Cl–Rh(N–N)/Au:Pd–SiO_2 (Au:Pd 4.2:1.0%), TO (128 mol H_2/mol Rh for 6 h) is significantly higher when the % Rh is 1.5 than it (91 mole H_2/mol Rh for 6 h) is when the % Rh is 3.6. Thus, TO decreases as the %Rh increases, which is similar to the trend in rates observed for the three catalysts with increasing Au content (Table 6). Thus, the observed changes in Cl–Rh(N–N)/Au:Pd–SiO_2 catalyst activity with Au loading may be due to changes in either the morphology of the Au:Pd–SiO_2 portion of the catalyst or the changing amounts of Rh complex tethered to the surface.

3.4.3. Effect of various palladium loadings with constant gold loading on Cl–Rh(N–N)/Au:Pd–SiO_2 catalytic activity

For the series of Cl–Rh(N–N)/Au:Pd–SiO_2 catalysts (Table 6) in which the % Au is held constant at 4.2%, the TO/h values increase as the % Pd increases in the order: 1.0% Pd (16 TO/h) $<$ 4.1% Pd (25 TO/h) $<$ 9.8% Pd (43 TO/h). Thus, the rate of toluene hydrogenation appears to increase linearly with the amount of Pd, which is somewhat surprising because the morphology of the Au:Pd–SiO_2 part of the catalysts undoubtedly changes as the amount of Pd increases [27]. Another explanation for the increasing rate with increasing % Pd involves considering the % Rh in the catalyst. Although the tethering process was the same for all of the Au:Pd–SiO_2 catalysts, the amount of complex tethered in these catalysts decreases as the % Pd increases. Since TO increases as the Rh loading decreases, as noted above, the trend in increasing TO/h values may be reasonably understood in terms of the decreasing Rh loading. Thus, the observed increase in TO/h values may be due to either the increase in % Pd loading or to the decrease in % Rh loading.

3.5. Comments on the form of the rhodium on the catalyst

The hydrogenation of toluene to methylcyclohexane is catalyzed by the series of TCSM catalysts of the composition X–Rh(N–N)/Au:Pd–SiO_2. Reactions of the catalysts with CO help to characterize the form of the catalysts. When PF_6–Rh(N–N)/Au:Pd–SiO_2 (Au:Pd wt.% 4.2:1.0 with Rh 1.2%) reacts with CO (1 atm) in toluene before use in a hydrogenation reaction, a Rh complex with ν(CO) bands at 2093(s) and 2047(vs) cm^{-1} is formed; the positions of these bands suggest that tethered $Rh(diamine)(CO)_2^+$ is formed. This result indicates that the COD ligand is displaced by CO in this reaction. The PF_6–Rh(N–N)/Au:Pd–SiO_2 catalyst, even after being used in three toluene hydrogenation cycles, exhibits the same ν(CO) bands after treatment with CO. This suggests that either the COD ligand is still present after the hydrogenation and is displaced by CO or the COD ligand is no longer present as a result of having been hydrogenated and some other donor groups stabilize the $Rh(diamine)^+$ fragment. In $Rh(COD)(PR_3)_2^+$-catalyzed olefin hydrogenation reactions, it is observed [37] that the COD ligand is hydrogenated at 25°C. It is also presumably hydrogenated off from the Rh complex in the PF_6–Rh(N–N)/Au:Pd–SiO_2 catalysts. Since PF_6^- is a very weakly coordinating ligand, it seems likely that surface oxygen atoms on the SiO_2 will occupy the sites formerly occupied by COD, thereby stabilizing the Rh(diamine)$^+$ unit. This SiO_2-stabilized Rh(diamine)$^+$ unit could also react with CO to give the Rh(diamine)$(CO)_2^+$ complex. It is also conceivable that under the conditions of the reaction Rh^I is removed from the diamino ligand and deposits on the Au:Pd–SiO_2 surface. Such a deposition has been observed when $Rh_2Cl_2(CO)_4$ complexed to phosphinated silicas is treated with H_2 for several days at room temperature [38]. These catalysts showed bands at 2048(s) and 1983(s) cm^{-1} which were attributed to CO adsorbed on metallic rhodium. In our studies, we see no band in the 1983 cm^{-1} region which suggests that metallic Rh is not present. However, $Rh^I(CO)_2$ has been identified in several studies [39] of Rh on silica. This species has bands at 2093, 2038 cm^{-1}, which are quite similar to those (2093, 2047 cm^{-1}) observed in our studies of the PF_6–Rh(N–N)/Au:Pd–SiO_2 catalyst both before and after toluene hydrogenation. Thus, these bands are consistent with the presence of a $Rh^I(CO)_2$ species or a tethered Rh(diamine)$(CO)_2^+$ complex. From the spectroscopic studies, it is not possible to distinguish these alternatives. If it were the $Rh^I(CO)_2$ species, one would expect the Rh^I on the surface to be an effective arene hydrogenation catalyst [40–42], which is observed. On the other hand, the catalyst prepared by tethering PF_6–Rh(N–N) to only SiO_2 is totally inactive as an arene hydrogenation catalyst (see PF_6–Rh(N–N)/SiO_2 in Table 1). If Rh were to be removed under the hydrogenation conditions to give Rh^I, it should be an active catalyst. Perhaps Pd must be present in order to remove the Rh from the complex and/or activate the Rh^I on the catalyst surface. Thus, it is not possible to definitely conclude whether the active rhodium species is a tethered Rh(diamine)$^+$ complex or Rh^I (or Rh°) on the surface.

4. Summary

The TCSM catalysts consisting of Rh(COD)[$NH_2CH_2CH_2NH(CH_2)_3Si(OCH_3)_3$](X) tethered on a SiO_2-supported Au–Pd bimetal catalyst are highly active for the hydrogenation of toluene under the mild conditions of 40°C and 1 atm H_2 pressure. These X–Rh(N–N)/Au:Pd–SiO_2 catalysts are most active with the weakly coordinating X^- anions PF_6^- and BPh_4^-. The Cl–Rh(N–N)/Au:Pd–SiO_2 catalyst retains its activity during three cycles over a period of 19 h and 2900 mol H_2/mol Rh turnovers. This and other evidence indicate that the Rh does not leach from the catalyst. The activity of the PF_6–Rh(N–N)/Au:Pd–SiO_2 catalyst changes little when the Pd loading is kept constant (9.8%) while the Au loading increases from 0.8 to 4.2%. In a series of catalysts in which the Au loading is held constant at 4.2% and the Pd% increases from 1.0 to 9.8% and Rh decreases from 3.6 to 1.5%, the rate (TO/h) of toluene hydrogenation increases by a factor of three which may be due either to the high loading of Pd or the lower loading of the Rh complex. Although other interpretations are possible, a mechanism involving H_2 adsorption on Pd followed by hydrogen spillover onto the SiO_2 where the tethered rhodium complex uses it to hydrogenate the arene substrate is consistent with the observed results.

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