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Hydrogenation of Arenes under Mild Conditions Using Rhodium Pyridylphosphine and Bipyridyl Complexes Tethered to a Silica-Supported Palladium Heterogeneous Catalyst

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The rhodium complexes [Rh(COD)(**1**)]BF_4 (Rh(N−P)) and [Rh(COD)(**2**)]BF_4 (Rh(N−N)), containing the new pyridylphosphine and bipyridyl ligands (**1** and **2**) with alkoxysilane groups, were tethered on the silica-supported palladium heterogeneous catalyst Pd−SiO_2 to give the TCSM (tethered complex on supported metal) catalysts Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2. Under the mild conditions of 70 °C and 4 atm of H_2, the two TCSM catalysts are very active for the hydrogenation of arenes ($PhCO_2Me$, PhOH, toluene, $PhOCH_3$, $PhCO_2Et$, 4-$CH_3C_6H_4CO_2Et$, dimethyl terephthalate) to cyclohexanes; the activities are higher than those of the separate homogeneous Rh(N−P) and Rh(N−N) complex catalysts, the silica-supported palladium catalyst Pd−SiO_2, or the rhodium complex catalysts tethered on just SiO_2. The catalysts are easily separated from the reaction mixtures and can be recycled several times without losing activity. Of the two TCSM catalysts, the higher activity for the hydrogenation of anisole to methyl cyclohexyl ether was observed for Rh(N−N)/Pd−SiO_2, which gives a TOF value of 3060 mol of substrate converted/((mol of Rh) h) and a TO value of 14 500 mol of substrate converted/(mol of Rh) in 6 h. Reactions of acetophenone lead to hydrogenation of the arene ring, the carbonyl group, or both, depending on the catalyst (Rh(N−P)/Pd−SiO_2 or Rh(N−N)/Pd−SiO_2) and the solvent (heptane or ethanol).

Introduction

Although much success has been achieved in the field of transition metal complex catalyzed hydrogenation of olefins,[1−3] arene hydrogenation catalyzed by transition metal complex catalysts is much less developed.[4−7] Hydrogenations of arenes using homogeneous metal complex catalysts generally occur at low rates unless high pressure (≥10 atm) and/or high catalyst/substrate ratios (≥1/500) are used.[4−7] Recently, we found [8−10] that transition metal complex catalysts can be activated for arene hydrogenation by tethering them to a silica-supported metal heterogeneous catalyst. The combined homogeneous−heterogeneous catalyst consisting of a tethered complex on a supported metal (TCSM) not only

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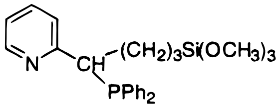
Chart 1



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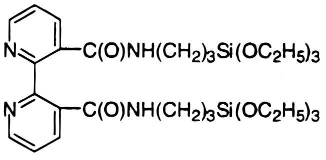

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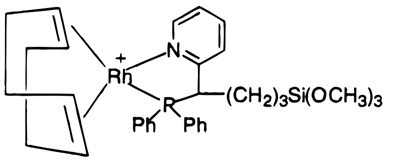

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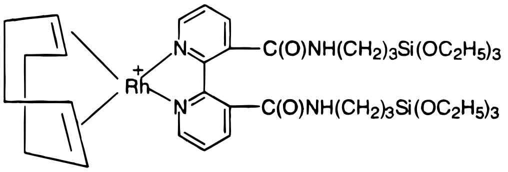

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has the advantages of a conventional SiO_2-tethered complex catalyst but also functions by synergistic action of the two catalyst components (tethered complex and supported metal) in the catalytic reactions. For example, the rhodium isocyanide complex $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ (Rh−CNR_3), when tethered on silica-supported palladium (Pd−SiO_2), gives the TCSM catalyst Rh−CNR_3/Pd−SiO_2, which is much more active for the hydrogenation of arenes than the separate homogeneous Rh−CNR_3 complex catalyst, the separate heterogeneous supported palladium catalyst, or the Rh−CNR_3 complex catalyst tethered on just SiO_2.[8] A possible explanation for the high activities of the TCSM catalysts involves considering Pd−SiO_2 as the site where H_2 is dissociated and spills over onto the SiO_2. Silica is also the site of the tethered homogeneous complex which may bind and activate the arene substrate for reaction with the “spillover” hydrogen. It should be emphasized, however, that the mechanism for arene hydrogenation is not known and other mechanisms must also be considered.[9a]

Our initial studies showed that the design of a TCSM catalyst with high activity depends on the proper choice of the two catalyst components (tethered complex and supported metal) for a specific reaction.[8−10] Bipyridyl and pyridylphosphine ligands have previously been used in homogeneous complex catalysts.[11−13] An important feature of these complexes is that the chelating ligand which binds strongly to the metal ion would reduce leaching of the metal ion if the ligand were tethered to a support. For this reason, we sought to determine the activities of Rh(I) complexes of bipyridyl and pyridylphosphine ligands in their TCSM catalysts. In the present study, we report details of the syntheses of the pyridylphosphine and bipyridyl ligands (**1** and **2**; see Chart 1) containing alkoxysilane anchors and their rhodium complexes [Rh(COD)(**1**)]BF_4 (**3**-BF_4) and [Rh(COD)(**2**)]BF_4 (**4**-BF_4), which were briefly described in a communication that reported their use for the catalytic hydrodefluorination of fluoroarenes.[10a] The rhodium complexes **3**-BF_4 (Rh(N−P)) and **4**-BF_4 (Rh(N−N)) were tethered on silica-supported palladium (Pd−SiO_2) to give the TCSM catalysts Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2. The catalytic activities of these two TCSM catalysts for the hydrogenation of a variety of arenes were investigated.

Experimental Section

All syntheses of the pyridylphosphine ligand and the rhodium complexes were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. Silica gel 100 (BET surface area, 400 m^2/g) was obtained from Fluka. Tetrahydrofuran (THF) and toluene were distilled under nitrogen from sodium benzophenone ketyl just before use. CH_2Cl_2 was distilled from CaH_2. Heptane and all the arene substrates were purchased from Aldrich and used without further purification. The silica-supported palladium (Pd−SiO_2) containing 10% Pd by weight was prepared as described previously.[8b]

NMR spectra were recorded on a Bruker AC 200 MHz or a Varian 300 MHz spectrometer. Solid-state ^{31}P NMR spectra were obtained on a Bruker MSL 300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer. FT-IR spectra were recorded on a Nicolet 560 spectrophotometer equipped with a TGS detector in the main compartment and an MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. Solution IR spectra were measured in the main compartment using a cell with NaCl plates. The DRIFT spectra were recorded with the sample 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 an HP 6890 GC using a 32 m HP-1 capillary column with a FID detector.

The rhodium content of the TCSM catalysts was determined using atomic emission spectroscopy. The samples for these analyses were prepared by treating the catalysts (50 mg) successively with 5 mL of aqua regia and 5 mL of aqueous HF (5%) at 90 °C; the resulting solution was diluted with water to 25 mL.

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Preparation of Ligands. Pyridylphosphine Ligand 1. To a diethyl ether solution (20 mL) of 2-[(diphenylphosphino)methyl]pyridine (1.10 g, 4.0 mmol), which was prepared according to the literature method,[12a] was added 2.5 mL of a 1.6 M hexane solution of *n*-butyllithium (4.0 mmol) at −40 °C. The solution was stirred for 1 h at −40 °C. Then, 1.15 g (4.0 mmol) of (3-iodopropyl)trimethoxysilane[14] was slowly added, and the solution was stirred for 3 h, during which time the temperature was allowed to rise to room temperature. The solvents were removed under vacuum, and the crude product was purified by column (2.7 × 7 cm) chromatography on silica gel using a CH_2Cl_2/Et_2O (4:1) mixture as the eluent. Ligand **1** was obtained in 53% yield as a yellow oil. ^1H NMR ($CDCl_3$): δ 8.47 (m, 1H, C_5H_4N), 7.01−7.65 (m, 13H, $2C_6H_5$ and C_5H_4N), 3.66 (m, 1H, PCH), 3.43 (s, 9H, 3 OCH_3), 2.12 (m, AB, $1H_a$, $CHCH_2$), 1.71 (m, AB, $1H_b$, $CHCH_2$), 1.27 (m, 2H, $CHCH_2CH_2$), 0.57 (m, 2H, $CHCH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.69 (s). Anal. Calcd for $C_{24}H_{30}NO_3PSi$: C, 65.57; H, 6.89; N, 3.19. Found: C, 65.32; H, 6.71; N, 3.04.

Bipyridyl Ligand 2. To a suspension containing 1.39 g (5.1 mmol) of 3,3′-binicotinic acid, which was prepared by the literature method,[13a] in 40 mL of dichloromethane was added 2.10 g (10.2 mmol) of 1,3-dicyclohexylcarbodiimide (DCC), and then 2.4 mL (10.2 mmol) of $H_2NCH_2CH_2CH_2Si(OEt)_3$ was added slowly. The mixture was stirred at room temperature overnight. Then, the solution was washed with water (3 × 50 mL). After the solvents were removed under vacuum, the residue was purified by column chromatography (2.7 × 15 cm) on silica gel using ethanol as the eluent. The bipyridyl ligand **2** was isolated as an orange-red oil (2.7 g, yield 82%). ^1H NMR ($CDCl_3$): δ 8.54 (m, 2H, $2C_5H_3N$), 7.88 (m, 2H, $2C_5H_3N$), 7.58 (m, 2H, $2C_5H_3N$), 7.18 (s, broad, 2H, 2NH), 3.74 (q, 12H, 6 OCH_2CH_3, J_{HH} = 6.9 Hz), 3.10 (m, 4H, $2NHCH_2$), 1.31 (m, 4H, $2NHCH_2CH_2$), 1.16 (t, 18H, 6 OCH_2CH_3, J_{HH} = 6.9 Hz), 0.40 (m, 4H, $2NHCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 168.0 (s, C=O), 156.5 (s, C_5H_3N), 149.5 (s, C_5H_3N), 135.7 (s, C_5H_3N), 132.4 (s, C_5H_3N), 123.1 (s, C_5H_3N), 58.4 (s, OCH_2CH_3), 42.4 (s, $NHCH_2$), 22.7 (s, $NHCH_2CH_2$), 18.3 (s, OCH_2CH_3), 7.7 (s, $NHCH_2CH_2CH_2$).

Preparation of the Rhodium Complexes [Rh(COD)(1)]BF_4 (3·BF_4) and [Rh(COD)(2)]BF_4 (4·BF_4). General Procedure. To a THF solution (10 mL) of $[Rh(COD)Cl]_2$[15] (0.20 g, 0.40 mmol) was added 0.16 g (0.80 mmol) of $AgBF_4$ at room temperature. The mixture was stirred for 30 min and then filtered to give a THF solution of $[Rh(COD)(THF)_2]BF_4$. Then, a solution of the appropriate ligand (**1** or **2**; 0.80 mmol) in THF (5 mL) was slowly added to the THF solution of $[Rh(COD)(THF)_2]BF_4$ at −40 °C. The reaction mixture was stirred for 1 h at −40 °C and then for 3 h at room temperature. The solvents were removed under vacuum. The residue was washed with diethyl ether (2 × 10 mL).

3·BF_4: yellow powder, 65% yield. ^1H NMR ($CDCl_3$): δ 8.26 (m, 1H, C_5H_4N), 7.81−7.42 (m, 13H, $2C_6H_5$ and C_5H_4N), 5.52 (m, 2H, COD), 4.36 (m, 1H, PCH), 4.16 (m, 2H, COD), 3.50 (s, 9H, 3 OCH_3), 2.18−2.56 (m, 10H, COD and $CHCH_2$), 1.64 (m, 2H, $CHCH_2CH_2$), 0.68 (m, 2H, $CHCH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.6 (d, J_{P-Rh} = 149.7 Hz). Anal. Calcd for $C_{32}H_{42}BF_4NO_3PRhSi$: C, 52.11; H, 5.75; N, 1.90. Found: C, 51.46; H, 5.65; N, 1.85.

4·BF_4: red-yellow powder, 84% yield. ^1H NMR ($CDCl_3$): δ 8.22 (m, 2H, 2 C_5H_3N), 7.84 (m, 2H, 2 C_5H_3N), 7.58 (m, 2H, 2 C_5H_3N), 7.18 (s, broad, 2H, 2 NH), 4.38−4.66 (m, 4H, COD), 3.79 (q, 12H, 6 OCH_2, J_{H-H} = 6.9 Hz), 3.22 (m, 4H, $NHCH_2$), 4.38−4.66 (m, 8H, COD), 1.80−2.31 (m, 8H, COD), 1.65 (m, 4H, 2 $NHCH_2CH_2$), 1.18 (t, 18H, 6 OCH_2CH_3, J_{H-H} = 6.9 Hz), 0.45 (s, broad, 4H, 2 $NHCH_2CH_2CH_2$). Anal. Calcd for $C_{38}H_{62}BF_4N_4O_8RhSi_2$: C, 48.10; H, 6.59; N, 5.90. Found: C, 48.87; H, 6.41; N, 6.34.

Preparation of the Tethered Rhodium Complex Catalysts Rh(N−P)/Pd−SiO_2, Rh(N−N)/Pd−SiO_2, Rh(N−P)/SiO_2, and Rh(N−N)/SiO_2. A mixture of 1.0 g of Pd−SiO_2 (or SiO_2) and 74 mg of **3**·BF_4 (or 95 mg of **4**·BF_4) in 10 mL of CH_2Cl_2 was stirred at room temperature for 6 h. After filtration, the solid was washed with CH_2Cl_2 (3 × 10 mL) and dried under vacuum to give the tethered rhodium complex catalysts Rh(N−P)/Pd−SiO_2 (Rh content, 0.60 wt %), Rh(N−N)/Pd−SiO_2 (Rh content, 0.71 wt %), Rh(N−P)/SiO_2 (Rh content, 0.68 wt %), and Rh(N−N)/SiO_2 (Rh content, 0.95 wt %).

Catalytic Hydrogenation Reactions. The hydrogenation reactions were carried out in a Fisher glass pressure reactor equipped with a stirring bar and connected to an H_2 cylinder and vacuum line. After the solid catalyst was placed in the reactor under a N_2 atmosphere, the atmosphere was replaced by H_2, and then solvent and substrate were added. The reactor was heated to 70 °C with an oil bath, and the hydrogen pressure in the reactor was adjusted to 4 atm. The reaction was started by turning on the magnetic stirrer and followed by taking samples periodically for GC analysis. The products were identified by comparison of their mass spectra with those of authentic samples. When the catalyst was used in several successive methyl benzoate hydrogenations, the reaction mixture after the first cycle was filtered and the solid catalyst was washed with heptane, dried under vacuum, and used for the hydrogenation of a new batch of methyl benzoate by following the same procedure as that in the first cycle. After the second cycle, the catalyst was treated as after the first cycle. The third and fourth cycles were performed similarly.

Results and Discussion

Synthesis of the TCSM Catalysts. The ligands **1** and **2** were synthesized from 2-[(diphenylphosphino)methyl]pyridine[12a] and 3,3′-dicarbomethoxy-2,2′-bipyridyl[13a] according to the steps illustrated in Scheme 1. Successive addition of *n*-butyllithium and (3-iodopropyl)trimethoxysilane to a diethyl ether solution of 2-[(diphenylphosphino)methyl]pyridine at −40 °C and final purification by chromatography on silica gel led to **1** as a yellow oil in 53% yield. The addition of *n*-butyllithium and (3-iodopropyl)trimethoxysilane must be conducted at −40 °C or lower to avoid a side reaction between the Si−OCH_3 groups and (phosphinopyridylmethyl)lithium.[16] When (3-chloropropyl)trimethoxysilane was used, the yield of **1** was lower compared with that from the iodo derivative. Ligand **2** was obtained as an orange-red oil in 76% yield by the reaction between (3-aminopropyl)triethoxysilane and 3,3′-dicarbomethoxy-2,2′-bipyridyl in CH_2Cl_2 in the presence of dicyclohexylcarbodiimide (DCC) at room temperature, followed by purification by column chromatography on silica gel. **1** is air-sensitive, but **2** is stable in air. Both **1** and **2** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

Ligands **1** and **2** react with $[Rh(COD)(THF)_2]BF_4$[12b] to give the complexes [Rh(COD)(**1**)]BF_4 (**3**·BF_4) and [Rh(COD)(**2**)]BF_4 (**4**·BF_4) in good yield according to eq 1.

$$[Rh(COD)(THF)_2]BF_4 + L \rightarrow [Rh(COD)(L)]BF_4 \quad (1)$$

$$L = \mathbf{1}, \mathbf{2}$$

These two complexes were characterized by ^1H and ^{31}P NMR spectroscopy and elemental analysis. **3**·BF_4 (Rh(N−P)) and **4**·BF_4 (Rh(N−N)) were reacted with hydroxyl groups on the surface of the SiO_2-supported

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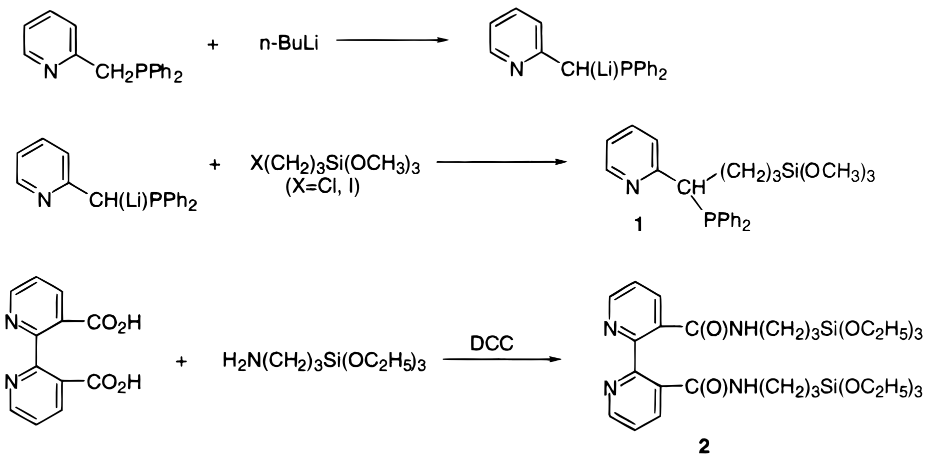
Scheme 1



palladium catalyst Pd−SiO$_2$ or just SiO$_2$ to give the TCSM catalysts Rh(N−P)/Pd−SiO$_2$ and Rh(N−N)/Pd−SiO$_2$ and the SiO$_2$-tethered complex catalysts Rh(N−P)/SiO$_2$ and Rh(N−N)/SiO$_2$. Solid-state ^{31}P NMR spectra of both Rh(N−P)/Pd−SiO$_2$ and Rh(N−P)/SiO$_2$ show a peak at 48.4 ppm, which is similar to that (47.6 ppm) of the untethered Rh(N−P) complex. When Rh(N−N)/Pd−SiO$_2$ and Rh(N−N)/SiO$_2$ were stirred in CH$_2$Cl$_2$ under a CO atmosphere at room temperature overnight, the IR (DRIFT) spectra of the resulting samples were about the same and exhibited four ν(CO) bands at 2104 (s), 2090 (w, sh), 2045 (s), and 2022 (w, sh) cm^{-1}, which are similar to those (2099 (s), 2088 (w, sh), 2040 (s), and 2016 (w, sh) cm^{-1} in CH$_2$Cl$_2$) of a solution sample obtained from the reaction of Rh(N−N) and CO in CH$_2$Cl$_2$ under the same conditions. Previously it was reported[17] that Rh(bipy)(COD)$^+$ reacts with CO at room temperature to form Rh(bipy)(CO)$_2$$^+$. These results suggest that the structures of the tethered Rh(N−P) and Rh(N−N) complexes on the surface of Pd−SiO$_2$ or SiO$_2$ are similar to those of the untethered complexes.

Hydrogenation of Arenes over the Tethered Rhodium Complex Catalysts. The TCSM catalysts Rh(N−P)/Pd−SiO$_2$ and Rh(N−N)/Pd−SiO$_2$ were used to catalyze the hydrogenation of methyl benzoate and phenol under the conditions of 70 °C and 4 atm of H$_2$. The GC-MS analyses of the hydrogenation solutions showed that methyl cyclohexanecarboxylate is the only product of the methyl benzoate hydrogenation, and both cyclohexanone and cyclohexanol were formed in the hydrogenation of phenol. Table 1 gives the hydrogenation activities of the TCSM catalysts, the separate homogeneous rhodium complex catalysts, the silica-supported palladium (Pd−SiO$_2$) heterogeneous catalyst, and the rhodium complex catalysts tethered on just SiO$_2$ (Rh(N−P)/SiO$_2$ and Rh(N−N)/SiO$_2$). From the data in Table 1, it can be seen that the homogeneous Rh(N−P) and Rh(N−N) complex catalysts are inactive for the hydrogenation of methyl benzoate under these mild conditions. However, the TCSM catalysts Rh(N−P)/Pd−SiO$_2$ and Rh(N−N)/Pd−SiO$_2$ are very active for this hydrogenation. The activities (as measured by turnover number (TO), or conversion) of Rh(N−P)/Pd−SiO$_2$ and Rh(N−N)/Pd−SiO$_2$ are at least 10 times and 32 times greater, respectively, than those of Pd−SiO$_2$ or Rh(N−P)/SiO$_2$ and Rh(N−N)/SiO$_2$.

Table 1. Hydrogenation of Methyl Benzoate and Phenol[a]

catalyst	reacn time (h)	TO[b]	conversn (%)[c]
	Methyl Benzoate		
Pd−SiO$_2$	3		18
Rh(N−P)	2	0	0
Rh(N−N)	2	0	0
Rh(N−P)/SiO$_2$	4	15	2
Rh(N−N)/SiO$_2$	4	120	23
Rh(N−P)/Pd−SiO$_2$	1	560	66
Rh(N−N)/Pd−SiO$_2$	0.5	720	100
	Phenol		
Pd−SiO$_2$	18	0	0
Rh(N−P)	10	0	0
Rh(N−N)	10	0	0
Rh(N−P)/SiO$_2$	18	0	0
Rh(N−N)/SiO$_2$	18	0	0
Rh(N−P)/Pd−SiO$_2$[d]	11	3400	100[e]
Rh(N−N)/Pd−SiO$_2$[d]	7	2900	100[f]

[a] Reaction conditions: 50 mg of solid catalysts (5 μmol of Rh(N−P) and Rh(N−N)); 5 mL of heptane; 2.5 mmol of substrates; 70 °C; 4 atm of H$_2$. [b] The turnover number, defined as moles of substrate converted per mole of rhodium, corresponds to the reaction time. [c] The conversion, determined by GC-MS (with authentic samples), corresponds to the reaction time. Methyl benzoate is converted to methyl cyclohexanecarboxylate; phenol is converted to cyclohexanol and cyclohexanone. [d] Conditions: 10 mL of heptane solvent; 25 mg of solid catalyst; 5 mmol of phenol. [e] Conversion:47.8% of cyclohexanone, 52.2% of cyclohexanol. [f] Conversion: 58.8% cyclohexanone, 41.2% of cyclohexanol.

The homogeneous Rh(N−P) and Rh(N−N) catalysts, the heterogeneous Pd−SiO$_2$ catalyst, and the SiO$_2$-tethered complex catalysts Rh(N−P)/SiO$_2$ and Rh(N−N)/SiO$_2$ are all inactive for the hydrogenation of phenol under the conditions of 70 °C and 4 atm, but the two TCSM catalysts Rh(N−P)/Pd−SiO$_2$ and Rh(N−N)/Pd−SiO$_2$ are very active for phenol hydrogenation under the reaction conditions. Thus, the rhodium complexes Rh(N−P) and Rh(N−N) are activated for the hydrogenation of methyl benzoate and phenol by tethering them on Pd−SiO$_2$. By comparison, catalysts consisting of Pd supported on metal oxides that hydrogenate phenol to cyclohexanone require temperatures of 200 °C or higher.[18] The hydrogenation of phenol with transition metal complex catalysts usually requires a high H$_2$ pressure ($\geq$50 atm).[7d−f]

The TCSM catalysts Rh(N−P)/Pd−SiO$_2$ and Rh(N−N)/Pd−SiO$_2$ are also very active for the hydrogenation

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Table 2. Hydrogenation of Arenes over Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2[a]

substrate	TOF[b]	TO[c]	product[d]
		Rh(N−P)/Pd−SiO_2	
toluene	2880	7770 (6)	methylcyclohexane
anisole	1790	8940 (6)	methyl cyclohexyl ether
phenol[e]	710	2720 (6)	cyclohexanol (52%), cyclohexanone (48%)
methyl benzoate	560	6120 (25)	methyl cyclohexanecarboxylate
ethyl benzoate	260	1990 (14)	ethyl cyclohexanecarboxylate
ethyl 4-methylbenzoate[e]	140	580 (6)	ethyl 4-methylcyclohexanecarboxylate (trans:cis = 3:2)
dimethyl terephthalate	76	1895 (25)	dimethyl cyclohexane-1,4-dicarboxylate (trans:cis = 1:4)
		Rh(N−N)/Pd−SiO_2	
toluene	2870	14500 (6)	methylcyclohexane
anisole	3060	14500 (6)	methyl cyclohexyl ether
phenol[e]	950	2800 (7)	cyclohexanol (41%), cyclohexanone (59%)
methyl benzoate	1120	11620 (25)	methyl cyclohexanecarboxylate
ethyl benzoate	1510	14500 (14)	ethyl cyclohexanecarboxylate
ethyl 4-methylbenzoate[e]	500	2520 (6)	ethyl 4-methylcyclohexanecarboxylate (trans:cis = 3:2)
dimethyl terephthalate	270	6720 (25)	dimethyl cyclohexane-1,4-dicarboxylate (trans:cis = 1:2)

[a] Reaction conditions: 25 mg of catalyst; 20 mL of heptane solvent; 25 mmol of substrate; 70 °C; 4 atm of H_2. [b] TOF is the average turnover frequency during the initial 2 h, defined as moles of the substrate converted per mole of rhodium per h. [c] Turnover number, defined as moles of substrate converted per mole of rhodium, corresponds to the reaction time in parentheses (in h). [d] Determined by GC-MS and comparison with authentic samples. [e] Conditions: 10 mL of heptane solvent; 5 mmol of substrate.

of other arenes under the conditions of 70 °C and 4 atm (Table 2). The higher rates of hydrogenation of toluene and anisole as compared with those of methyl and ethyl benzoates in the presence of either catalyst suggest that electron-donating substituents in the arene accelerate the rate. The least reactive substrate is dimethyl terephthalate, which has two electron-withdrawing ester groups. Neither hydrogenolysis products nor products formed from the hydrogenation of the ester groups were detected in any of the hydrogenation reactions.

A comparison of the hydrogenation activities of the two TCSM catalysts indicates that the Rh(N−N)/Pd−SiO_2 catalyst is more active for arene hydrogenations than Rh(N−P)/Pd−SiO_2. Under the conditions of 70 °C and 4 atm and a substrate/Rh mole ratio of 14 500 (Table 2), the initial TOF (mol of substrate converted/((mol of Rh) h)) values of the Rh(N−N)/Pd−SiO_2 catalyst for hydrogenations of toluene and anisole are 2870 and 3060, and the TO (mol of the substrate converted/(mol of Rh)) values during a 6 h period are 14 500 for both of the substrates. To the best of our knowledge, this catalyst is more active for the hydrogenation of arenes under these mild conditions than any other reported homogeneous or immobilized complex catalyst. Corma et al.[19] used the rhodium complex [Rh(COD)(N−N)]PF_6 (COD = 1,5-cyclooctadiene, N−N = 2-((3-(triethoxysilyl)propyl)aminocarboxyl)pyrroline) anchored on zeolites to catalyze the hydrogenation of arenes under the conditions of 80 °C and 6 atm of H_2. The initial TOF (mol of the substrate converted/((mol of Rh) h)) values of this catalyst for the hydrogenation of toluene and anisole are 994 and 945, and the times for achieving a TO (mol of substrate converted/(mol of Rh)) of 12 000 are 18 and 70 h for toluene and anisole hydrogenations, respectively. Thus, this catalyst is much less active than Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2. For the immobilized complex catalyst prepared from $[Rh(Cl)(nbd)]_2$ (nbd = norbornadiene) and phosphinated silica, the TO value for the hydrogenation of toluene is 200 at 80 atm of H_2 and 30 °C during 1.5 h.[20] Hydrogenations of arenes in the presence of homogeneous or immobilized complex catalysts are generally performed under high H_2 pressure (≥10 atm).[4a,b,7] In previous papers,[8,9a] we reported that the TCSM catalysts Rh−CNR_3/Pd−SiO_2 and Rh−NEt_2/Pd−SiO_2, prepared by tethering $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ (Rh−CNR_3) and $RhCl(CO)_2[Et_2N(CH_2)_3Si(OCH_3)_3]$ (Rh−NEt_2) on Pd−SiO_2, are very active for the hydrogenation of arenes under 40 °C and 1 atm of H_2; the TOF and TO values of these two catalysts for toluene hydrogenation are 330 mol of H_2/((mol of Rh) h) and 2420 mol of H_2/(mol of Rh) in 8.5 h for Rh−CNR_3/Pd−SiO_2 and 432 mol of H_2/((mol of Rh) h) and 1916 mol of H_2/(mol of Rh) in 5 h for Rh−NEt_2/Pd−SiO_2. A few homogeneous complex catalysts are also reported to be active for the hydrogenation of arenes using 1 atm of H_2, but their activities (TOF and TO values) are very low.[5a,b,6]

From the results in Table 1, it is clear that both the tethered complex (Rh(N−P) or Rh(N−N)) and supported metal (Pd−SiO_2) components are necessary for the high catalytic activities of the TCSM catalysts. This activity may be attributed to a combination of functions of both the supported palladium and the tethered rhodium complexes. It is well-known[21] that inorganic oxide supported metal heterogeneous catalysts such as Pd−SiO_2, Pd−Al_2O_3, Pt−SiO_2, etc. can dissociatively adsorb hydrogen, which spills over onto the oxide surface. This behavior suggests that the Pd−SiO_2 component of TCSM catalysts functions by activating H_2 to produce the spillover hydrogen on the SiO_2 surface. The resulting spillover hydrogen on the silica surface is then in the vicinity of the tethered Rh(N−P) or Rh(N−N) complex, which coordinates and activates arene substrates for reaction with the spillover hydrogen. Another possible mechanism for the hydrogenation of arenes on

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Table 3. Effect of Solvent on the Rate of Methyl Benzoate Hydrogenation over Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2 Catalysts[a]

catalyst	reacn time (h)	solvent	conversn (%)[b]
Rh(N−P)/Pd−SiO_2	4	ethanol	86
	1	heptane	66
Rh(N−N)/Pd−SiO_2	1	CH_2Cl_2	24
	1	THF	71
	1	ethanol	79
	0.5	heptane	100

[a] Reaction conditions: 50 mg of solid catalyst; 5 mL of solvent; 2.5 mmol of methyl benzoate; 70 °C; 4 atm of H_2. [b] Conversion, determined by GC, corresponds to the reaction time.

Table 4. Effect of Substrate Concentration on Arene Hydrogenation Rate over Rh(N−N)/Pd−SiO_2 Catalyst[a]

substrate (amt, mmol)	heptane solvent (mL)	reacn time (h)	TO[b]
toluene (25)	0	6	14500
	10	6	14500
	20	6	14500
methyl benzoate (25)	0	20	2800
	10	10	3080
	20	20	6020
ethyl 4-methylbenzoate (5)	5	10	1456
	10	10	2520

[a] Reaction conditions: 25 mg of Rh(N−N)/Pd−SiO_2 catalyst; 70 °C; 4 atm of H_2. [b] See footnote *c* in Table 2.

Table 5. Durability of Rh(N−N)/Pd−SiO_2 and Rh(N−P)/Pd−SiO_2 in the Hydrogenation of Methyl Benzoate[a]

cycle	reacn time (h)	conversn (%)
	Rh(N−P)/Pd−SiO_2	
first	1.0	66
second	1.0	87
third	1.0	100
fourth	1.0	100
	Rh(N−N)/Pd−SiO_2	
first	0.5	100
second	0.5	100
third	0.5	100
fourth	0.5	100

[a] Reaction conditions are the same as those in Table 1.

the TCSM catalysts requires the close proximity of the tethered rhodium complex and the supported palladium. In such a mechanism, the tethered rhodium complex may coordinate to the arene via only two carbons of the benzene ring. Then, the remaining four carbons of the benzene ring are hydrogenated on the supported palladium if the tethered rhodium complex is near a Pd island. A model for this type of mechanism is the known hydrogenation of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ to the cyclohexene complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_{10})]^{2+}$ in the presence of Pd/C under the conditions of 1 atm of H_2 and 30 °C. Under the same conditions, Pd/C is inactive for the hydrogenation of benzene.[22] Another possible mechanism is one in which a small amount of Rh(I) is removed from the tethered complex and deposited on the SiO_2 or Pd in a highly active form for arene hydrogenation.[9a] It should be noted, however, that the solid-state ^{31}P NMR spectrum of the used Rh(N−P)/Pd−SiO_2 catalyst isolated at the end of the reaction time (11 h, Table 1) by filtering the catalyst from the reaction mixture, washing it with heptane, and drying under vacuum is similar to that of the fresh, unreacted Rh(N−P)/Pd−SiO_2 catalyst. This suggests that at least the majority of the N−P ligand remains coordinated to the rhodium.

Tables 3 and 4 show the effects of solvent and substrate concentration on the rates of arene hydrogenation over the TCSM catalysts Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2. Table 3 shows that the hydrogenation rate for methyl benzoate over both of the TCSM catalysts is greater in heptane than in ethanol. The rates for methyl benzoate hydrogenation over the Rh(N−N)/Pd−SiO_2 catalyst decrease with the solvents in the order heptane > ethanol > THF > dichloromethane. The lower rate in THF and ethanol compared to that in heptane may be due to weak coordination of the solvent to the rhodium center, which inhibits coordination with the arene substrate.

From the data in Table 4, it can be seen that the effect of substrate concentration on arene hydrogenation rates varies with the arene substrate used. The concentration of toluene has no effect on the rate of toluene hydrogenation over Rh(N−N)/Pd−SiO_2 in heptane. However, for the hydrogenation of methyl benzoate and ethyl 4-methylbenzoate over Rh(N−N)/Pd−SiO_2, the hydrogenation rate increases as the substrate concentration decreases. This may be due to ester group coordination to the rhodium center, which reduces the activity of the complex for arene hydrogenation.

The two TCSM catalysts exhibit very good durabilities for arene hydrogenation (Table 5), which were determined by using the catalysts for several successive hydrogenations of methyl benzoate under the conditions in Table 1. The data in Table 5 show that after four cycles with the Rh(N−N)/Pd−SiO_2 catalyst the conversion of methyl benzoate remains 100%. The activity of the Rh(N−P)/Pd−SiO_2 catalyst actually increases, suggesting that the catalyst slowly converts to a more active form. The durability of Rh(N−N)/Pd−SiO_2 was also tested by using a large amount of methyl benzoate (substrate/Rh = 50 000) and prolonging the reaction time under the same reaction conditions. It was found that after the catalyst was used for 100 h, the activity of the used catalyst isolated from the reaction mixture was the same as that of the fresh, unreacted catalyst. An atomic spectroscopic analysis of the Rh content of the liquid phase that was separated from the reaction mixture showed that no detectable Rh (<0.1 ppm) had leached into the liquid phase.

Hydrogenation of Acetophenone over the TCSM Catalysts. The hydrogenation of acetophenone is usually catalyzed by supported metal heterogeneous catalysts under relatively high H_2 pressure (>10 atm) and/or high temperature (around 200 °C).[23] The phenylethanol and cyclohexylethanol products are industrially important. Cyclohexylethanol finds application in the manufacture of poly(vinylcyclohexane), which is a high-temperature-resistant polymer, while phenylethanol is used in the manufacture of perfumery products

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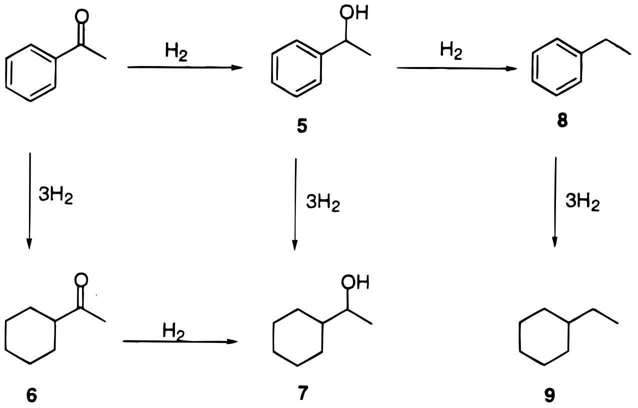
Table 6. Hydrogenation of Acetophenone over Tethered Rhodium Complex Catalysts[a]

catalyst	solvent	reacn time (h)	yield (%)[b] 5	6	7	8	9
Pd−SiO$_2$	heptane	1.0	100	0	0	0	0
		3.0	99	0	0	1.0	0
	ethanol	0.5	9	0	0	91	0
		4.0	0	0	0	96	4
Rh(N−N)	heptane	4.0	0	0	0	0	0
Rh(N−P)	heptane	4.0	0	0	0	0	0
Rh(N−N)/SiO$_2$	heptane	3.0	1.3	0	0	0	0
Rh(N−P)/SiO$_2$	heptane	3.0	3.9	0	0	0	0
Rh(N−N)/ Pd−SiO$_2$	heptane	1.0	10.4	23	66.6	0	0
		2.0	0	23	76	0	1
		12	0	11.6	87	0	1.4
	ethanol	0.5	0	4	69.5	26.5	0
		2.0	0	3	70.5	0	26.5
Rh(N−P)/ Pd−SiO$_2$	heptane	0.5	80	3.5	9.5	7	0
		3.0	0	17	53	22	7
		4.0	0	15	55	0	30
	ethanol	2.0	41	0	6	52	0
		5.0	18	2.6	10	65.4	4.0

[a] Reaction conditions: 50 mg of solid catalyst; 2.5 mmol of acetophenone; 5 mL of solvent; 70 °C; 4 atm of H$_2$. [b] The yields of products (see Scheme 2) were determined by GC-MS using authentic samples.

Scheme 2



and pharmaceuticals. Although many rhodium, ruthenium, and iridium complexes have been shown to be efficient catalysts for the reduction of acetophenone to phenylethanol under hydrogen-transfer conditions,[24] the reduction of acetophenone with H$_2$ catalyzed by transition metal complex catalysts usually gives poor results, especially under mild conditions.[6b,c,7c,d,f,i,20] Our TCSM catalysts Rh(N−N)/Pd−SiO$_2$ and Rh(N−P)/Pd−SiO$_2$ are also very active for the hydrogenation of acetophenone under the conditions of 70 °C and 4 atm of H$_2$ (Table 6). Scheme 2 shows the products that are formed and possible pathways for their formation. As the data illustrate in Table 6, the hydrogenation of acetophenone on Pd−SiO$_2$ in heptane gives only the carbonyl reduction product 1-phenylethanol (**5**) in 100% yield in 1 h. After 3 h, 1.0% of the hydrogenolysis product ethylbenzene (**8**) forms, but there are no other products except **5**. The homogeneous complex catalysts Rh(N−N) (**4**·BF$_4$) and Rh(N−P) (**3**·BF$_4$) are inactive for acetophenone hydrogenation in heptane under the reaction conditions. The SiO$_2$-tethered complex catalysts Rh(N−N)/SiO$_2$ and Rh(N−P)/SiO$_2$ exhibit very low activity for acetophenone hydrogenation. After 3 h, only product **5** is observed in a yield of 1.3% using Rh(N−N)/SiO$_2$ and 3.9% using Rh(N−P)/SiO$_2$. When the hydrogenation of acetophenone was conducted with the TCSM catalysts Rh(N−N)/Pd−SiO$_2$ and Rh(N−P)/Pd−SiO$_2$ in heptane, complete conversion of acetophenone was achieved in 1 and 0.5 h, respectively. The Rh(N−N)/Pd−SiO$_2$ catalyst gives benzene ring reduction products, methyl cyclohexyl ketone (**6**) and 1-cyclohexylethanol (**7**), in a total yield of 89.6%, together with 10.4% of **5**. The Rh(N−P)/Pd−SiO$_2$ catalyst gives only a 13% combined yield of **6** and **7**, along with 80% **5** and 7% **8**. After hydrogenation on Rh(N−N)/Pd−SiO$_2$ for 12 h, the yields of **6** and **7** are 11.6% and 87%, respectively, together with only 1.4% ethylcyclohexane (**9**). On the Rh(N−P)/Pd−SiO$_2$ catalyst, after the reaction proceeded for 4 h, the yields of **6** and **7** were 15% and 55%, respectively, and 30% of the acetophenone was already converted to **9**. Thus, under the conditions of 70 °C and 4 atm in heptane solvent, the SiO$_2$-supported palladium catalyst Pd−SiO$_2$ is very active for the hydrogenation of the carbonyl group in acetophenone, but it is inactive for the benzene ring hydrogenation. The homogeneous rhodium complex catalysts Rh(N−N) and Rh(N−P) are inactive for the hydrogenation of both the carbonyl group and benzene ring of acetophenone, and the SiO$_2$-tethered rhodium complex catalysts Rh(N−N)/SiO$_2$ and Rh(N−P)/SiO$_2$ exhibit only very low activity for carbonyl group reduction. However, on the TCSM catalysts Rh(N−N)/Pd−SiO$_2$ and Rh(N−P)/Pd−SiO$_2$, the benzene ring and carbonyl group of acetophenone are easily hydrogenated to give **7**. At short reaction times, Rh(N−N)/Pd−SiO$_2$ hydrogenates both the benzene and carbonyl groups to give **7**, whereas Rh(N−P)/Pd−SiO$_2$ hydrogenates only the carbonyl group to give **5**. The high activity and selectivity of the TCSM catalysts for the hydrogenation of acetophenone to 1-cyclohexylethanol may be attributed to the presence of the two catalyst components; i.e., the carbonyl group is hydrogenated on the Pd−SiO$_2$, and the arene ring hydrogenation is catalyzed by the tethered Rh complexes that are activated by the Pd−SiO$_2$. The higher selectivity of Rh(N−N)/Pd−SiO$_2$ for **7**, as compared with that of Rh(N−P)/Pd−SiO$_2$, may be related to the fact that Rh(N−N)/Pd−SiO$_2$ is more active for the hydrogenation of arene rings than Rh(N−P)/Pd−SiO$_2$ (Table 1).

Table 6 also demonstrates that the product composition of the acetophenone hydrogenation is strongly affected by the solvent. When ethanol is used as the solvent, acetophenone is completely converted to the hydrogenolysis products **8** (96%) and **9** (4.0%) on the Pd−SiO$_2$ catalyst in 4 h, and no other product is observed. On the Rh(N−N)/Pd−SiO$_2$ catalyst, the complete conversion of acetophenone is achieved in 0.5 h, giving the benzene ring hydrogenation products **6** (4.0%) and **7** (69.5%), along with 26.5% **8**. This high yield (26.5%) of **8** in ethanol as compared with that (0%) in heptane is consistent with the high yield (91%) of **8** that is formed over Pd−SiO$_2$ in ethanol, and with the lower arene hydrogenation activity of Rh(N−N)/Pd−SiO$_2$ in ethanol as compared with that in heptane. With the Rh-

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(N−P)/Pd−SiO_2 catalyst, the acetophenone is completely converted in 2 h and the major products are **5** (41%) and **8** (52%). The yield of the benzene ring reduction product **7** is only 6.0%, and no **6** was detected. However, when the reaction is allowed to proceed for 5 h, the yields of **6** and **7** are still low (2.6% and 10%, respectively), but the yield of **8** is up to 65.4%, which suggests that the Pd−SiO_2 component of the Rh(N−P)/Pd−SiO_2 catalyst plays a more important role in controlling product distribution in ethanol than in heptane. It is evident from these studies of TCSM-catalyzed hydrogenation of acetophenone that product distributions are critically dependent on the tethered complex (Rh(N−N) or Rh(N−P)) as well as the solvent.

Summary

Activities of the Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2 TCSM catalysts for arene hydrogenation are higher than those of any other homogeneous or immobilized complex catalyst in the literature under the mild conditions of 70 °C and 4 atm of H_2. Both the tethered rhodium complexes and the supported palladium are essential to their high hydrogenation activities. Relatively unreactive arenes such as $PhCO_2Me$, PhOH, and arenes with electron-withdrawing groups are readily hydrogenated. They retain their activities even during four successive runs. Acetophenone hydrogenations give products in which the arene ring, the carbonyl group, or both are hydrogenated; the distribution of products depends on the TCSM catalyst (Rh(N−P)/Pd−SiO_2 or Rh(N−N)/Pd−SiO_2), the reaction time, and the reaction solvent. These two-component TCSM catalysts offer high activities and selectivities that are not possible with other catalysts under the mild conditions.

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