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Combined Homogeneous and Heterogeneous Catalysts. Rhodium and Platinum Isocyanide Complexes Tethered on Silica-Supported Metal Heterogeneous Catalysts: Arene and Cyclohexanone Hydrogenation[†]

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Rhodium and platinum isocyanide complexes $RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$ ($Rh-CNR_2$), $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ ($Rh-CNR_3$), and $PtCl_2[CN(CH_2)_3Si(OC_2H_5)_3]_2$ ($Pt-CNR_2$) were tethered to the silica-supported metal heterogeneous catalysts $M-SiO_2$ (M = Pd, Pt, Ru) to give the TCSM (tethered complex on supported metal) catalysts $Rh-CNR_2/Pd-SiO_2$, $Rh-CNR_3/M-SiO_2$ (M = Pd, Pt, Ru), and $Pt-CNR_2/Pd-SiO_2$. These TCSM catalysts were used to catalyze the hydrogenation of arenes ($Rh-CNR_2/Pd-SiO_2$ and $Rh-CNR_3/M-SiO_2$) and cyclohexanone ($Pt-CNR_2/Pd-SiO_2$) under the mild conditions of 40 °C and 1 atm. They exhibit activities that are higher than those of the separate homogeneous rhodium (or platinum) isocyanide complex, the separate silica-supported metal heterogeneous catalyst, or the rhodium (or platinum) complex catalyst tethered on just SiO_2. The activities of the TCSM catalysts are strongly affected by the nature and loading of the supported metal in the catalyst. Among the three silica-supported metal $M-SiO_2$ (M = Pd, Pt, Ru) catalysts, the rhodium complex $Rh-CNR_3$ tethered on $Pd-SiO_2$ exhibits the highest activity for the hydrogenation of toluene (TOF = 5.5 mol H_2/(mol Rh min) and TO = 2420 mol H_2/mol Rh during 8.5 h). The $Rh-CNR_3/Pd-SiO_2$ catalyst with 10 wt % Pd is more active than its counterparts with higher or lower palladium loadings. IR (DRIFT) spectral studies of the TCSM catalysts before and after being used for toluene hydrogenation show that the isocyanide ligands remain coordinated to the rhodium (or platinum) center even after extended use. Atomic emission spectroscopic analysis of hydrogenation solutions shows that there is no rhodium (or platinum) leaching into the solutions.

Introduction

Heterogenizing transition metal complex catalysts by tethering them to insoluble supports has been one of the interesting directions of research in the field of catalysis in recent decades.[1−3] We recently reported that transition metal complexes can be tethered to silica-supported heterogeneous metal catalysts by the same methods that have been used for tethering complexes on just SiO_2.[4] The resulting combined catalysts (Figure 1) consisting of a metal complex tethered on a supported metal (TCSM) not only have the advantages of conventional SiO_2-tethered complex catalysts but also function by synergistic action of the two catalyst components. The design of a TCSM catalyst with high activity depends on the proper choice of the two catalyst components (the tethered complex and supported metal) for a specific reaction. Our initial experiments showed that rhodium complex catalysts tethered to a SiO_2-supported heterogeneous palladium metal catalyst ($Pd-SiO_2$) are much more active for the hydrogenation of

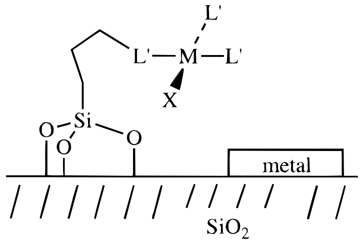

Figure 1. Conceptual illustration of a TCSM catalyst consisting of a tethered homogeneous complex catalyst on a supported metal heterogeneous catalyst.

[†] Dedicated to Herr Wolf-Peter Fehlhammer on the occasion of his 60th birthday.

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arenes than the separate homogeneous rhodium complex catalysts, the separate Pd−SiO$_2$, or the rhodium complex catalysts tethered on just silica.[4] 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. While this explanation accounts for the high activities of the TCSM catalysts and is consistent with the known ability of Pd−SiO$_2$ to produce spillover hydrogen,[5] it is possible that the combined effect of both catalyst components occurs by some other mechanism.

Isocyanide ligands form homo- and heteroleptic metal complexes with many transition metals.[6] Such complexes have been immobilized on organic polymers,[7a−c] and immobilized isocyanide complexes have been used as catalysts for olefin isomerization,[7d] hydroformylation,[7e] olefin hydrogenation,[7d,f] and diene telomerization.[7d] In the present application, we use the isocyanide ligand $C{\equiv}N(CH_2)_3Si(OC_2H_5)_3$ to coordinate to a transition metal complex and the siloxy end to tether the complex to SiO$_2$. The isocyanide group has a strong characteristic $\nu(C{\equiv}N)$ absorption in the IR region which facilitates the characterization of the insoluble tethered-complex catalysts. In a previous communication,[4] we first described the preparation of the rhodium isocyanide complexes $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ and $RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$ and the TCSM catalysts resulting from tethering these two complexes to a silica-supported palladium (Pd−SiO$_2$) catalyst. These TCSM catalysts exhibit very high activities for the hydrogenation of arenes under the mild conditions of 40 °C and 1 atm of H$_2$. In this paper, we report details of the catalyst syntheses and additional catalytic studies of arene hydrogenation using different supported metals (Pd−SiO$_2$, Ru−SiO$_2$, and Pt−SiO$_2$). Also, we describe the catalytic activity of the platinum isocyanide complex $PtCl_2[CN(CH_2)_3Si(OC_2H_5)_3]_2$ tethered on Pd−SiO$_2$ in the hydrogenation of cyclohexanone.

Experimental Section

Materials and Analysis. $Rh_2Cl_2(CO)_4$, H_2PtCl_6, $RuCl_3{\cdot}xH_2O$ (Ru, 42%), PtCl$_2$, and PdCl$_2$ were purchased from Strem. Silica gel 100 (BET surface area, 400 m^2/g) and 3-aminopropyltriethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$) were obtained from Fluka. All solvents were dried by refluxing over CaH$_2$ under nitrogen prior to use. Cyclohexanone was distilled before use. The arene substrates were used as obtained from commercial sources without further purification.

FTIR and DRIFT spectra were recorded on a Nicolet 560 spectrophotometer equipped with a TGS detector in the main compartment and a MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. The solution IR spectra were measured in the main compartment using a solution cell with NaCl salt plates. The DRIFT spectra were recorded with samples in the Harrick microsampling cup. NMR spectra were recorded on a Nicolet NT 300-MHz spectrometer. 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 Varian 3400 GC using a 25 m HP-1 capillary column with a FID detector.

The rhodium content of the TCSM catalysts was determined by atomic emission spectroscopy. The sample was prepared by treating the catalyst (50 mg) successively with 5 mL of aqua regia and 5 mL of aqueous HF (5%) at 90 °C and then diluting the resulting solution with water to 25 mL.

Preparation of the Isocyanide Siloxane and Its Rhodium and Platinum Complexes. $(C_2H_5O)_3Si(CH_2)_3NC$. This isocyanide siloxane was prepared from $(C_2H_5O)_3Si(CH_2)_3NHCHO$ and diphosgene ($Cl_3CO(C{=}O)Cl$) following a procedure developed for the synthesis of other alkyl isocyanides.[8] A solution of $Cl_3COC({=}O)Cl$ (3.23 g, 17 mmol) in 10 mL of CH$_2$Cl$_2$ was added dropwise to a three-necked flask (which was fitted with a reflux condenser maintained at −30 °C) containing a mixture of $(C_2H_5O)_3Si(CH_2)_3NHCHO$ (8.30 g, 34 mmol, which was prepared by refluxing $(C_2H_5O)_3Si(CH_2)_3NH_2$ in ethyl formate overnight and purified by distillation) and triethylamine (10 mL, 70 mmol) in 30 mL of CH$_2$Cl$_2$ with stirring at 0 °C. After stirring at 0 °C for 30 min, the temperature was allowed to rise to ca. 20 °C, and the solution was extracted with water (30 mL) and then 7.5% aqueous solution (50 mL) of NaHCO$_3$. The organic phase was separated and dried over 4-Å molecular sieves. The solvent was evaporated in a vacuum, and the crude isocyanide $(C_2H_5O)_3Si(CH_2)_3NC$ was purified by distillation under low pressure (0.15 mmHg). IR (CH$_2$Cl$_2$): ν(CN) 2150 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.81 (q, 6H, OCH_2CH_3), 3.38 (m, 2H, $CNCH_2$), 1.78 (m, 2H, $CH_2CH_2CH_2$), 1.20 (t, 9H, OCH_2CH_3), 0.72 (t, 2H, $SiCH_2$).

$RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$ (Rh−CNR$_2$). Rh−CNR$_2$ was prepared by a method similar to that described in the literature[9] for the synthesis of other rhodium alkyl isocyanide complexes. A solution of $CN(CH_2)_3Si(OC_2H_5)_3$ (0.34 g, 1.44 mmol) in 5 mL of toluene was added dropwise to a 15 mL toluene solution of $[RhCl(CO)_2]_2$ (0.14 g, 0.36 mmol), and the mixture was stirred at room temperature for 1 h. The resulting solution was evaporated and chromatographed on silica gel (2.4 × 5 cm). Elution with acetone gave the blue-black oily Rh−CNR$_2$ complex. ^{1}H NMR (CDCl$_3$): δ 3.82 (q, 12H, OCH_2CH_3), 3.67 (t, 4H, $CNCH_2$), 1.90 (m, 4H, $CH_2CH_2CH_2$), 1.21 (t, 18H, OCH_2CH_3), 0.75 (t, 4H, $SiCH_2$). IR (toluene): ν(CN) 2192(s) cm^{-1}, ν(CO) 1996(s) cm^{-1}.

$RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ (Rh−CNR$_3$). Rh−CNR$_3$ was prepared according to a procedure used for the preparation of RhCl[CN(2,6-xylyl)]$_3$.[10] A solution of $CN(CH_2)_3Si(OC_2H_5)_3$ (0.51 g, 2.16 mmol) in 5 mL of toluene was added dropwise to a 15 mL toluene solution of $[RhCl(COD)]_2$ (0.18 g, 0.36 mmol); the mixture was stirred at room temperature for 1 h. The resulting solution was evaporated and chromatographed on silica gel. Elution with acetone gave the deep purple oily Rh−CNR$_3$ complex. ^{1}H NMR (CDCl$_3$): δ 3.82 (q, 18H, OCH_2CH_3), 3.58 (t, 4H, $CNCH_2$), 3.46 (t, 2H, $CNCH_2$), 1.85 (m, 6H, $CH_2CH_2CH_2$), 1.23 (t, 27H, OCH_2CH_3), 0.73 (t, 6H, $SiCH_2$). IR (toluene): ν(CN) 2158(s), 2119(m) cm^{-1}. Anal. Calcd for $C_{30}H_{63}O_9N_3Si_3ClRh$: C, 43.28; H, 7.63; N, 5.05. Found: C, 42.70; H, 7.37; N, 4.57.

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$PtCl_2[CN(CH_2)_3Si(OC_2H_5)_3]_2$ (Pt−CNR$_2$). A solution of $PtCl_2(C_6H_5CN)_2$[11] (0.28 g, 0.60 mmol) and $CN(CH_2)_3Si(OC_2H_5)_3$ (0.28 g, 1.2 mmol) in 15 mL of CH_2Cl_2 was stirred at room temperature for 1 h. After the solvent was evaporated under vacuum, the oily residue was washed with pentane and then dried under vacuum to give the yellow oily Pt−CNR$_2$ complex. ^{1}H NMR ($CDCl_3$): δ 3.87−3.71 (m, 16H, OCH_2CH$_3$ and CNCH_2), 1.95 (m, 4H, CH$_2$CH_2CH$_2$), 1.22 (t, 18H, OCH$_2$CH_3), 0.75 (m, 4H, SiCH_2). IR (CH_2Cl_2): ν(CN) 2263(s), 2237(m) cm^{-1}. Anal. Calcd for $C_{20}H_{42}O_6N_2Si_2Cl_2Pt$: C, 32.97; H, 5.81; N, 3.84. Found: C, 33.42; H, 6.06; N, 4.05.

Preparation of the SiO$_2$-Supported Metal Heterogeneous Catalysts. Pd−SiO$_2$. This SiO$_2$-supported palladium was prepared by a procedure similar to that described in the literature.[12] An aqueous solution of H_2PdCl_4 (prepared by dissolving 1.2 g of $PdCl_2$ in 80 mL of aqueous HCl (0.2 M)) was added to a flask containing 7.0 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 in an oven for 5 h and then calcined in a tube furnace at 500 °C in an air flow for 4 h. The calcined sample 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 the black Pd−SiO$_2$ (Pd, 10 wt %) powder. The Pd−SiO$_2$ catalysts with a palladium content of 5 wt % or 15 wt % were prepared by the same procedure.

Ru−SiO$_2$.[13] An aqueous solution of $RuCl_3$ (prepared by dissolving 1.9 g of $RuCl_3{\cdot}xH_2O$ (Ru, 42%) in 30 mL of water) was added to a flask containing 8.0 g of SiO$_2$. After the mixture was stirred at room temperature overnight, the water was removed by continuously stirring the mixture at 120 °C on a hot plate for 3 h. The resulting solid was calcined under a flow of air at 500 °C for 6 h and then a flow of oxygen for 1 h at 400 °C. The sample was finally reduced with a flow of H$_2$ at 500 °C for 5 h to give the black Ru−SiO$_2$ (Ru, 10 wt %) powder.

Pt−SiO$_2$. Pt−SiO$_2$ (Pt, 10 wt %) was prepared by the same procedure as that used for the preparation of Ru−SiO$_2$ by using H_2PtCl_6 instead of $RuCl_3{\cdot}xH_2O$.

Preparation of the Tethered Complex Catalysts. Rh−CNR$_2$/Pd−SiO$_2$. A mixture of 0.60 g of Pd−SiO$_2$ and $RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$ (0.11 g, 0.18 mmol) in 10 mL of toluene was refluxed for 4 h. After filtration, the solid was washed with toluene until the filtrate was colorless. The tethered rhodium isocyanide complex catalyst (Rh−CNR$_2$/Pd−SiO$_2$) with a rhodium content of 1.10 wt % was obtained after drying under vacuum. IR (DRIFT): ν(CN) 2197(s); ν(CO) 2016(s) cm^{-1}.

Rh−CNR$_2$/SiO$_2$. This catalyst was prepared in the same manner as Rh−CNR$_2$/Pd−SiO$_2$ by using SiO$_2$ instead of Pd−SiO$_2$. The rhodium content was 1.30 wt %. IR (DRIFT): ν(CN) 2200(s), ν(CO) 2017(s) cm^{-1}.

Rh−CNR$_3$/Pd−SiO$_2$ and Rh−CNR$_3$/SiO$_2$. These two catalysts were prepared by the same procedure used for the preparation of Rh−CNR$_2$/Pd−SiO$_2$ and Rh−CNR$_2$/SiO$_2$ by using 0.18 mmol of Rh−CNR$_3$ instead of Rh−CNR$_2$. The rhodium contents were 1.35 wt % for Rh−CNR$_3$/Pd−SiO$_2$ and 1.00 wt % for Rh−CNR$_3$/SiO$_2$. IR (DRIFT): ν(CN) 2176(s), 2124(w, sh) cm^{-1} for Rh−CNR$_3$/Pd−SiO$_2$ and 2178(s), 2128(w, sh) cm^{-1} for Rh−CNR$_3$/SiO$_2$.

Rh−CNR$_3$/Pt−SiO$_2$ and Rh−CNR$_3$/Ru−SiO$_2$. These two TCSM catalysts were prepared in the same manner as that used in the preparation of Rh−CNR$_3$/Pd−SiO$_2$ by using 0.60 g of Pt−SiO$_2$ or Ru−SiO$_2$ instead of Pd−SiO$_2$. The rhodium contents were 1.34 wt % for Rh−CNR$_3$/Pt−SiO$_2$ and 1.00 wt % for Rh−CNR$_3$/Ru−SiO$_2$. IR (DRIFT): ν(CN) 2176(s), 2125(w, sh) cm^{-1} for Rh−CNR$_3$/Pt−SiO$_2$ and 2178(s), 2126(w, sh) cm^{-1} for Rh−CNR$_3$/Ru−SiO$_2$.

Table 1. Hydrogenation of Toluene to Methylcyclohexane[a]

catalyst	reaction time (h)	TOF[b] (mol H$_2$/ mol Rh min)	TO[c] (mol H$_2$/ mol Rh)	H$_2$ uptake[c] (mmol)
Pd−SiO$_2$	23			1.0
Rh−CNR$_2$[d]	18	0.08	57	1.1
Rh−CNR$_2$/SiO$_2$	8.5	0	0	0
Rh−CNR$_2$/Pd−SiO$_2$	8.5	4.8	1750	9.4
Rh−CNR$_3$[d]	6.0	0	0	0
Rh−CNR$_3$/SiO$_2$	8.5	0.7	143	0.69
Rh−CNR$_3$/Pd−SiO$_2$	8.5	5.5	2420	15.9

[a] Reaction conditions: 50 mg of solid catalyst, 5 mL of toluene, 40 °C, 1 atm of H$_2$. [b] Turnover frequency is the maximum TOF defined as moles of H$_2$ per mole rhodium per min. [c] Turnover and H$_2$ uptake correspond to the reaction time. [d] 20 μmol of Rh−CNR$_2$ and Rh−CNR$_3$.

Pt−CNR$_2$/Pd−SiO$_2$ and Pt−CNR$_2$/SiO$_2$. A mixture of 1.0 g of Pd−SiO$_2$ and 0.22 g (0.30 mmol) of $PtCl_2[CN(CH_2)_3Si(OC_2H_5)_3]_2$ in 15 mL of CH_2Cl_2 was refluxed for 4 h. After filtration, the solid was washed with CH_2Cl_2 until the filtrate was colorless; then the solid was dried under vacuum to give the tethered platinum isocyanide complex catalyst (Pt−CNR$_2$/Pd−SiO$_2$) with a platinum content of 1.90 wt %. IR (DRIFT): ν(CN) 2265(m), 2236(s) cm^{-1}. Pt−CNR$_2$/SiO$_2$ with a platinum content of 2.90 wt % was prepared by the same procedure as that used for the preparation of Pt−CNR$_2$/Pd−SiO$_2$ by using 1.0 g of SiO$_2$ instead of Pd−SiO$_2$. IR(DRIFT): ν(CN) 2267(s), 2245(m) cm^{-1}.

Catalytic Hydrogenation Reactions. The hydrogenation reactions were carried out in a three-necked, jacketed vessel with a stirring bar and closed with a self-sealing silicon rubber cap; the bottle was connected to a vacuum/hydrogen line and a constant pressure gas buret. The temperature of the ethylene glycol that circulated through the jacket was maintained with a constant-temperature bath. The reaction temperature and H$_2$ pressure were 40 °C and 1 atm, respectively. After the catalyst was added and the atmosphere in the vessel was replaced with hydrogen, the solvent and substrate were added and the hydrogen uptake was followed with the constant-pressure gas buret. The reaction solutions were analyzed by GC. Products of the reactions were identified by GC−MS.

Results

Hydrogenation of Arenes over the Tethered Rhodium Complex Catalysts. The rates of hydrogenation (Table 1) of toluene to methylcyclohexane at 40 °C under 1 atm of H$_2$ in the presence of the TCSM catalysts or the separate homogeneous and heterogeneous catalysts were determined by following the rate of H$_2$ uptake. It is evident that the Rh−CNR$_2$/Pd−SiO$_2$ catalyst activity (as measured by the maximum TOF, TO, or H$_2$ uptake) is at least 8 times greater than that of the simple heterogeneous SiO$_2$-supported Pd (Pd−SiO$_2$), the homogeneous catalyst (Rh−CNR$_2$) even with relatively large amounts of Rh (20 μmol) as compared with 6.3 μmol in Rh−CNR$_2$/Pd−SiO$_2$, or the Rh−CNR$_2$ complex tethered to just SiO$_2$ (Rh−CNR$_2$/SiO$_2$). Similarly, Rh−CNR$_3$/Pd−SiO$_2$ is at least 15 times more active than Pd−SiO$_2$, homogeneous Rh−CNR$_3$, or tethered Rh−CNR$_3$/SiO$_2$. The most active TCSM catalyst, Rh−CNR$_3$/Pd−SiO$_2$, has a maximum turnover frequency (TOF) of 5.5 mol H$_2$/(mol Rh min) and a turnover number (TO) of 2420 during an 8.5 h period. Its activity is, to our knowledge, higher than that of any other

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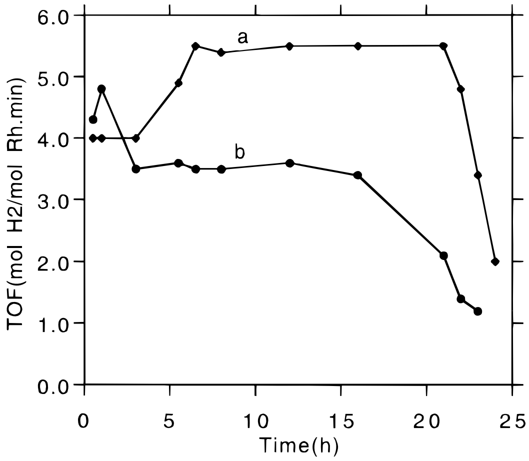

Figure 2. Toluene hydrogenation activities of TCSM catalysts as a function of reaction time: (a) Rh−CNR_3/Pd−SiO_2, (b) Rh−CNR_2/Pd−SiO_2. Reaction conditions are the same as those in Table 1.

Table 2. Hydrogenation of Arenes over Rh−CNR_3/Pd−SiO_2 and Rh−CNR_2/Pd−SiO_2[a]

substrate (mmol)	TOF[b]	TO[c]	product
Rh−CNR_3/Pd−SiO_2 Catalyst			
methyl benzoate (4)	1.5	1760(26)	methyl cyclohexane-carboxylate
diphenylmethane (3)	1.5	1910(24)	dicyclohexylmethane (7.6%)[d] cyclohexylphenylmethane (47.9%)[d]
phenyl ether (3.1)	2.8	2760(22)	cyclohexyl ether (24.3%)[d] cyclohexylphenyl ether (42.3%)[d]
naphthalene (5)	4.7	3700(19)	tetrahydronaphthalene (88%)[d] decahydronaphthalene (12%)[d]
toluene (4.7)	5.6	1120(9)	methylcyclohexane
anisole (4.6)	6.6	2810(9)	methylcyclohexyl ether
Rh−CNR_2/Pd−SiO_2 Catalyst			
methyl benzoate (8)	1.6	1050(12)	methyl cyclohexane-carboxylate
anisole (9.2)	5.7	1390(7)	methylcyclohexyl ether
naphthalene (5)	6.3	1560(6)	tetrahydronaphthalene
toluene (9.4)	6.5	1750(8)	methylcyclohexane

[a] Reaction conditions: 25 mg of Rh−CNR_3/Pd−SiO_2 or 50 mg of Rh−CNR_2/Pd−SiO_2; 5 mL of heptane solvent; 40 °C; 1 atm of H_2; mmol of arene substrate is given in parentheses. Products were identified by GC−MS. [b] Turnover frequency is the maximum TOF defined as moles of H_2 uptake per mole rhodium per min. [c] Turnover number corresponds to the reaction time in parentheses (in h). [d] Yield of the product determined by GC.

homogeneous or immobilized complex catalyst reported in the literature for the hydrogenation of arenes under these mild conditions. Under similar conditions, Blum et al.[14a] used $RhCl_3$−Aliquat-336 to catalyze the hydrogenation of toluene in a medium of H_2O−CH_2Cl_2. After 5 h, ca. 3 mol of toluene was converted to methylcyclohexane per mole of rhodium. The TO value for immobilized complexes prepared from $[RhCl(nbd)]_2$ (nbd = norbornadiene) and phosphinated silica was 200 at 80 atm of H_2 and 30 °C for 1.5 h.[15] Recently, Corma et al.[16] reported that the rhodium complex $[Rh(COD)(N-N)]PF_6$ (COD = 1,5-cyclooctadiene, N−N = 2-(3-triethoxysilypropylaminocarbonyl)pyrrolidine) anchored on zeolites catalyzes the hydrogenation of arenes under 6 atm of H_2 and 80 °C. Hydrogenation of arenes in the presence of homogeneous catalysts is generally performed under high H_2 pressures (≥10 atm).[17] Only a few homogeneous catalysts are active using 1 atm of H_2, but their activities are low.[14]

Figure 2 shows the activities (TOF) of the two rhodium−TCSM catalysts (Rh−CNR_2/Pd−SiO_2 and Rh−CNR_3/Pd−SiO_2) in the hydrogenation of toluene as a function of time. Both of the TCSM catalysts are active from the outset. The activities of these catalysts increase initially but reach maximum values of 4.8 for Rh−CNR_2/Pd−SiO_2 after 1 h and 5.5 for Rh−CNR_3/Pd−SiO_2 after 6.5 h. The TOF value for Rh−CNR_2/Pd−SiO_2 then decreases to ca. 3.5. After remaining at 3.5 for about 12 h, the TOF of Rh−CNR_2/Pd−SiO_2 decreases further. The TOF of Rh−CNR_3/Pd−SiO_2 remains at the maximum value for more than 14 h before decreasing. After the hydrogenation proceeds for about 20 h, the catalysts in the reaction mixtures become compacted by the stirring, which causes the reaction rates to decrease dramatically (Figure 2). However, after the catalysts are separated from the mixture, washed with toluene, and dried in a vacuum, the activities of both catalysts are restored.

The two TCSM catalysts, Rh−CNR_2/Pd−SiO_2 and Rh−CNR_3/Pd−SiO_2, are also very active for the hydrogenation of other arenes under the same mild conditions (Table 2). The higher rate of hydrogenation of anisole as compared with methyl benzoate in the presence of either catalyst indicates that electron-donating substituents in the arene accelerate the rate. The lower rates for diphenyl methane and phenyl ether compared to those for toluene and anisole indicate that steric effects may be involved. No hydrogenolysis products were detected in any of the hydrogenations.

Catalyst durability was tested by using the Rh−CNR_3/Pd−SiO_2 catalyst for 3 successive hydrogenations of toluene under the conditions in Table 1. In the first cycle, the maximum TOF was 5.5 and TO was 6920 after 24.5 h. Then, the catalyst was filtered from the mixture, washed two times with toluene in air, and dried under vacuum at room temperature. In the second hydrogenation cycle, this catalyst gave a maximum TOF of 4.6 and TO values of 5710 after 24.5 h and 6950 after 31 h. After treating the catalyst as described after the first cycle, it was used in a third cycle for which the maximum TOF was 4.0 and TO was 6770 after 24.5 h and 7160 after 27 h. Thus, after three cycles and a total use period of 82.5 h, the catalyst has essentially the same TO activity

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Table 3. Hydrogenation of Toluene to Methycyclohexane[a]

catalyst	TOF[b] (mol H_2/mol Rh min)	TO[c] (mol H_2/mol Rh)	H_2 uptake[c] (mmol)
Pd−SiO_2			1.0(23)
Rh−CNR_3[d]	0	0(6)	0(6)
CNR/Pd−SiO_2[e]			0.63(14)
Rh−CNR_3/SiO_2	0.7	240(16)	1.2(16)
Rh−CNR_3[d] + Pd−SiO_2	3.3	1643(9)	16.4(9)
RhCl(CNBu^n)$_3$[f] + Pd−SiO_2	1.0	426(9)	8.5(9)
Rh−CNR_3/Pd−SiO_2	5.5	2420(8.5)	15.9(8.5)

[a] Reaction conditions are the same as those in Table 1. [b] Turnover frequency is the maximum TOF defined as moles of H_2 uptake per mole rhodium per min. [c] Turnover number and H_2 uptake correspond to the reaction time in parentheses (in h). [d] 10 μmol of Rh−CNR_3. [e] This catalyst was prepared by the reaction of Pd−SiO_2 with $CN(CH_2)_3Si(OC_2H_5)_3$ under the same conditions that were used for the preparation of Rh−CNR_3/Pd−SiO_2. [f] 20 μmol of RhCl(CNBu^n)$_3$.

Table 4. Hydrogenation of Toluene to Methylcyclohexane over Tethered Rh−CNR_3 Catalysts with Different Supported Metals[a]

catalyst	reaction time (h)	TO[c] (mol H_2/mol Rh)	H_2 uptake[c] (mmol)
Pd−SiO_2	23		1.0
Ru−SiO_2	8.0		2.3
Pt−SiO_2	8.0		11.5
Rh−CNR_3/Ru−SiO_2	8.0	762	3.7
Rh−CNR_3/Pt−SiO_2	8.0	2768	18.1
Rh−CNR_3/Pd−SiO_2	8.5	2420	15.9

[a,c] Reaction conditions and footnotes are the same as those in Table 1.

Table 5. Hydrogenation of Toluene to Methylcyclohexane over Rh−CNR_3/Pd−SiO_2 with Different Pd Loadings[a]

Pd content (wt %)	TOF[b] (mol H_2/mol Rh min)	TO[c] (mol H_2/mol Rh)
0[d]	0.7	143
5[e]	3.5	696
10[f]	5.5	2420
15[g]	3.5	1855

[a] Reaction time: 8.5 h. The other reaction conditions are the same as those in Table 1. [b,c] Footnotes are the same as those in Table 3. [d] 1.00% Rh. [e] 0.78% Rh. [f] 1.35% Rh. [g] 0.70% Rh.

as in the first cycle, and the total number of turnovers during this period was 21 000. After each cycle, the liquid toluene phase that was separated from the reaction mixture was examined for catalytic activity in the hydrogenation of toluene under the same conditions used with the solid catalyst. The results show that the liquid phases are inactive for hydrogenation. Also, atomic emission analyses did not detect rhodium in the liquid phases from the first, second, and third cycles. Based on the lower detection limit of the instrument, the amount of rhodium leaching into the liquid phases must be less than 0.2% of the Rh on the catalyst.

To determine whether tethering of the rhodium isocyanide complex on the surface of Pd−SiO_2 was essential to the high activity of the TCSM catalysts, the soluble, nontethered RhCl(CNBu^n)$_3$ (or Rh−CNR_3) together with Pd−SiO_2 was used to catalyze the hydrogenation of toluene (Table 3). The RhCl(CNBu^n)$_3$ was prepared by the procedure used for the synthesis of RhCl(2,6-xylyl)$_3$.[10] It is evident that the activity of RhCl(CNBu^n)$_3$ together with Pd−SiO_2 is only one-fifth that of Rh−CNR_3/Pd−SiO_2. The hydrogenation rate of the mixture of Rh−CNR_3 and Pd−SiO_2 in toluene is about 3 times greater than that of the mixture of RhCl(CNBu^n)$_3$ and Pd−SiO_2 in toluene but is still lower than that of the tethered complex catalyst Rh−CNR_3/Pd−SiO_2. The higher activity of the mixture of Rh−CNR_3 and Pd−SiO_2 compared to the mixture of RhCl(CNBu^n)$_3$ and Pd−SiO_2 may be due to the fact that during the hydrogenation some of the Rh−CNR_3 complex becomes tethered to the Pd−SiO_2 to form the TCSM catalyst Rh−CNR_3/Pd−SiO_2. These results indicate that the tether is required for the high TCSM catalyst activity.

It should be noted that the activity of RhCl(CNBu^n)$_3$ (or Rh−CNR_3) together with Pd−SiO_2 is greater than that of the Rh−CNR_3 complex catalyst alone or Rh−CNR_3/SiO_2. This suggests that Pd−SiO_2 can also promote the hydrogenation activity of the soluble rhodium isocyanide complex, although it is not as efficient as the TCSM catalyst Rh−CNR_3/Pd−SiO_2. It can also be seen (Table 3) that the activity of the non-rhodium-containing catalyst CNR/Pd−SiO_2, which was prepared by tethering the isocyanide−siloxane $CN(CH_2)_3Si(OC_2H_5)_3$ to Pd−SiO_2 under the same conditions as those used for making the tethered complex catalyst Rh−CNR_3/Pd−SiO_2, is much lower than that of Rh−CNR_2/Pd−SiO_2 or Rh−CNR_3/Pd−SiO_2 and is even lower than that of Pd−SiO_2. This indicates that the tethering conditions are not, in some manner, activating the Pd−SiO_2.

Effect of Supported Metal on TCSM Catalyst Activity. Table 4 shows the hydrogenation activities of the Rh−CNR_3 complex catalysts tethered on SiO_2-supported metals M−SiO_2 (M = Pd, Pt, Ru). It can be seen that the activities of the three SiO_2-supported metals for the hydrogenation of toluene decrease in the order Pt−SiO_2 > Ru−SiO_2 > Pd−SiO_2; in the same reaction, the activities of the TCSM catalysts decrease in the order Rh−CNR_3/Pt−SiO_2 > Rh−CNR_3/Pd−SiO_2 > Rh−CNR_3/Ru−SiO_2. The high activity of the Rh−CNR_3/Pt−SiO_2 catalyst may be ascribed to the high activity (Table 4) of the supported platinum, Pt−SiO_2. The activity of Rh−CNR_3/Pd−SiO_2 is at least 15 times higher than that of Pd−SiO_2, but Rh−CNR_3/Pt−SiO_2 and Rh−CNR_3/Ru−SiO_2 are only about 1.6 times more active than Pt−SiO_2 and Ru−SiO_2, respectively. Thus, tethering Rh−CNR_3 to Pd−SiO_2 enhances the activity of the tethered complex more than to Pt−SiO_2 or Ru−SiO_2.

The loading of the supported metal (Pd) also affects the hydrogenation activity of the Rh−CNR_3/Pd−SiO_2 catalyst (Table 5). It is obvious that the Rh−CNR_3/Pd−SiO_2 catalyst with 10 wt % Pd loading is more active for the hydrogenation of toluene than the catalysts with 5 and 15 wt % Pd. SEM (scanning electron microscopic) and TEM (transmission electron microscopic) analyses of the three Pd−SiO_2 catalysts (before Rh−CNR_3 was tethered to them) with different Pd loadings show that although they are prepared by the same procedure, the Pd particle sizes of the Pd−SiO_2 catalyst with 10 wt % Pd loading are more uniform than those on the catalysts with 5 wt % and 15 wt % Pd loadings. Also, the average Pd particle size of 10 wt % Pd−SiO_2 (4.5 nm) is much smaller than that of 5 wt % (25 nm) and 15 wt % (83 nm) Pd−SiO_2. The lower activity of the Rh−CNR_3/Pd−SiO_2 catalyst with 5 wt % Pd loading may be due to the fact that the tethered Rh−CNR_3 complexes are further from Pd islands, and the synergistic functioning of the

Table 6. Hydrogenation of Cyclohexanone to Cyclohexanol over Tethered Platinum Complex Catalysts[a]

catalyst	TOF[b] (mol H_2/mol Pt min)	TO[c] (mol H_2/mol Pt)	H_2 uptake[c] (mmol)
$Pd-SiO_2$			0.45(3.5)
$Pt-CNR_2$[d]	0.4	113(6)	0.56(6)
$Pt-CNR_2/SiO_2$	0	0(10)	0(10)
$Pt-CNR_2/Pd-SiO_2$	1.9	562(6)	2.74(6)

[a] Reaction conditions: 50 mg of solid catalyst; 1 mL of cyclohexanone; 5 mL of ethanol; 40 °C, 1 atm of H_2. [b,c] Footnotes are the same as those in Table 3. [d] 20 μmol of $Pt-CNR_2$.

two catalyst components is less effective. In the $Rh-CNR_3/Pd-SiO_2$ catalyst with 15 wt % Pd loading, some Pd particles may be too large to activate H_2 efficiently,[18] so that its hydrogenation activity is low.

Hydrogenation of Cyclohexanone over Tethered Platinum Complex Catalysts. The TCSM catalyst $Pt-CNR_2/Pd-SiO_2$ was used to catalyze the hydrogenation of cyclohexanone to cyclohexanol under the conditions of 40 °C and 1 atm. Its activity, along with those of the homogeneous $Pt-CNR_2$ complex catalyst and SiO_2-supported Pd ($Pd-SiO_2$), is given in Table 6. The activity of the TCSM catalyst $Pt-CNR_2/Pd-SiO_2$ is about 5 times greater than that of the homogeneous $Pt-CNR_2$ catalyst and 3 times greater than that of $Pd-SiO_2$. On the other hand, when $Pt-CNR_2$ is tethered on just SiO_2, the resulting SiO_2-tethered complex catalyst $Pt-CNR_2/SiO_2$ is inactive for the hydrogenation of cyclohexanone under the mild conditions. Thus, just as for the highly active TCSM catalysts, $Rh-CNR_2/Pd-SiO_2$ and $Rh-CNR_3/Pd-SiO_2$, in the hydrogenation of arenes, both the supported Pd and the tethered $Pt-CNR_2$ complex are essential to the high activity of the $Pt-CNR_2/Pd-SiO_2$ catalyst in the hydrogenation of cyclohexanone to cyclohexanol. To our knowledge, the most active catalysts for the reduction of cyclohexanone are complexes of rhodium, ruthenium, and iridium,[19] which function under hydrogen-transfer reactions. The reduction of cyclohexanone with hydrogen, catalyzed by transition metal complex catalysts, usually requires conditions of high pressure and temperature.[20] Only a few cationic rhodium complex catalysts are known to be active for the hydrogenation of cyclohexanone under atmospheric pressure with satisfactory catalytic activity.[21]

IR Spectroscopic Studies. The IR (DRIFT) spectrum of the TCSM catalyst $Rh-CNR_2/Pd-SiO_2$ shows one ν(CN) band at 2197(s) cm^{-1} and one ν(CO) band at 2016(s) cm^{-1}. The positions and relative intensities of these bands are similar to those of the free $Rh-CNR_2$ complex (ν(CN) 2192(s) cm^{-1}, ν(CO) 1996(s) cm^{-1} in toluene) and the $Rh-CNR_2$ complex tethered on just SiO_2 ($Rh-CNR_2/SiO_2$, ν(CN) 2200(s) cm^{-1}, ν(CO) 2017(s) cm^{-1}). After the $Rh-CNR_2/Pd-SiO_2$ catalyst was used for the hydrogenation of toluene for 23 h, IR analysis of the used catalyst isolated from the reaction mixture showed that the ν(CN) and ν(CO) bands at 2197 and 2017 cm^{-1} had almost disappeared, but two new ν(CN) bands appeared at 2229(w) and 2175(s) cm^{-1}. This spectrum suggests that during the hydrogenation the CO ligand was removed from the rhodium center and a new $RhCl(CNR)_2$ species was formed. There was no evidence for a ν(CN) band in the 2150 cm^{-1} region corresponding to uncoordinated $CN-R$ groups nor for a band in the ν(N−H) region (3300−3500 cm^{-1}) that would indicate hydrogenation of the isocyanide groups to CH_3NH-. The IR (DRIFT) absorptions (ν(CN−): 2174(s), 2124(w, sh) cm^{-1}) of $Rh-CNR_3/Pd-SiO_2$ are also similar to those of the free $Rh-CNR_3$ complex (ν(CN): 2158(s), 2119(m) cm^{-1} in toluene) and the SiO_2-tethered catalyst $Rh-CNR_3/SiO_2$ (ν(CN) (DRIFT): 2178(s), 2128(w, sh) cm^{-1}). After the $Rh-CNR_3/Pd-SiO_2$ catalyst was used for the hydrogenation of toluene for three cycles (82.5 h), the IR spectrum of the used catalyst isolated from the reaction mixture was about the same as that of the fresh catalyst. No other bands corresponding to uncoordinated $CN-R$ or CH_3NH- groups were observed either. These results indicate that the isocyanide ligand-tethers remain coordinated to the rhodium center in the $Rh-CNR_3/Pd-SiO_2$ catalyst even after extended use.

When fresh $Rh-CNR_3/Pd-SiO_2$ was stirred in toluene under a CO atmosphere at room temperature overnight, the resulting catalyst gave an IR (DRIFT) spectrum that exhibited one ν(CN) band at 2191(s) cm^{-1} and one ν(CO) band at 2020(s) cm^{-1}, which are nearly identical to those (ν(CN) 2197(s), ν(CO) 2016(s) cm^{-1}) of the unreacted $Rh-CNR_2/Pd-SiO_2$ catalyst. After the fresh $Rh-CNR_3/Pd-SiO_2$ catalyst was used for the hydrogenation of toluene for three cycles, it was treated with CO as for the unreacted catalyst. The DRIFT spectrum of the resulting sample exhibited the characteristic two bands at 2197(s) cm^{-1} for ν(CN) and 2020(s) cm^{-1} for ν(CO). No other ν(CO) bands were observed, which suggests that even after $Rh-CNR_3/Pd-SiO_2$ was used for three hydrogenation cycles, the tethered $Rh-CNR_3$ complex on the catalyst retains its structure.

The IR (DRIFT) spectrum of fresh $Pt-CNR_2/Pd-SiO_2$ shows two ν(CN) bands at 2265(m) and 2236(s) cm^{-1}, which are similar to those of the free *cis*-$Pt-CNR_2$ complex (2263(s), 2237(m) cm^{-1} in CH_2Cl_2) and the SiO_2-tethered $Pt-CNR_2$ complex catalyst $Pt-CNR_2/SiO_2$ (2267(s), 2245(m) cm^{-1}). The difference in relative intensities, (s)(m) vs (m)(s), may indicate the presence of different amounts of cis and trans isomers.[22] After $Pt-CNR_2/Pd-SiO_2$ was used for the hydrogenation of cyclohexanone for 6 h, the catalyst isolated from the reaction mixture gave two ν(CN) adsorptions at 2262(m) and 2232(s) cm^{-1}, and no absorptions corresponding to uncoordinated $CN-R$ groups or CH_3NH- groups were observed. Thus, the tethered $Pt-CNR_2$ complex in the

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TCSM catalyst appears to retain its structure during the hydrogenation.

Discussion

The catalytic hydrogenation of arenes has long been dominated by heterogeneous catalysts containing metals such as Ni, Rh, Pt, and Ru.[23] The homogeneous metal complex catalyzed hydrogenation of arenes has generally been performed under high pressure and/or high catalyst/substrate ratios.[13−16] To the best of our knowledge, only (η^3-C_3H_5)CoL_3 (L = phosphine or phosphite) and $RhCl_3$ (or [(1,5-hexadiene)RhCl]$_2$) together with a quaternary ammonium salt have been reported[14] to catalyze the hydrogenation of arenes under atmospheric pressure. Unfortunately, the TO values of all these complex catalysts were not high (substrate/catalyst $\leq$ 100).[14] In the present study, homogeneous catalysts have been activated for arene hydrogenation by tethering them to SiO_2 that also supports a metal. The homogeneous Rh−CNR_2 and Rh−CNR_3 catalysts, the SiO_2-supported palladium (Pd−SiO_2), and the two rhodium isocyanide complexes tethered on just SiO_2 are inactive or exhibit low activity for the hydrogenation of toluene under the conditions of 40 °C and 1 atm. However, when the Rh−CNR_2 and Rh−CNR_3 complexes were tethered on Pd−SiO_2, the resulting combined catalysts (TCSM catalysts) Rh−CNR_2/Pd−SiO_2 and Rh−CNR_3/Pd−SiO_2 are very active and efficient for the hydrogenation of toluene. Thus, both the tethered complex (Rh−CNR_2 or Rh−CNR_3) and supported metal (Pd−SiO_2) components are necessary for the high catalytic activities of the TCSM catalysts.

The higher activities of the TCSM catalysts (Rh−CNR_2/Pd−SiO_2, Rh−CNR_3/Pd−SiO_2, and Pt−CNR_2/Pd−SiO_2) may be attributed to a combination of functions of both the supported palladium and the tethered rhodium or platinum complex. As is known,[5,24] Pd−SiO_2 can dissociatively adsorb hydrogen which spills over onto the silica surface. Thus, the supported palladium provides a very active form of hydrogen on SiO_2 where the rhodium or platinum isocyanide complex is tethered. At the same time, the substrate (arene or cyclohexanone) binds to the tethered complex where it is activated to react with the spillover hydrogen.

The results shown in Table 3 indicate that although the combination of nontethered RhCl($CNBu^n$)$_3$ (or Rh−CNR_3) with Pd−SiO_2 is more active for the hydrogenation of toluene than Rh−CNR_3, Pd−SiO_2, or Rh−CNR_3/SiO_2 alone, its activity is lower than that of the TCSM catalyst Rh−CNR_3/Pd−SiO_2.

To test the possibility that spillover hydrogen generated on a Pd−SiO_2 particle could spill over onto a separate SiO_2 particle containing tethered Rh−CNR_3, we used 1:1 amounts of Rh−CNR_3/SiO_2 and Pd−SiO_2 to catalyze the hydrogenation of toluene under the conditions in Table 1. After 23 h, the H_2 uptake was only 2.38 mmol, which is close to the sum of the H_2 uptakes (2.66 mmol in 23 h) for toluene hydrogenation over Rh−CNR_3/SiO_2 and Pd−SiO_2 separately. These results suggest that the synergistic functioning of the supported palladium and rhodium complex is only efficient when the rhodium complex is tethered on the Pd−SiO_2 surface. Also, the higher activity of the Rh−CNR_3/Pd−SiO_2 catalyst with a 10 wt % palladium loading indicates that the amount of supported metal is important to the high activities of the TCSM catalysts.

IR (DRIFT) spectra of the used TCSM catalysts (Rh−CNR_2/Pd−SiO_2, Rh−CNR_3/Pd−SiO_2, and Pt−CNR_2/Pd−SiO_2) isolated from reaction mixtures show that the isocyanide ligand-tethers remain coordinated to the rhodium (or platinum) center in the used catalysts. Even after being used for the hydrogenation of toluene for three cycles (82.5 h), Rh−CNR_3/Pd−SiO_3 exhibits the same IR spectrum as that of the unreacted catalyst. The isocyanide ligand seems not to undergo hydrogenation under the reaction conditions. The IR spectrum of the CO-treated, used Rh−CNR_3/Pd−SiO_2 catalyst did not show any ν(CO) bands that are characteristic of Rh^I-$(CO)_2$ (ν(CO) 2097(s), 2027(s) cm^{-1})[25a,b] or CO adsorbed on Rh(0) metal species (ν(CO) 2058−2065, 1830−1890 cm^{-1}).[25] This suggests that the isocyanide ligands are strongly coordinated to the rhodium center, and no detectable silica-supported rhodium species are formed during the hydrogenation reactions. Also, atomic emission spectroscopic analyses of the hydrogenated solutions showed that no detectable rhodium leached into the solutions during the hydrogenations. All of these results indicate that in the TCSM catalysts, Rh−CNR_2/Pd−SiO_2, Rh−CNR_3/M−SiO_2 (M = Pd, Pt, Ru), and Pt−CNR_2/Pd−SiO_2, the rhodium (or platinum) isocyanide complexes remain attached to the Pd−SiO_2 surface through the isocyanide tethers.

Summary

Under the mild conditions of 40 °C and 1 atm, the TCSM catalysts, Rh−CNR_2/Pd−SiO_2 and Rh−CNR_3/M−SiO_2 (M = Pd, Pt, Ru), are very active for the hydrogenation of arenes. Also, the TCSM catalyst Pt−CNR_2/Pd−SiO_2 is very active for the hydrogenation of cyclohexanone. The high activities of these catalysts require the presence of both components, the tethered rhodium (or platinum) isocyanide complex and the supported metal on the SiO_2 surface. Activities of the catalysts are significantly affected by the nature and loading of the supported metal. Their durabilities and ease of separation make these TCSM catalysts useful in arene and cyclohexanone hydrogenations.

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