

Combination Catalysts Consisting of a Homogeneous Catalyst Tethered to a Silica-Supported Palladium Heterogeneous Catalyst: Arene Hydrogenation

Hanrong Gao and Robert J. Angelici*

Department of Chemistry and Ames Laboratory
Iowa State University, Ames, Iowa 50011

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Transition metal complex catalysts tethered to organic or inorganic supports¹ have received much attention in the past few decades because they can, in principle, combine the advantages of homogeneous and heterogeneous catalysts. Such complexes can be easily tethered on silica surfaces through a ligand in the complex which has alkoxy- or chlorosilane functional groups that react with surface hydroxyl groups on the SiO₂.² Silica-supported heterogeneous metal catalysts such as Pd-SiO₂, Rh-SiO₂, and Pt-SiO₂ also have surface hydroxyl groups that could be used to tether transition metal complex homogeneous catalysts. These combination catalysts consisting of a tethered complex on a supported metal (TCSM) catalyst (Figure 1) could function by synergistic action of both catalyst components. For hydrogenation reactions of unsaturated organic substrates, one might imagine that these TCSM catalysts could function in a way that H₂ is activated on the supported metal (e.g., Pd, Rh, or Pt) with the resulting hydrogen atoms spilling over onto the silica where they could react with the unsaturated organic substrate that is simultaneously coordinated and activated by the tethered complex. This mechanism for the functioning of a TCSM catalyst depends on the well-known phenomenon of hydrogen spillover on supported metal catalysts.³ In other mechanisms, the tethered complex may interact more directly with molecules that are activated on the supported metal. In this paper, we report an example, the first to our knowledge, of a tethered complex on a supported metal (TCSM) catalyst, whose activity for the hydrogenation of arenes is substantially higher than that of the tethered complex or the supported metal separately. In fact, its activity is higher than that of any reported homogeneous or immobilized metal complex catalyst under the mild conditions of 1 atm of H₂ and 40 °C.

Two TCSM catalysts were prepared by tethering either of the rhodium isocyanide complexes, RhCl[CN(CH₂)₃Si(OC₂H₅)₃]₃ or RhCl(CO)[CN(CH₂)₃Si(OC₂H₅)₃]₂, to a silica-supported palladium metal catalyst (Pd-SiO₂). The rhodium isocyanide complex RhCl(CO)[CN(CH₂)₃Si(OC₂H₅)₃]₂ (Rh-CNR₂)⁴ was prepared by the reaction of [Rh(CO)₂Cl]₂⁵ with 4 equiv of

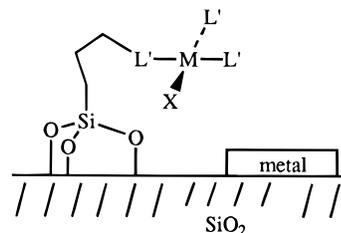


Figure 1. Conceptual illustration of a TCSM catalyst consisting of a tethered homogeneous complex catalyst on a supported metal heterogeneous catalyst.

CN(CH₂)₃Si(OC₂H₅)₃⁶ in toluene, in a reaction similar to that described for the synthesis of RhCl(CO)[CNBu₄]₂.⁷ The complex RhCl[CN(CH₂)₃Si(OC₂H₅)₃]₃ (Rh-CNR₃)⁸ was prepared in the reaction of [Rh(COD)Cl]₂⁹ (COD = cyclooctadiene) with 6 equiv of CN(CH₂)₃Si(OC₂H₅)₃ according to a procedure used for the preparation of RhCl[CN(2,6-xylyl)]₃.¹⁰ The toluene solution containing RhCl(CO)[CN(CH₂)₃Si(OC₂H₅)₃]₂ or RhCl[CN(CH₂)₃Si(OC₂H₅)₃]₃ was refluxed with the silica-supported palladium catalyst Pd-SiO₂¹¹ (Pd, 10 wt %) for 4 h. After filtration, the solid was washed with toluene and then dried in vacuum at room temperature. The resulting tethered catalysts, Rh-CNR₂/Pd-SiO₂ (Rh content, 1.10 wt %) and Rh-CNR₃/Pd-SiO₂ (Rh content, 1.35 wt %), gave IR spectra (DRIFTS) with $\nu(\text{CN}^-)$ and $\nu(\text{CO})$ bands (2197 (s) and 2017 (s) cm⁻¹ for Rh-CNR₂/Pd-SiO₂; 2176 (s) and 2124 (w) cm⁻¹ for Rh-CNR₃/Pd-SiO₂) that are very similar in position and relative intensity to those of the untethered Rh-CNR₂ and Rh-CNR₃ complexes,^{4,8} which indicates that the complexes retain their structures after being tethered to the Pd-SiO₂ surface.

The rates of hydrogenation (Table 1) of toluene to methylcyclohexane at 40 °C while being stirred under 1 atm of H₂ in the presence of the TCSM catalysts or the separate homogeneous and heterogeneous catalysts were determined by following the rate of H₂ uptake. The catalysts are active from the outset but the TOF (turnover frequency) values increase to a maximum value of 4.8 for Rh-CNR₂/Pd-SiO₂ after 1 h and to 5.5 for Rh-CNR₃/Pd-SiO₂ after 6.5 h. After several hours at the maximum TOF levels, the activities decrease slightly. From the data in Table 1, it can be seen that the Rh-CNR₂/Pd-SiO₂ catalyst activity (as measured by the maximum TOF, turnover number (TO), or H₂ uptake) is at least 7 times greater than that of the simple heterogeneous SiO₂-supported Pd (Pd-SiO₂), the Rh-CNR₂ complex tethered to just SiO₂(Rh-CNR₂/SiO₂), just the ligand (CN(CH₂)₃Si(OC₂H₅)₃) tethered to Pd-SiO₂(CNR/Pd-SiO₂), or the homogeneous catalyst (Rh-CNR₂) even with relatively large amounts of Rh (20 μmol) as compared with 6.3 μmol in Rh-CNR₂/Pd-SiO₂. Similarly, Rh-CNR₃/Pd-SiO₂ is at least 9 times more active than Pd-SiO₂, homogeneous Rh-CNR₃, tethered Rh-CNR₃/SiO₂, or CNR/Pd-SiO₂. The most active TCSM catalyst, Rh-CNR₃/Pd-SiO₂, has a maximum turnover frequency of 5.5 mol H₂/(mol of Rh min) and a turnover number

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(4) Selected data for RhCl(CO)[CN(CH₂)₃Si(OC₂H₅)₃]₂: ¹H NMR (CDCl₃) δ 3.82 (q, 12H, OCH₂CH₃), 3.67 (t, 4H, CNCH₂), 1.90 (m, 4H, CH₂CH₂CH₂), 1.21 (t, 18H, OCH₂CH₃), 0.75 (t, 4H, SiCH₂); IR (in toluene) $\nu(\text{CN}^-)$ 2192 (s) cm⁻¹, $\nu(\text{CO})$ 1996 (s) cm⁻¹.

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(6) (CH₃CH₂O)₃SiCH₂CH₂CH₂NC was prepared from (CH₃CH₂O)₃-SiCH₂CH₂CH₂NHCHO and Cl₃COC(=O)Cl following a procedure developed for the synthesis of other alkyl isocyanides (Skorna, G.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 259); IR (in CH₂Cl₂), $\nu(\text{CN}^-)$ 2150 cm⁻¹; ¹H NMR (CDCl₃) δ 3.81 (q, 6H, OCH₂CH₃), 3.38 (m, 2H, CNCH₂), 1.78 (m, 2H, CH₂CH₂CH₂), 1.20 (t, 9H, OCH₂CH₃), 0.72 (t, 2H, SiCH₂).

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(8) Selected data for RhCl[CN(CH₂)₃Si(OC₂H₅)₃]₃: ¹H NMR (CDCl₃) δ 3.82 (q, 18H, OCH₂CH₃), 3.58 (t, 4H, CNCH₂), 3.46 (t, 2H, CNCH₂), 1.85 (m, 6H, CH₂CH₂CH₂), 1.23 (t, 27H, OCH₂CH₃), 0.73 (t, 6H, SiCH₂); IR (in toluene) $\nu(\text{CN}^-)$ 2158 (s), 2119 (m) cm⁻¹. Anal. Calcd for C₃₀H₆₃O₉N₃Si₃ClRh: C, 43.28; H, 7.63; N, 5.05. Found: C, 42.70; H, 7.37; N, 4.57.

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(11) Pd-SiO₂ was prepared by the incipient wetness method by impregnation of SiO₂ using an aqueous solution of H₂PdCl₄, calcining at 500 °C for 4 h and reducing with H₂ at 380 °C for 4 h.

Table 1. Hydrogenation of Toluene to Methylcyclohexane^a

catalyst	Rh content ^e (wt %)	reaction time (h)	maximum TOF ^f		H ₂ uptake ^g (mmol)
			(mol of H ₂ /mol of Rh min)	TO ^g (mol of H ₂ /mol of Rh)	
Pd-SiO ₂	0	23			1.0
CNR/Pd-SiO ₂ ^b	0	15			0.62
Rh-CNR ₂ ^c		18	0.08	57	1.1
Rh-CNR ₂ /SiO ₂ ^d	1.30	8.5	0	0	0
Rh-CNR ₂ /Pd-SiO ₂	1.10	8.5	4.8	1750	8.4
Rh-CNR ₃ ^c		6.0	0	0	0
Rh-CNR ₃ /SiO ₂ ^d	1.00	8.5	0.7	143	0.94
Rh-CNR ₃ /Pd-SiO ₂	1.35	8.5	5.5	2420	9.5

^a Reaction conditions: 50 mg of solid catalyst, 5 mL of toluene, 40 °C, 1 atm of H₂. Methylcyclohexane was identified by GC-MS. ^b This catalyst was prepared in the same way as described for the TCSM catalysts except CN(CH₂)₃Si(OC₂H₅)₃ was used instead of Rh-CNR₂ or Rh-CNR₃. ^c Using 20 μmol of the homogeneous catalysts, Rh-CNR₂ or Rh-CNR₃. ^d These catalysts were prepared in the same way as that used for the corresponding catalysts tethered on Pd-SiO₂, except SiO₂ was used instead of Pd-SiO₂. ^e Rhodium content determined by atomic emission analysis. ^f Turnover frequency defined as moles of H₂ per mole of rhodium per minute. ^g Turnover and H₂ uptake during the entire reaction time; they also coincide with the amounts of product formed as determined by GC analyses.

of 2420 during an 8.5 h period. To 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.^{12a-14} Hydrogenation of arenes in the presence of homogeneous catalysts is generally performed under high H₂ pressures (≥ 10 atm).¹⁵ Only a few homogeneous catalysts are active using 1 atm of H₂, but their activities are low.¹²

The two TCSM catalysts 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 suggests 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 hydrogenation reactions.

The durability of the Rh-CNR₃/Pd-SiO₂ catalyst was tested by using it for three successive hydrogenations of toluene using 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 the catalyst was treated 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 as in the first cycle, which indicates that the Rh has not been leached from the tether.

Even after three catalytic cycles, the Rh-CNR₃/Pd-SiO₂ catalyst still exhibits ν(CN-) absorptions in the DRIFT spectrum at 2177(s) and 2124(w) cm⁻¹, which are the same as those in the freshly prepared catalyst. Also, there neither is any evidence for a ν(CN-) band in the region of 2150 cm⁻¹ corresponding to

Table 2. Hydrogenation of Arenes over Rh-CNR₃/Pd-SiO₂ and Rh-CNR₂/Pd-SiO₂^a

substrate (mmol)	TOF ^b	TO ^c	product
Rh-CNR ₃ /Pd-SiO ₂ catalyst			
methyl benzoate (4.0)	1.5	1760 (26)	C ₆ H ₁₁ CO ₂ Me
diphenylmethane (3.0)	1.5	1910 (24)	(C ₆ H ₁₁) ₂ CH ₂ (7.6%) C ₆ H ₁₁ (Ph)CH ₂ (47.9%)
phenyl ether (3.1)	2.8	2760 (22)	(C ₆ H ₁₁) ₂ O (24.3%) C ₆ H ₁₁ OPh (42.3%)
naphthalene (5.0)	4.7	3700 (19)	C ₁₀ H ₁₂ (88%) C ₁₀ H ₁₈ (12%)
toluene (4.7)	5.6	1120 (9)	C ₆ H ₁₁ CH ₃
anisole (4.6)	6.6	2810 (9)	C ₆ H ₁₁ OCH ₃
Rh-CNR ₂ /Pd-SiO ₂ catalyst			
methyl benzoate (8.0)	1.6	1050 (12)	C ₆ H ₁₁ CO ₂ Me
anisole (9.2)	5.7	1390 (7)	C ₆ H ₁₁ OCH ₃
naphthalene (5.0)	6.3	1560 (6)	C ₁₀ H ₁₂
toluene (9.4)	6.5	1750 (8)	C ₆ H ₁₁ CH ₃

^a Reaction conditions: 25 mg of Rh-CNR₃/Pd-SiO₂ (Rh, 1.35 wt %) or 50 mg of Rh-CNR₂/Pd-SiO₂ (Rh, 1.10 wt %); 5 mL of heptane solvent; 40 °C; 1 atm of H₂; mmole of arene substrate is given in the table. Products were identified by GC-MS. ^b Turnover frequency is the maximum TOF defined as moles of H₂ uptake per mole rhodium per minute. ^c Turnover number corresponds to the reaction time in parentheses (in hours); it also coincides with the amount of product formed as determined by GC analysis.

uncoordinated CN-R groups nor a band in the ν(N-H) region (3300 ~ 3500 cm⁻¹) that would indicate hydrogenation of the isocyanide groups to CH₃NH-. Thus, the tethered Rh-CNR₃ complex on the Rh-CNR₃/Pd-SiO₂ catalyst appears to retain its structure even after extended use. In order to determine whether the tether is essential to the activities of these catalysts, the soluble, nontethered RhCl(CNBU)₃ together with Pd-SiO₂ was used to catalyze the hydrogenation of toluene, but the activity was only one-fifth that of Rh-CNR₃/Pd-SiO₂, which indicates that the tether is required for the high TCSM catalyst activity.

Although it has not been established whether these arene hydrogenation reactions proceed by a hydrogen spillover mechanism or by some other process, it is clear that the tethered homogeneous complex and the supported metal cooperate in a manner that gives these TCSM catalysts activities higher than either of the catalysts separately. It is expected that this type of catalyst could incorporate a wide range of tethered homogeneous complexes and supported metals, which would permit the design of TCSM catalysts for a variety of reactions. Studies are in progress.

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