A new catalytic hybrid material from simple acid–base hydrolytic chemistry

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Abstract

The synthesis of a new inorganic–organic hybrid material in a non-aqueous medium from acid–base hydrolysis of octadecyltri(amino)silane with tri(hydroxypropyl)phosphine, is reported. Rh(I) metal centers are easily introduced into the network by reacting it with the dimer, $[Rh(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})]_2$, and the resulting organometallic–inorganic hybrid shows preference for the fully hydrogenated product (bibenzyl) in the catalytic hydrogenation of diphenylacetylene. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The design of solid supports to immobilize soluble transition metal catalysts continues to be a topical area of research, and offers several advantages by heterogenizing homogeneous catalysis [1–3]. Some of the commonly used systems to support transition metal complexes include functionalized polymers [4,5], silica [6,7], thin films [8–11], and sol–gels [12]. The sol–gel technique is a promising approach in building organometallic–inorganic hybrid materials, and the traditional route to synthesize such materials involves co-condensation of hydrolyzed tetra(alkoxy)silane with functionalized tri-alkoxysilane in an acid or base catalyzed cross-linking process [12]. The concentration of the donor ligands in the resulting silica matrix is dependent on the molar ratios of the tetra- and trialkoxysilanes used, and the curing temperatures. The structural control in this traditional sol–gel process that requires a definite H_2O:silane molar ratio, is dependent on a number of factors such as pH of the solution. The inductive effects on reaction kinetics also affect the diverse series of reactions that are involved in the process to different extents [13]. We have recently developed a highly versatile route to the functionalization of the inorganic oxide surfaces, and synthesis of siloxane-linked polymers and networks based on simple acid–base hydrolytic chemistry [8–11,14–20]. It involves the reaction of [Si]-NEt$_2$ moieties with molecules containing terminal OH groups. We were in-

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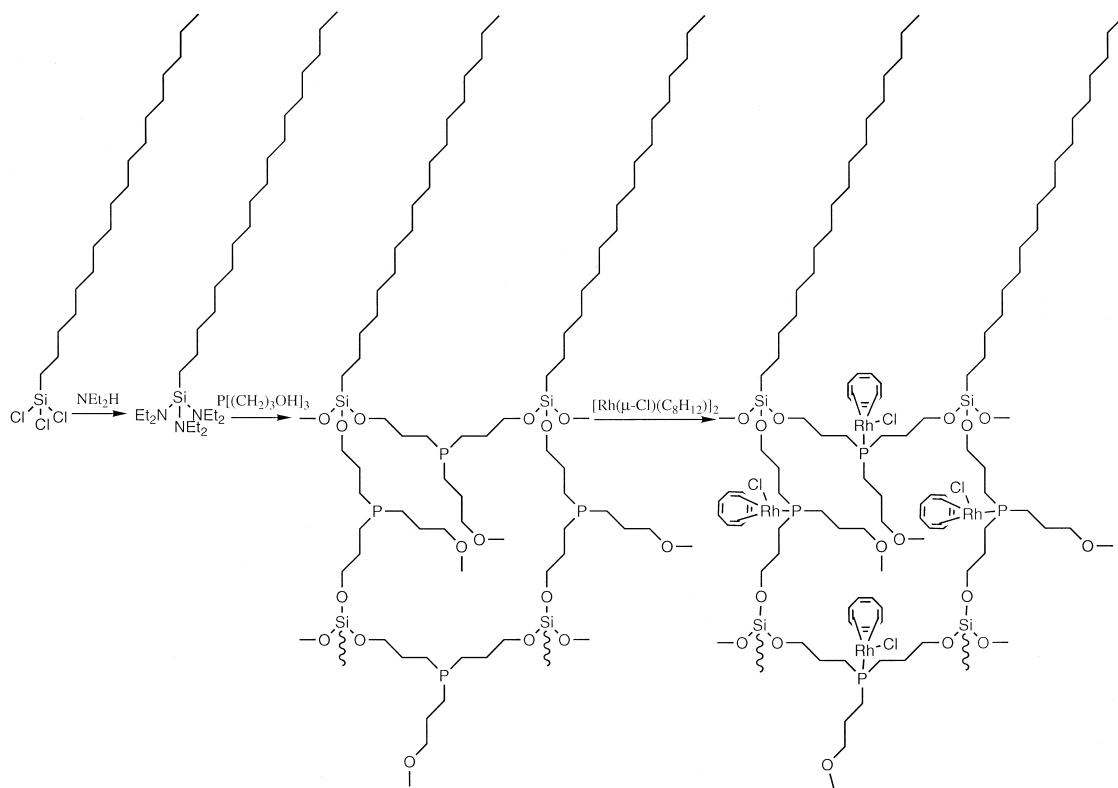
trigued by the possibility of generating a novel organometallic network material using this simple chemistry and mild reaction conditions. We report herein, synthesis of a new inorganic–organic hybrid material from the reaction of octadecyltri(amino)silane with tri(hydroxypropyl)phosphine. The reaction is carried out in a non-aqueous medium, and is compatible with sensitive trialkylphosphine ligands that are commonly employed in anchoring transition metal complexes. The resulting network will have a core of phosphine donor ligands with an envelope of long hydrocarbon chains on the top, and may offer a unique behavior of the bound metal complexes in catalysis. The phosphine sites in the above hybrid easily bind covalently to Rh(I) centers upon reacting with $[Rh(\mu\text{-Cl})(1,5\text{-}C_8H_{12})]_2$. The organometallic network is found to be highly active and selective in the catalytic

hydrogenation of diphenylacetylene. The long hydrocarbon chains seem to act as a trap for diphenylacetylene when it binds to the active metal centers, leading to a fully hydrogenated product (bibenzyl). The corresponding solution analog, $[(Me_3Si(CH_2)_3)_3PRhCl(1,5\text{-}C_8H_{12})]$, produces a mixture of *cis*-stilbene, *trans*-stilbene and bibenzyl.

2. Results and discussion

2.1. Synthesis

Aminosilanes which can be easily prepared from the corresponding chlorosilanes and excess diethylamine, react with molecules containing

Scheme 1.

Fig. 1. ^{29}Si NMR of the organometallic–inorganic hybrid material before (B) and after (A) functionalization with Rh(I) complex.

terminal OH groups via acid–base hydrolysis [8–11,14–21]. Using a similar reaction methodology, $CH_3(CH_2)_{17}Si(N(C_2H_5)_2)_3$ was prepared from octadecyltrichlorosilane (OTS) in an almost quantitative yield (Scheme 1). It was then reacted with 1 molar equivalent of tri(hydroxypropyl)phosphine to give a gelatinous viscous liquid, which upon further drying under vacuum for a long time yielded a white solid. It showed a singlet at −30.9 ppm in its solid state $^{31}P\{^1H\}$ NMR spectrum, indicating that the environment around phosphorous in the conden-

sate is equivalent at all positions. The solid state ^{29}Si NMR showed a major peak at −45.9 ppm which is consistent [22] with a T^0 type of network structure, $(RO)_3Si-(CH_2)_{17}CH_3$ ($R = CH_2-CH_2-CH_2-P$ moiety), and a vary small peak at −53.9 ppm which can be assigned to the terminal T^1 network Si groups (Scheme 1 and Fig. 1).

The solubility of the network polymer was examined in a number of different solvents, and it was virtually insoluble. It was found to swell in THF, toluene and benzene with a little bit less swelling in benzene than the former two solvents. In chloroform, large chunks were broken into smaller ones, and a suspension of relatively large particles was obtained.

The thermal stability of the hybrid material was determined by thermogravimetric analysis, and a 5% weight loss was observed at 230–235°C in a nitrogen atmosphere. The high thermal stability can be ascribed to mechanical strength imparted by stable and strong Si–O bonds.

The metal was successfully introduced into the network by adding the dimer, $[Rh(\mu\text{-Cl})(1,5\text{-}C_8H_{12})]_2$, to a suspension of the material in THF. Solid state $^{31}P\{^1H\}$ NMR of the organometallic hybrid showed a broad peak at 15.0 ppm which is similar to its solution analog $[((CH_3)_3Si(CH_2)_3)_3PRhCl(1,5\text{-}C_8H_{12})]$. The solid state ^{29}Si NMR of the sol–gel containing bound metal centers was identical to that for the original unfunctionalized sol–gel, and suggests that the silicon network structure is not affected by the addition of the metal complex.

Solution analog of the organometallic network, $[(CH_3)_3SiO(CH_2)_3]_3PRhCl(1,5\text{-}C_8H_{12})$, was easily prepared by reacting two molar

Scheme 2.

equivalents of $[(CH_3)_3SiO(CH_2)_3]_3P$ with $[Rh-(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})]_2$, and was characterized using standard techniques.

2.2. Hydrogenation of diphenylacetylene

Rh(I) complexes catalyze a variety of organic transformations [23,24]. We chose to investigate hydrogenation of diphenylacetylene (tolan) since it can lead to three products, *cis*-stilbene, *trans*-stilbene and bibenzyl, and offers a way of evaluating catalytic activity and selectivity. The sol–gel bound Rh(I) complex was found to be highly active in the catalytic hydrogenation of tolan, and at 10 bar pressure of hydrogen, 25°C and 30 min of reaction time, yielded a product distribution of 90.2% bibenzyl and 9.8% *trans*-stilbene (Scheme 2). The solution analog of the above surface bound complex, $[(CH_3)_3SiO-(CH_2)_3]_3PRhCl(1,5\text{-}C_8H_{12})$, was also found to be active in catalyzing hydrogenation of tolan, however, gave a product distribution that was very different than the network bound Rh(I) complex: 51.4% bibenzyl, 46.8% *trans*-stilbene and 1.7% *cis*-stilbene.

The above results suggest the Rh(I) supported catalyst in the hybrid material shows selectivity for the fully hydrogenated product. This may be attributed to the structure of the support that contains long hydrocarbon chains which encapsulate the active metal centers, and once diphenylacetylene enters the reactive site in the network, it is trapped in there, and gets completely reduced to fully hydrogenated product.

3. Conclusions

Acid–base hydrolysis of $CH_3(CH_2)_{17}$-$Si(N(C_2H_5)_2)_3$ with $[HO\text{-}(CH_2)_3]_3P$ in a non-aqueous medium, offers a convenient route to synthesize an inorganic–organic hybrid material that contains phosphine donor ligands in its backbone structure. The resulting polymeric network easily binds to Rh(I) centers through the latter ligands upon reacting with $[Rh(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})]_2$. The organometallic hybrid is active in catalyzing hydrogenation of diphenylacetylene, and shows selectivity towards fully hydrogenated product, bibenzyl. The unique structure of the network material helps in trapping diphenylacetylene when bound to Rh(I) centers, and may be responsible for the observed selectivity.

4. Experimental

4.1. General

All manipulations were performed under a nitrogen atmosphere using either standard Schlenk line techniques or in a Braun Labmaster glove box. Solvents were dried and distilled over sodium and stored under nitrogen. Solution NMR spectra were measured on a Jeol 270 MHz spectrometer, and the solid state spectra were recorded on a Chemagnetics (CMX-300) instrument. Chemical shifts are reported relative to tetramethylsilane as an internal standard for ^1H NMR spectra, and to H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra. Mass spectra were obtained using a low resolution KRATOS Kompact MALDI-TOF spectrometer using didronel/LiBr as the matrix, and by FAB. The compounds reported in the manuscript were obtained as gels or oils which were difficult to dry, and the elemental analyses presented are of compounds that were dried for long periods of time. The remaining traces of solvent may be responsible for lower percentage of carbon in the analytical data. The FT–IR spectra were recorded on a Bruker IFS-48 spectrometer, and elemental analysis were performed by Guelph Chemical Laboratories. Thermogravimetric analysis was performed using a Seiko TK/DTA-220 instrument with a heating rate of 20°C min^{-1}. OTS was purchased from Aldrich and tri(hydroxypropyl)phosphine

from Strem Chemicals, and used as received. GC–MS evaluations were performed in a Hewlett Packard 6840 GC and HP 5973 mass spectrometer, using He as the carrier gas and an initial temperature of 100°C increased to 250°C over a 30-min run.

4.2. $[(CH_3)_3Si-O-(CH_2)_3]_3P$

Tri(hydroxypropyl)phosphine (1.10 g, 5.26 mmol) in 15 ml of THF was added dropwise to N,N'-diethyltrimethylsilylamine (2.98 ml, 15.7 mmol) in 5 ml of THF. The mixture was allowed to stir at ambient temperature for 20 h. Diethylamine and THF were removed by distillation resulting in a clear, colorless oily liquid; yield, 2.16 g, 96.5%. ^{1}H NMR (270 MHz, C_6D_6): δ 0.06 (27H, s, $(CH_3)_3Si$), 1.35 (6H, br t, $J_{H-H} = 7.3$ Hz, CH_2P), 1.63 (6H, m, $J_{H-H} = 6.6$ Hz, CH_2), 3.51 (6H, t, $J_{H-H} = 6.2$ Hz, CH_2O) ppm. $^{31}P\{^1H\}$ NMR (270 MHz, C_6D_6): $\delta - 31.9$ (s) ppm. FT–IR (KBr): ν 686.1, 748.0, 841.2, 935.3, 1097.5, 1250.6, 1384.9, 1436.7, 1652.7, 2847.0, 2891.0, 2954.7 cm^{-1}. EI–MS: m/z 425. Anal. calcd. for $C_{18}H_{45}O_3Si_3P$ (424.78): C, 50.89%; H, 10.68%. Found: C, 51.64%; H, 10.45%.

4.3. $[(CH_3)_3Si-O-(CH_2)_3]_3PRhCl(1,5-C_8H_{12})$

A total of 97.2 mg of (**1**) (0.23 mmol) in 10 ml of C_6H_6 was added dropwise to 56.4 mg of $[RhCl(\eta^2-C_8H_{12})]_2$ (0.114 mmol) in 5 ml of benzene. The mixture was stirred for 2.5 h, followed by removal of the solvent in vacuo resulting in a red residue. The product was recrystallized from a toluene/hexanes mixture affording a red microcrystalline solid; yield, 140 mg, 90.7%. ^{1}H NMR (270 MHz, C_6D_6): δ 0.09 (27H, s, $(CH_3)_3Si$), 1.72 (6H, m, PCH_2), 1.77 (8H, m, $2CH_2CH_2$), 2.19 (6H, m, CH_2), 3.53 (6H, t, $J_{H-H} = 6$ Hz, CH_2O), 5.67 (4H, br s, $CH=CH$) ppm. $^{31}P\{^1H\}$ NMR (270 MHz, C_6D_6): δ 15.14 (d, $J_{Rh-P} = 146.5$ Hz) ppm. FT–IR (KBr): ν 687.4, 748.5, 841.5, 938.5, 096.7, 1170.4, 1206.6, 1250.3, 1332.2, 1384.6,

1432.9, 2735.6, 2832.1, 2880.2, 2953.7 cm^{-1}. MALDI-TOF MS (LiBr/gentisic acid): m/z 673.2. Anal. calcd. for $C_{26}H_{60}O_3Si_3PClRh$ (674.35): C, 46.31%; H, 8.79%. Found: C, 46,78%; H, 7.83%.

4.4. $CH_3(CH_2)_{17}Si(N(C_2H_5)_2)_3$

OTS ($CH_3(CH_2)_{17}SiCl_3$, 15 g, 38.6 mmol) was dissolved in dry THF, and a 10-fold excess of diethylamine (30 ml) was added dropwise at 0°C. The reaction mixture was left to stir overnight, and it was then vacuum filtered to remove a white solid ($N(C_2H_5)_2H \cdot HCl$). THF was then removed in vacuo to obtain a colorless liquid (16.5 g, 87% yield). ^{1}H NMR (270 MHz, C_6D_6, ppm) δ 1.00 (18H, t, $J_{H-H} = 5.91$ Hz, CH_3-CH_2N), 1.29–1.50 (37H, m, $-(CH_2)_{17}-CH_3$), 2.89 (12H, q, $J_{H-H} = 6.94$ Hz, CH_3-CH_2N). MS: m/z 500. Anal. ($C_{30}H_{67}N_3Si$); found: C, 68.40%; H, 13.53%. Calcd.: C, 70.36%; H, 13.56%.

4.5. Hybrid

$CH_3(CH_2)_{17}Si(N(C_2H_5)_2)_3$ (4.94 g, 9.93 mmol) was dissolved in 10 ml of THF, and was added to a solution of tri(hydroxypropyl)phosphine (2.07 g, 9.93 mmol), and the mixture was left to stir for 48 h. THF was removed under vacuum to yield a gelatinous viscous liquid which upon further drying under vacuum gave a white solid (4.7 g, 97% yield). ^{1}H NMR (270 MHz, C_6D_6, ppm) δ 0.94 (3H, m, $CH_3(CH_2)_{17}Si$), 1.50 (34H, m, $CH_3(CH_2)_{17}Si$), 2.90 (4H, m, $J_{H-P} = 14.01$ Hz, $P(CH_2)_2-CH_2-O$), 3.49 (2H, m, $P(CH_2)_2-CH_2-O$). $^{31}P\{^1H\}$ NMR $\delta - 30.9$. ^{29}Si NMR (solid state) -45.9 ppm. FT–IR ν_{Si-O} 1092.6 cm^{-1}. Anal. ($C_{27}H_{55}SiO_3P$); found: C, 65.06%; H, 11.27%. Calcd.: C, 66.66%; H, 11.32%.

4.6. Organometallic hybrid

A THF mixture of the above OTS sol–gel polymer (1.1 g) was added to a solution of

$[Rh(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})]_2$ (0.50 g) in 10 ml of THF, and left to stir overnight giving a light orange solution. The solvent was removed leaving a yellow powder (1.52 g, 92% yield). Anal. $(C_{35}H_{67}SiO_3PRhCl)$; found: C, 56.58%; H, 9.72%. Calcd.: C, 57.34%; H, 9.15%.

4.7. Hydrogenation of diphenylacetylene using $[(CH_3)_3Si\text{-}O(CH_2)_3]_3 PRh(1,5\text{-}C_8H_{12})(Cl)$

$RhCl(1,5\text{-}C_8H_{12})[P((CH_2)_3OSi(CH_3)_3)_3]$ (100 mg, 0.149 mmol) was dissolved in 15 ml of C_6H_6 containing 4.11 g (0.023 mol) of diphenylacetylene. The mixture was pressurized with 150 psi of hydrogen and allowed to stir at room temperature for 30 min. The solution was distilled to remove benzene, resulting in an off-white solid characterized by ^{1}H NMR, FT–IR, melting points and GC–MS. Total product yield: 4 g, 95%. Turnover number: $(mol_{sub} \, mol_{cat}^{-1})$ 150. Turnover frequency: $(mol_{sub} \, mol_{cat}^{-1} \, h^{-1})$ 290 h^{-1}.

4.8. Bibenzyl

^{1}H NMR (270 MHz, C_6D_6): δ 2.74 (4H, br s, CH_2CH_2), 6.97, 7.11 (10H, m, $2C_6H_5$) ppm. FT–IR (KBr): ν 3082.1, 3056.8, 3024.4, 2927.3, 1601, 1494, 759.2, 698.5 cm^{-1}. Melting point: 52°C. GC–MS (C_6H_6): 9.075 min, m/z 182, 51.44%.

4.9. cis-Stilbene

^{1}H NMR (270 MHz, C_6D_6): δ 7.16 ($CH=CH$), 7.22, 7.32 (10H, m, $2C_6H_5$) ppm. FT–IR (KBr): ν 2927.2, 2854.8, 1652.1, 1450.6, 963.8, 770.7 cm^{-1}. GC–MS (C_6H_6): 11.298 min, m/z 180, 1.72%.

4.10. trans-Stilbene

^{1}H NMR (270 MHz, C_6D_6): δ 6.46 ($CH=CH$), 7.10, 7.17 (10H, m, $2C_6H_5$) ppm. FT–IR (KBr): ν 3076.3, 3060, 3021.5, 2938.6, 1599.1, 1492.5, 753.8, 685.3 cm^{-1}. Melting point: 119°C. GC–MS (C_6H_6): 12.024 min, m/z 180, 46.83%.

4.11. Hydrogenation of diphenylacetylene using OTS hybrid catalyst

A total of 4.73 g (0.027 mol) of diphenylacetylene was added to a suspension of the OTS hybrid catalyst (0.100 g, 0.136 mmol) in 30 ml of THF containing 4.73 g (0.027 mol) of diphenylacetylene. The solution was pressurized with 150 psi of hydrogen and was allowed to react at room temperature for 30 min. The gel was filtered off and the solution was distilled to remove THF. The white solid was characterized by ^{1}H NMR, FT–IR, and GC–MS. Total product yield: 4.5 g, 94%. Turnover number: $(mol_{sub} \, mol_{cat}^{-1})$ 180. Turnover frequency: $(mol_{sub} \, mol_{cat}^{-1} \, h^{-1})$ 360 h^{-1}.

4.12. Bibenzyl

A total of 90.12%, *trans*-stilbene: 9.82%.

Acknowledgements

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