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Synthesis of silica-supported rhodium carbene complex as efficient catalyst for the addition of phenylboronic acid to aldehydes

Ismail Özdemir[1]*, Nevin Gürbüz[1], Turgay Seçkin[1] and Bekir Çetinkaya[2]

[1]Inönü University, Department of Chemistry, 44069 Malatya, Turkey
[2]Ege University, Department of Chemistry, 35100 Bornova-İzmir, Turkey

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Silica-supported catalytically active functional materials, such as the rhodium(I) carbene complex with 1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidine-2-ylidine (L), were prepared using the sol–gel method. The complex (1; COD = 1,5-cyclooctadiene) RhCl(COD)[1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidin-2-ylidine] was characterized by conventional spectroscopic methods and elemental analyses and the silica-supported functional material RhCl(COD)(L) were tested for the catalytic addition of phenylboronic acid to aldehydes. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: silica-supported catalysis; *N*-heterocyclic carbene; imidazolidinylidine

INTRODUCTION

Silica-supported materials are of rapidly growing interest in science, as well as for industrial applications such as catalysts,[1–3] ceramics,[4,5] fillers,[6,7] and coatings.[8] For all these purposes, the synthesis of silica-supported materials exhibiting well-defined properties, such as particle size distribution and particle shape, is an important challenge to preparative chemistry. Moreover, the adjustment of specific properties of silica-supported materials for catalytic properties is becoming of considerable interest. Various methods of synthesis have been developed in order to fulfill the requirements.[9,10] These include chemical vapor deposition, laser ablation, the micro-emulsion process, hydrothermal methods and sol–gel processes.[9–12]

Recently, transition-metal complexes of *N*-heterocyclic carbenes have been the focus of considerable attention, since they can act as a catalyst or catalyst precursor to important transformations, such as palladium-catalyzed Heck-type or Suzuki coupling,[13–17] CO–C_2H_4 copolymerizations,[18] ruthenium-catalyzed olefin metathesis,[19–25] cyclopropanations,[26] furan synthesis[27,28] and rhodium-catalyzed hydrogenation,[29] hydroformylation[30] and hydrosilylations.[31]

In contrast to the widely used phosphine complexes, they have been shown to be remarkably stable towards heat, oxygen and moisture. The metal–carbon bonds in the carbene complexes are much stronger than the metal–phosphorus bond of typical phosphine complexes. This property eliminates the problems associated with weak ligand–metal interactions, including deposition of free metal under catalytic conditions.

Homogeneous catalysts have been used industrially on small scales, mainly because of the difficulty of separation from the reaction products. A good way to combine the advantages of homogeneity with those of heterogeneous catalysts is to attach the soluble and catalytic active metal complexes to suitable materials.[32–34] Inorganic supports possess a rigid structure that is not deformed by solvent swelling during catalytic reactions. Fumed silica is a better support because it offers high surface area, high mechanical strength, and heat and chemical stability.

The advantages to be gained in heterogenizing *N*-heterocyclic carbene complexes through polymer attachment have been described.[35–37] Recyclable polymer-supported catalyst **I** was used for ring-closing metathesis.[35,36] Ruthenium(II) complexes of *N*-heterocyclic carbenes (**II**) attached to silica exhibit very high efficiencies as catalyst for the

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*Correspondence to: Ismail Özdemir, Inönü University, Department of Chemistry, 44069 Malatya, Türkiye.
E-mail: handongyin@lctu.edu.cn
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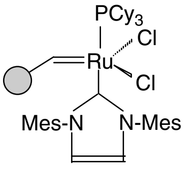
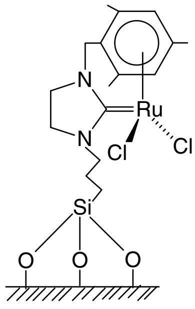
intramolecular cyclization of (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran reaction.[38]



I



II

Rhodium carbene complexes have been studied extensively. However, there are few reports on the catalytic activity of rhodium carbene complexes in rhodium-mediated processes.[30,39,40] Miyaura and co-workers reported that rhodium catalyzes the addition of aryl and alkenylboronic acids to aldehydes, giving secondary alcohols. The reactions were facilitated by the presence of an electron-withdrawing group on the aldehyde and an electron-donating group on the arylboronic acid, suggesting that the mechanism involves nucleophilic attack of the aryl group on the aldehyde.[41] An catalytic system generated *in situ* for the addition of phenylboronic acid to aldehydes is prepared by combination of rhodium salt, 1,3-bis(alkyl or aryl) imidazolium chloride and base.[42]

In this contribution, the preparation of silica-supported catalyst material is described. This includes the preparation of the new RhCl(COD)[1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidin-2-ylidine] (**1**; COD = 1,5-cyclooctadiene). Special focus is given to the application and relevant catalytic properties, of the immobilized materials with regard to reactivity and recyclability for the addition of phenylboronic acid to aldehydes.

Based on the findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of rhodium complexes for the addition of phenylboronic acid to aldehydes.

EXPERIMENTAL

Manipulations were prepared with standard Schlenk techniques under an inert atmosphere of nitrogen with previously dried solvents. The complex $[RhCl(COD)]_2$[43] and 1,3-dialkyl-imidazolinylidene were prepared according to known methods.[44] IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrometer. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) were recorded on a Bruker AM 300 WB FT spectrometer with chemical shifts referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TÜBITAK Analyses Center. Differential thermal analysis (DTA) and thermogravimetric analysis. (TGA) were performed with Shimadzu DTA-50 and TGA-50 thermal analyzers respectively.

Amorphous mesoporous silicate synthesis

Tetraethyloxysilane (13.86 g) was dissolved in 8 g of ethanol and 8.26 g of ethylene glycol with stirring at 80 °C in an oil bath. After 1 h of stirring, a mixture of 24 g of ethanol, 6 g of water, and a catalytic amount of acetic acid was added to the system. After 3 h of reaction under the same conditions, a clear, transparent gel was obtained. The resulting gel was aged at ambient conditions for 2 days, dried in a vacuum oven at 110 °C, and calcined at 500 °C for 12 h in a flow of oxygen. BET surface area was measured to be $317 \pm 4\ m^2\ g^{-1}$, with pore volume of $0.37 \pm 0.02\ ml\ g^{-1}$.

Grafting of rhodium carbene complexes (1) on amorphous mesoporous silicate

In order to enhance the number of silanol (SiOH) groups that can be used to attach **1** to the surface, etching of particles (grain size 2–20 μm) with CH_3SO_3H was performed. Typically, 5 g of silica was stirred in 100 ml of CH_3SO_3H at room temperature overnight. The silica was recovered by ultracentrifuging (9000 rpm, 45 min), filtered, washed with water several times until the solution was neutral, and finally dried in a vacuum oven at 100 °C overnight.

Grafting was carried out under nitrogen atmosphere with different amounts of **1** and the silica particles. Each time, to the mixer loaded with 5 g of silica in 50 ml toluene and **1**, dimethylsulfoxide/water in 3 : 10 ratio was added drop-wise in order to avoid gel formation; the solutions were prepared just before the process. The resulting solutions were heated under reflux and stirred for 4 h. The modified particles were then poured off and extracted with methanol in a Soxhlet apparatus for 12 h. Finally, particles were dried under reduced pressure at 120 °C for 24 h.

Preparation of the rhodium carbene complex (1)

A solution of bis[1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidin-2-ylidine] (**L**; 0.5 mmol) and $[RhCl(COD)]_2$ (0.5 mmol) in toluene (15 ml) was heated under reflux for 2 h. Upon cooling to room temperature, yellow–orange crystals of **1** were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 ml) and dried under vacuum.

^1H NMR (δ, $CDCl_3$): 0.66 (t, $J = 7.6$ Hz, 2H, $SiCH_2CH_2CH_2-N$); 1.17 (t, $J = 7.0$ Hz, 9H, $SiOCH_2CH_3$); 1.59–1.64 (m, 2H, $SiCH_2CH_2CH_2N$); 2.97 (t, $J = 9.5$ Hz, 2H, $SiCH_2CH_2CH_2N$); 3.25 and 3.308 (m, 2H, NCH_2CH_2N); 3.79 (q, $J = 7.0$ Hz, 6H, $SiOCH_2CH_3$); 2.22 and 2.31 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.96 and 5.42 (d, $J = 13.8$ Hz, 4H, CH_{COD}); 1.84–1.94 (m, 8H,

CH_{2COD}); 6.79 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.42 (m, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6).

^{13}C NMR (δ, $CDCl_3$): 213.9 ($C_{carbene}$); 8.2 ($SiCH_2CH_2CH_2N$); 18.8 ($SiOCH_2CH_3$); 22.5 ($SiCH_2CH_2CH_2N$); 48.1 (NCH_2-CH_2N); 54.3 ($SiCH_2CH_2CH_2N$); 58.9 ($SiOCH_2CH_3$); 21.0 and 21.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 99.4 and 69.2 (d, $J = 6.49$ and 14.88 Hz, CH_{COD}); 29.5 (CH_{2COD}); 138.6; 137.9; 129.6; 129.5 and 129.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 48.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6).

General procedure for rhodium-carbene-catalyzed addition of phenylboronic acid to aldehydes

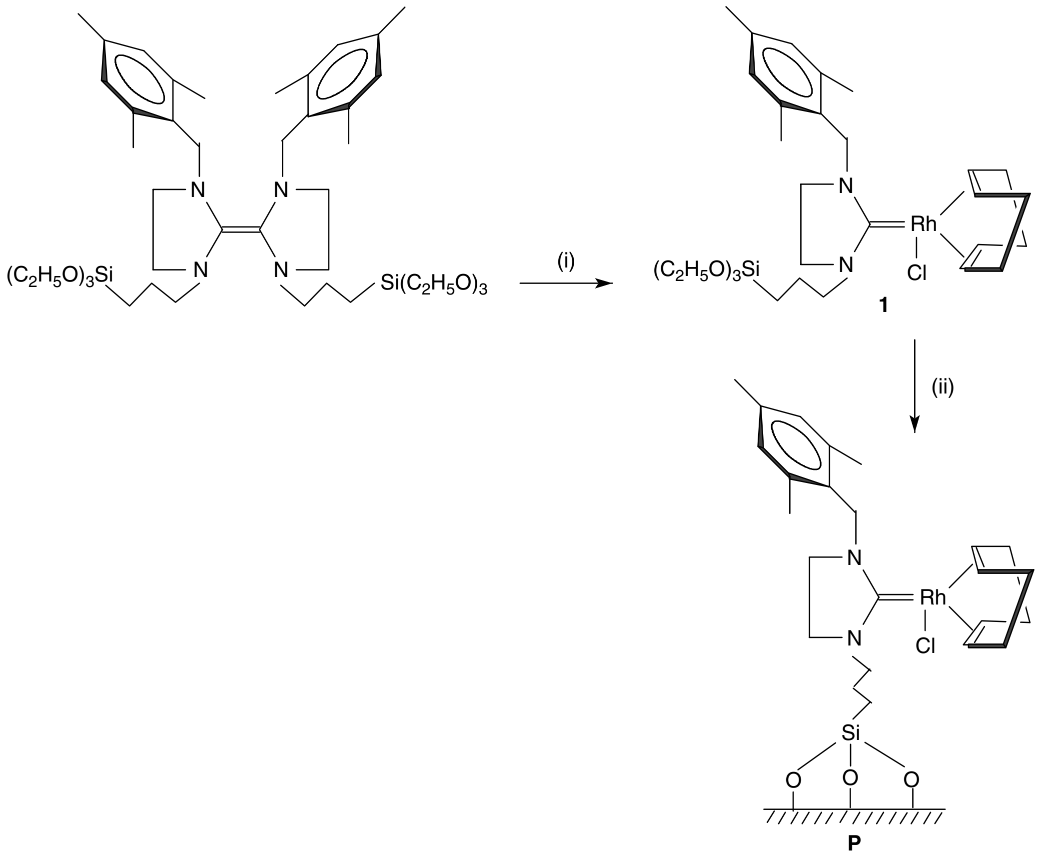
Phenylboronic acid (1.20 g, 9.8 mmol), KO^{t}Bu (4.9 mmol), substituted aldehydes (4.9 mmol), rhodium carbene catalyst (1 mol%), and dimethoxyethane (15 ml) were introduced to a Schlenk tube and then water (5 ml) was added. The resulting mixture was heated for 0.5–2.0 h at 80 °C, cooled to ambient temperature, and extracted with ethyl acetate (30 ml). After drying over $MgSO_4$, the organic phase was evaporated and the residue was purified by flash chromatography. Isolated yield (purity of yield and yields based on aldehydes) was checked by NMR; all reactions were monitored by thin-layer chromatography (TLC).

RESULTS AND DISCUSSION

The tetraaminoethene **L** was synthesized using a method similar to that reported by Çetinkaya *et al.*[44] The reaction of tetraaminoethene **L** with the binuclear $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) complex proceeded smoothly in refluxing toluene to give the RhCl(COD)[1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidine-2-ylidine] complex (**1**) as a crystalline solid in 89% yield (Scheme 1).

Complex **1**, which is very stable in the solid state, has been characterized by analytical and spectroscopic techniques. Rhodium complexes exhibit a characteristic $\nu_{(NCN)}$ band typically at 1598 cm^{-1}.[27,28,45] The ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. δ ($^{13}C_{carb}$) is 214 ppm and is similar to those found for other carbene complexes. The coupling constant $J(^{103}Rh-^{13}C)$ for the rhodium complex **1** is 47.5 Hz. This new complex shows typical spectroscopic signatures that are in line with those recently reported for other RhCl(COD)(1,3-dialkyl-imidazolinylidene) complexes.[26,28,45]

The silica-supported material (**P**) derived from the reaction of tetraaminoethene **L** with the binuclear $[RhCl(COD)]_2$



Scheme 1. Synthesis of the [1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidin-2-ylidine]Rh(I) complex: (i) $[RhCl(COD)]_2$ (0.5 mmol) in toluene (15 ml); (ii) DMSO, water, 150 min at reflux temperature.

complex to give the RhCl(COD)[1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidine-2-ylidine] (**1**) was characterized by thermal analysis carried out in nitrogen at a heating rate of 10 °C min^{-1}. DTA and TGA were used to evaluate the thermal properties of the material. DTA and TGA curves of the complex and silica-modified complex **1** are shown in Figs 1 and 2 respectively. For the complex, the mass loss between 116 and 473 °C is attributed to the

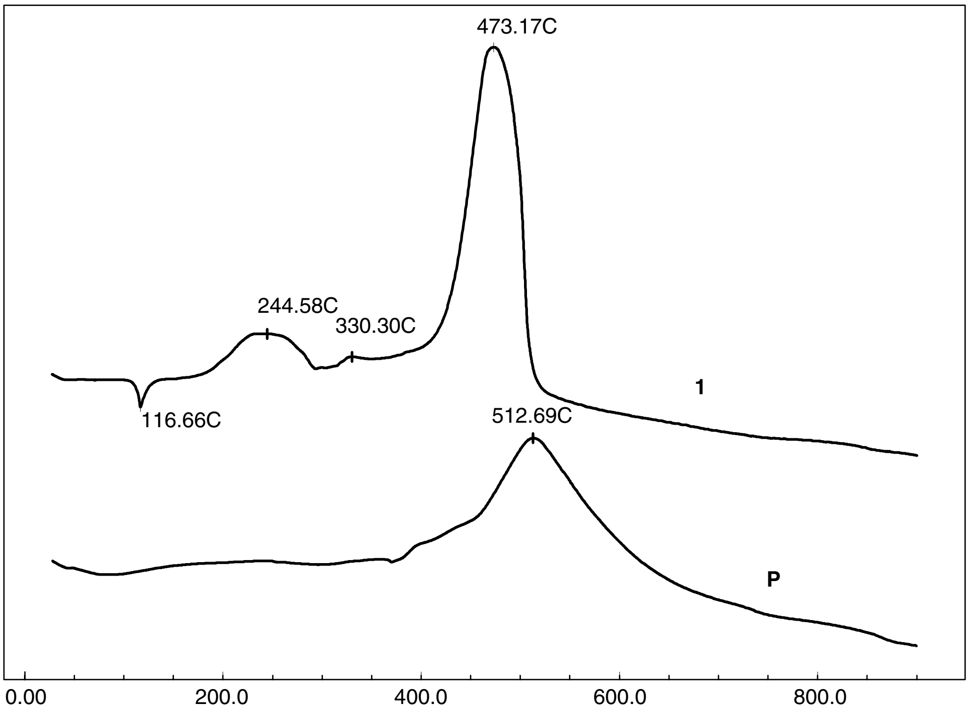


Figure 1. DTA pattern of complex **1** and the silica-supported material **P**.

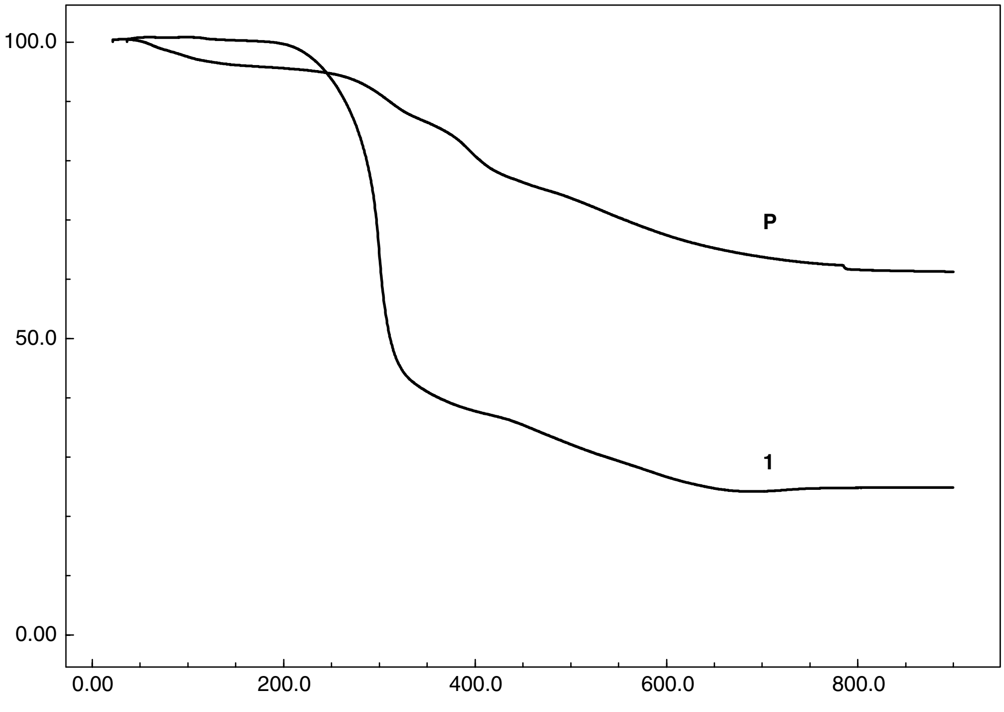
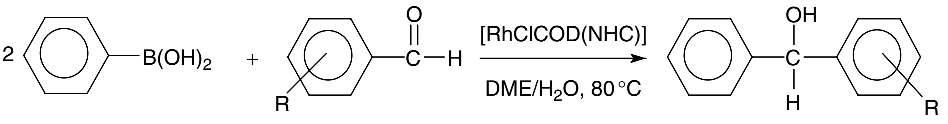


Figure 2. TGA profile of complex **1** and the silica-supported material **P**.



Scheme 2.

thermal degradation of the organic groups. This evidence was supported by the TGA spectra of the complex, where the main mass loss took place at 470 °C. For the silica-modified complex, the total mass loss between 250 and 670 °C was 15.45%. This is due to the complex grafted on the silica. By subtracting 2.86% (pure silica mass loss, 250–670 °C) from 15.45% (silica-modified complex **1** mass loss, 250–670 °C), the weight loss caused exclusively by grafting should be 12.59%, since many of the SiOH groups were used in the coupling process and do not lose water in the SiOH condensation step.

The catalytic activity of the complex and the silica-supported materials were tested for the addition of phenylboronic acid to aldehydes (Scheme 2).

Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered that functionalized organometallic reagents required. Rhodium complexes **1** and **P** were found to be active catalysts for the addition of phenylboronic acid to aldehydes and proved to be thermally robust at high temperature. The addition of phenylboronic acid to aldehydes proceeds in high yields and quite rapidly, even with a low catalyst loading. The results are summarized in Table 1. Under these conditions, 4-methoxybenzaldehyde, 2,4,6-trimethylbenzaldehyde, 3,4,5-trimethoxybenzaldehyde and 4-chlorobenzaldehyde react very cleanly with phenylboronic acid in goods yields (Table 1, entries 1, 4, 6 and 9).

Table 1. Rhodium-carbene-catalyzed addition of phenylboronic acid to aldehydes

Entry	Catalyst	R	Time (h)	Yield (%)^a
1	**1**	OCH_3	0.5	98
2	**1**	2,4,6-$(CH_3)_3$	0.5	89
3	**1**	3,4,5-$(OCH_3)_3$	0.5	90
4	**1**	2,4,6-$(OCH_3)_3$	0.5	93
5	**1**	Cl	0.5	91
6	**P**	OCH_3	2	89^b
7	**P**	2,4,6-$(CH_3)_3$	2	79^b
8	**P**	3,4,5-$(OCH_3)_3$	2	81^b
9	**P**	2,4,6-$(OCH_3)_3$	2	82^b
10	**P**	Cl	2	79^b

[a] Isolated yield (purity of yield checked by NMR); yields based on aldehydes; all reactions were monitored by TLC.
[b] Fourth run.

CONCLUSIONS

Silica-supported functional material with RhCl(COD)[1-(triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidine-2-ylidine] complex was prepared and the relevant catalytic properties in the addition of phenylboronic acid to aldehydes were tested. Introducing a complex with catalytic properties onto the silica surface improved the catalyst usability without the loss of efficiency.

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