Immobilization of a Boron Center-Functionalized Scorpionate Ligand on Mesoporous Silica Supports for Heterogeneous Tp-Based Catalysts

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Supporting Information

ABSTRACT: To develop novel immobilized metallocomplex catalysts, allyltris(3-trifluoromethylpyrazol-1-yl)borate (allyl-TpCF₃) was synthesized. A boron-attached allyl group reacts with thiol to afford the desired mesoporous silica-immobilized TpCF₃. Cobalt(II) is an efficient probe for estimating the structures of the immobilized metallocomplexes. The structures of the formed cobalt(II) complexes and their catalytic activity depended on the density of the organic thiol groups and on the state of the remaining sulfur donors on the supports.

1. INTRODUCTION

Hydrotris(pyrrozolyl)borates (TpK) and related multidentate "scorpionate" ligands have been utilized extensively in coordination chemistry, with applications in areas such as organometallic and biomimetic catalysis. An attractive characteristic of TpK is the feasibility for molecular designing by incorporation of the appropriate substituent groups on the pyrazolyl rings. Both electronic and structural properties of the substituent groups on the R₁−R₃ positions of the pyrazolyl rings influence the reactivity at the metal center of the resulting complex. Recently, interest in the modification of the boron center of TpK has increased. Replacement of a boron-attached hydride to a suitable functional group might yield a corresponding boron center-functionalized ligand (FG-TpK) that is applicable to various conjugate materials, with retention of the facially capping tridentate metal-supporting scaffolds.

Immobilization of FG-TpK on organic polymer-based supports has been achieved. Notably, the molecular structures of TpK−metal complexes correlate with the flexibility of the base polymer. On the flexible polymer support, metalation of the immobilized TpK yields a coordinatively saturated [M−(TpK)₃] species because the flexible polymer backbone results in two approaching TpK moieties. Although the formed [M(TpK)₃]ₙ sites function as cross-linking points of the polymers, these sites appear to be catalytically inert. By contrast, TpK can be immobilized while retaining a high dispersion state on the rigid supports. In fact, the Tp ligand immobilized on the less flexible, highly cross-linked polystyrene resin support yields the desired coordinatively unsaturated [M(TpK)(L)ₙ] species, some of which exhibit catalytic activity. Even in the successful resin-supported compounds, the correlation between the structure of the formed metal−TpK complexes and the local environments of the immobilized TpK ligands (which are affected by the morphology of the support, density of TpK, interaction of metals with functional groups other than immobilized ligands, etc.) has never been examined.

A few TpK-based heterogenized metallocomplex catalysts in which the boron centers of TpK are not functionalized (i.e., in which a hydride group remains) and silica and resin beads are used as supports have been reported thus far. Also, iron complexes of tris(pyrrozolyl)methane, which is a carbon-centered Tp analogue, have been immobilized on zeolite and carbon materials with similar manner, and catalytic activities of the immobilized complexes are higher than those of the corresponding homogeneous parent. By contrast, immobilization of FG-TpK on rigid inorganic supports has not been reported so far. Controlling the three-dimensional environments surrounding the immobilized FG-TpK and its metallocomplexes can be achieved using these inorganic supports with an ordered structure. In this context, we have been developing ordered mesoporous, silica-immobilized metallocomplex catalysts based on FG-TpK, as reported herein.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Allyl-TpCF₃ and Its Complexes of Cobalt(II). Our imidazole-based scorpionate analogue, allylbis(imidazolyl)methylborate (Lᵣᵤₛₕ), can be immobilized onto thiol-functionalized inorganic supports using thiol−ene coupling. A similar ligand immobilization method has also been used with the N₅N₅O-type carbon-based scorpionate compound. Therefore, we have designed an allyl-functionalized tris(3-trifluoromethylpyrazol-1-yl)borate (allyl-TpCF₃) as a metal-supporting ligand for a biomimetic
oxidation catalyst because fluoroalkyl groups resist oxidation. Thus far, a nonsubstituted pyrazole-based ligand, allyl-Tp\(^{PF_3}\), has been synthesized by Camerano et al. Our target ligand, allyl-Tp\(^{PF_3}\), can be synthesized in a similar manner: condensation of allyl(alkoxy)borane with two equiv of 3-trifluoromethylpyrazole (pz\(^{PF_3}\)) and nucleophilic addition of a potassium salt of pz\(^{PF_3}\).

Before immobilization of the synthesized allyl-Tp\(^{PF_3}\) onto inorganic supports, we examined coordination properties of the ligand toward cobalt(II) and characterized the resulting complexes. We selected cobalt(II) because of its usefulness as a structural probe stemming from the rich chemistry associated with the correlation between coordination geometries of cobalt(II) centers and their UV–vis spectral patterns. Reaction of the potassium salt of allyl-Tp\(^{PF_3}\) and CoBr\(_2\cdot6\)H\(_2\)O in tetrahydrofuran (THF) yielded a blue solution. From this solution, blue crystalline solids of a bromide complex, [CoBr(allyl-Tp\(^{PF_3}\))] (1), were obtained as the major product. In addition, a small amount of a pale-pink compound, the homoleptic complex [Co(allyl-Tp\(^{PF_3}\))]\(_2\) (2), was also obtained. The molecular structures of 1 and 2 were determined using X-ray crystallography (Figure 1). The geometries of the cobalt(II) centers of 1 and 2 were pseudotetrahedral and octahedral, respectively. In both 1 and 2, the allyl-Tp\(^{PF_3}\) coordinated to the cobalt(II) centers in a facially capping tridentate mode through three pyrazolyl nitrogen donors. No flipping from 3-CF\(_3\)-pyrazolyl to 5-CF\(_3\)-pyrazolyl occurred. The allyl groups in 1 and 2 did not coordinate to the cobalt centers, although coordination of a boron-attached allyl group in a hybrid scorpionate ligand, [(allyl)B(pz\(^{PF_3}\))\(_2\)(CH\(_2\)PPh\(_2\))]\(^+\), to an iridium(I) center has been reported by Camerano et al. Compounds 1 and 2 retained their molecular structures when dissolved in appropriate solvents, as indicated by the similarity of the spectral features of visible-light absorption by the solutions (1 in CH\(_2\)Cl\(_2\) and 2 in THF) and the solids. Reaction of allyl-Tp\(^{PF_3}\) with Co(OAc)\(_2\)·4H\(_2\)O yielded a violet-colored compound 3, which exhibited a \(\lambda_{max}\) of approximately 580 nm in both solid and solution states. Although attempts to obtain single crystals suitable for X-ray analysis were not successful, compound 3 is tentatively assigned as a \(\kappa^2\)-acetate complex with a penta-coordinated cobalt(II) center.

2.2. Synthesis and Characterization of Immobilized Cobalt Complex Catalysts. Allyl-Tp\(^{PF_3}\) was anchored onto organothiol-functionalized silica using a thiol–ene coupling reaction. As we reported previously, the structural properties of the support, such as the support surface morphology and the loading density of the organic linker group, are the dominant factors controlling the structure and performance of the resulting metallocomplex active sites of the immobilized catalysts. Therefore, in this study, SBA-15-type mesoporous SiO\(_2\) with controlled thiol group (SBA-SH) loadings was used as the support. This support was prepared through one-pot condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of a polymer micelle template. The condensation ratios of TEOS and MPTMS were controlled as TEOS:MPTMS = (100 - \(x\)):\(x\), where \(x\) = 0.5 or 1.0. The resultant thiol-functionalized SBA-15-type supports (SBA-SH(\(x\))), which were obtained by removing the template using Soxhlet extraction, had a desired mesoporous structure, as confirmed by XRD analysis and \(N_2\) isotherm absorption/desorption behavior. Remaining Si–OH groups on the surface of the mesopore walls were end-capped by treatment with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) at 323 K. The end-capping of the Si–OH groups led to a decrease in the acidity and an increase in the hydrophobicity of the silica support; these characteristics should avoid degradation of the Tp\(^{PF_3}\) moiety through hydrolysis of the B–N linkages. The loading amount of the thiol groups was consistent with the value of \(x\) estimated by \(^1\)H NMR analysis of the alkyl groups. The densities of the loaded thiol on SBA-SH(\(x\)) were approximately 0.06 molecules/nm\(^2\) for \(x\) = 0.5 and 0.12 molecules/nm\(^2\) for \(x\) = 1.0.

The coupling reaction of SBA-SH(\(x\)) with a CHCl\(_3\) solution of allyl-Tp\(^{PF_3}\), which gave SBA-SH-\(T\)\(_p\)\(^{PF_3}\)(\(x\)), was initiated by adding a small amount of AIBN under heating. The immobilized amount of Tp\(^{PF_3}\) for SBA-SH-\(T\)\(_p\)\(^{PF_3}\)(\(0.5\)) was approximately the same as the loadings of thiol groups. For SBA-SH-\(T\)\(_p\)\(^{PF_3}\)(1.0), some of the loaded thiol groups were not connected with Tp\(^{PF_3}\). Further reaction of the remaining thiol groups for SBA-SH-\(T\)\(_p\)\(^{PF_3}\)(1.0) with additional allyl-Tp\(^{PF_3}\) did not occur. The steric bulkiness of allyl-Tp\(^{PF_3}\) resulted in a saturation of the ligand loadings. Therefore, to prevent the formation of thiolato complexes, the remaining thiol groups were transformed to thioacetate ester by the reaction with acetyl chloride and the resultant supports were named as SBA-SH-\(T\)\(_p\)\(^{Ac}\) (\(x\)).

The coupling reaction of Tp\(^{PF_3}\)-anchored supports with an MeCN solution of CoBr\(_2\)·6H\(_2\)O yielded the corresponding immobilized cobalt complex catalysts Co/SBA-SH-\(T\)\(_p\)\(^{PF_3}\)(\(x\)) (4; \(x\) = 0.5 and 5; \(x\) = 1.0) and Co/SBA-SH-\(T\)\(_p\)\(^{PF_3}\)(\(x\)) (4'; \(x\) = 0.5 and 5'; \(x\) = 1.0) (Scheme 1). Loading amounts of the cobalt ion on the catalysts varied depending on the initial SH loadings and on the state of the non-Tp-anchored sulfur groups as SH or SAC (see Table S2). Coordination environments of the cobalt(II) center of the immobilized complexes were explored using diffuse reflectance UV–vis spectrophotometry; the results are shown in Figure 2. Comparison of the spectral patterns of the immobilized complexes and those of 1–3 in the solid state revealed the
For the lower thiol loading supports (where \( x = 0.5 \)), a tetrahedral cobalt(II) species was mainly formed, as suggested by the similarity between the spectral patterns of 1 and those of the catalysts 4 and 4’. Although the loading amounts of cobalt and the states of the remaining sulfur groups on 4 and 4’ were somewhat different, the similar spectral patterns of 4 and 4’ indicated that the dispersive immobilization of Tp\(^{CF_3}\) resulted in the formation of the tetrahedral cobalt species.

The spectral patterns of the higher-thiol-loaded catalysts (\( x = 1.0 \)) clearly differed from that of the catalysts with \( x = 0.5 \) and that of tetrahedral complex 1. The spectrum of 5 (SBA\(^{SH-Tp}\) derivative) appears to contain both hexa- and pentacoordinated cobalt(II), similar to the mixture of 2 and 3. The cobalt loadings on 5 were higher than the amounts of the immobilized Tp\(^{CF_3}\) (see Table S2). Notably, only trace amounts of cobalt were immobilized onto the reaction of the non-Tp\(^{CF_3}\)-anchored support SBA\(^{SH}(1.0)\) and the MeCN solution of CoBr\(_2\)·6H\(_2\)O. Therefore, the co-existence of Tp\(^{CF_3}\) and the thiol groups would lead to the formation of some multinuclear cobalt complexes on the support. By contrast, the UV–vis spectrum of the SBA\(^{Sac-Tp}\) derivative 5’ suggested that the major species was the penta-coordinate species and that small amounts of hexa- and tetra-coordinate species also existed. From the densities of the loaded thiol groups, their average distances were estimated to be 2.9 nm for SBA\(^{SH}(1.0)\) and 4.1 nm for SBA\(^{SH}(0.5)\). In such situations, the immobilized Tp\(^{CF_3}\) appears to be isolated even on SBA\(^{SH}(1.0)\), and it might be difficult to access the other groups (SH, SAc, and Tp\(^{CF_3}\)) of the formed Tp\(^{CF_3}\)-Co moieties on the supports (SBA\(^{SH-Tp}\) and SBA\(^{Sac-Tp}\)). However, the location of the immobilized complexes was not a flat surface but a curved inner wall of the straight pore. As a result, the distances between the functional groups and the cobalt center of Tp\(^{CF_3}\)-Co were sufficiently small for them to coordinate and form the penta-coordinate complexes. Therefore, the structures of the immobilized complexes were affected by the structures of the supports, the density of the organic functional groups, and the state of the remaining sulfur donors.

We also examined Co(OAc)\(_2\)·4H\(_2\)O as the metal source instead of CoBr\(_2\)·6H\(_2\)O (Table S2 and Figure S6). In the reaction of the non-Tp\(^{CF_3}\)-immobilized support SBA\(^{SH}\) with an MeCN solution of Co(OAc)\(_2\)·4H\(_2\)O, some cobalt species were anchored on the support. By contrast, no cobalt species was anchored onto SBA\(^{SH}(0.5)\) when CoBr\(_2\)·6H\(_2\)O was used as a precursor. Additionally, the reaction of SBA\(^{Sac-Tp}\) with an
MeCN solution of Co(OAc)₂·4H₂O resulted in the immobilized cobalt ions were in excess of the amount of the anchored Tp³CF³. The spectral patterns of the cobalt species on each of the supports [i.e., SBA¹⁶SH(0.5), SBA¹⁶SH–Tp³CF³(0.5 and 1.0), and SBA¹⁶SAC–Tp³CF³(0.5 and 1.0)] shown in Figure S6] varied depending on the anion of the precursor. These different behaviors of the cobalt species when anchoring to the functionalized supports imply that the counterions of cobalt(II) dominate control of the structure of the immobilized cobalt compounds. The acetate anions tend to become bridging ligands that yield multinuclear cobalt species that interact with the Tp³CF³ and even with the SH groups on the supports.

2.3. Correlation between the Structure and Activity of Immobilized Cobalt Complex Catalysts. Substrate-oxidizing activities of the obtained immobilized cobalt complex catalysts were examined by using cyclohexene as a substrate.

First, we compared the activity of the catalysts prepared from CoBr₂·6H₂O to clarify the performance of the cobalt centers supported by the Tp³CF³ scaffold. When aqueous H₂O₂ was used as the oxidant, the immobilized catalysts exhibited catalase-like H₂O₂ degradation activity, with the formation of O₂ bubbles. On the contrary, when tert-BuOOH was used as the oxidant, catalytic allylic oxygenation of cyclohexene occurred. No leaching of the cobalt species was observed under these reaction conditions. The major product was dialkylperoxide in all reactions, which indicated the reactions proceeded through a Haber–Weiss mechanism. Similar reactivity toward cyclohexene oxidation with tert-BuOOH has been observed on a cobalt-based MOF catalyst.¹⁹ The turnover number (TON) order of the cobalt centers was 4′ > 5′ > 4 > 5 > 1 (homogeneous conditions). It is worth noting that the immobilized Tp³CF³Co complex catalysts exhibited higher activity compared with the homogeneous cobalt species derived from genuine cobalt(II) salts (CoBr₂·6H₂O and Co(OAc)₂·4H₂O; Table S3). The higher activities of the immobilized catalysts are attributed to the suppression of bimolecular reactions that lead to catalyst decomposition. The differences in the TONs of the immobilized catalysts indicate that the structures of the cobalt centers affect the catalytic efficiencies. The most active catalyst was 4′, which was composed of isolated Tp³CF³Co sites without free thiol groups. The remaining thiol groups suppress the catalytic activity, as clearly demonstrated by comparisons with the activities of 5 and 5′. The lowest activity of 5 suggests that the hexa-coordinated cobalt center is less reactive than the coordinatively unsaturated tetra- and penta-coordinated cobalt species formed on the other immobilized catalysts. Catalyst 5′, the second-most active catalyst, exhibited better selectivity toward epoxidation than that observed for 4′ (Figure 3).

The activities of the immobilized cobalt complex catalysts derived from Co(OAc)₂·4H₂O were also examined (Table S3). The non-Tp³CF³-coordinated cobalt species formed on SBA¹⁶SH also exhibited better activity and epoxidation selectivity. In the catalysts derived from Co(OAc)₂·4H₂O, the supports of the most active and the second-most active catalysts were SBA¹⁶SAC–Tp³CF³(0.5) and SBA¹⁶SH–Tp³CF³(1.0), respectively. Trends of the product selectivity of these catalysts were similar to those observed for 4′ and 5′ (derived from CoBr₂·6H₂O). The catalysts supported on the highly dispersed Tp³CF³ (i.e., x = 0.5) exhibited a strong radical character that is sufficient to induce the oxygenation of the allylic position. For the catalysts formed on the support with higher loadings of Tp³CF³ and thiol (i.e., x = 1.0), a small increase in epoxide selectivity was observed.

Therefore, the local structure of the functionalized supports might be a controlling factor for the structures and activities of the metal centers. In the case of the cobalt-acetate-based catalysts, however, the nature of acetate makes selective formation of the isolated cobalt centers supported by Tp³CF³ difficult.

3. CONCLUSIONS

The boron-functionalized scorpionate ligand was successfully immobilized onto mesoporous silica through covalent bonds. The structures of the formed cobalt(II) complexes and their catalytic activities depended on the density of the organic thiol groups and on the state of the remaining sulfur donors on the inner wall of the mesopores. Additionally, the nature of the anions of the metal sources was a dominant factor affecting the structures of the immobilized metallocomplexes. As demonstrated herein, cobalt(II) is an efficient probe for estimating the structures of the immobilized species.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All solvents used for the synthesis of the ligand and catalytic reaction (THF, toluene, CH₃Cl₂, and MeCN) were purified over a Glass Contour Solvent Dispersing System under an Ar atmosphere. Other reagents of the highest grade that were commercially available were used without further purification. Atomic absorption analysis was performed on a Shimadzu AA-6200. Elemental analysis was performed on a Perkin-Elmer CHNS/O Analyzer 2400II. GC analysis was performed on a Shimadzu GC2010 gas chromatograph with an Rtx-5 column (Restek, length = 30 m, i.d. = 0.25 mm, and thickness = 0.25 μm). IR spectra were recorded on a JASCO FTIR 4200 spectrometer. NMR spectra were recorded on a JEOL ECA-600 spectrometer. UV–vis spectra of solution samples were recorded on a JASCO V650 spectrometer, and solid reflectance spectra were recorded on the same instrument with a PIN-757 integrating sphere attachment for solid. Nitrogen sorption studies were performed at liquid nitrogen temperature (77 K) using Micromeritics TriStar 3000. Before the adsorption experiments, the samples were outgassed under reduced pressure for 3 h at 333 K.
4.2. Synthesis of Potassium Salt of Allyltris(3-triluoromethylpyrazol-1-yl)borate ([K(allyl-TpCF₃)]). Potassium salt of 3-triluoromethylpyrazole (pzCF₃K) was obtained by the condensation reaction of KOH (0.33 g, 5.0 mmol) with pzCF₃H (0.68 g, 5.0 mmol) in dry methanol (30 mL) at ambient temperature for 1 h and the volatiles were removed by evaporation. The obtained white solids of pzCF₃K, pzCF₃H (2.66 g, 19.0 mmol), and allyldiisopropoxyborane ([B(allyl)(OiPr)₂]; 1.0 mL, 4.89 mmol) were suspended in pentane and washed with pentane. An analytically pure product was obtained by re-crystallization with ZnCl₂ as a catalyst.

4.3. Reaction of [K(allyl-TpCF₃)] and CoBr₂·6H₂O (Formation of [CoBr(allyl-TpCF₃)] (1) and [Co(allyl-TpCF₃)] (2)). A THF (100 mL) solution of [K(allyl-TpCF₃)] (1.00 g, 2.02 mmol) was added slowly to CoBr₂·6H₂O (0.529 g, 2.42 mmol) dissolved in THF (90 mL) at ambient temperature. After stirring for 1 h, volatiles were removed under reduced pressure. The resultant solids were suspended in pentane and then decanted. The resultant solids were dissolved in CH₂Cl₂ and insoluble materials were removed by filtration through a Celite plug. From the filtrate, the volatiles were removed under reduced pressure, and the resultant solids were dissolved in a mixture of CH₂Cl₂ and n-hexane. Refrigration of this solution at 243 K afforded a small amount of pale yellow crystalline solids of 243 K, yielding a blue powder of the desired bromide complex 1 (220 mg, 0.369 mmol, 18% yield). 1H NMR (CDCl₃, rt): δ (ppm) = 4.70 (s, 6H, pz-H). IR (KBr): νC=H = 3161 cm⁻¹; νC≡N = 1605 cm⁻¹; νC=C = 1258 cm⁻¹. UV−vis (CH₂Cl₂, rt): λ (nm (M⁻¹ cm⁻¹)) = 561 (56).

4.4. Reaction of [K(allyl-TpCF₃)] and Co(OAc)₂·4H₂O (Formation of [Co(allyl-TpCF₃)] (3)). A THF (90 mL) solution of [K(allyl-TpCF₃)] (0.870 g, 1.75 mmol) was added slowly to Co(OAc)₂·4H₂O (0.371 g, 2.10 mmol) at ambient temperature. After stirring for 1 h, volatiles were removed under reduced pressure. The resultant solids were suspended in pentane and then decanted. The resultant solids were dissolved in CH₂Cl₂ and insoluble materials were removed by filtration through a Celite plug. From the filtrate, the volatiles were removed under reduced pressure, and purple species were obtained from the resultant solids by extraction with MeCN. From this solution, MeCN was removed by evaporation, and the resultant solids were dissolved in a mixture of CH₂Cl₂ and n-hexane. Refrigration of this solution at 243 K yielded reddish purple solids of 3. IR (KBr): νC=H = 3161 cm⁻¹; νC≡N = 1605 cm⁻¹; νC=C = 1258 cm⁻¹. UV−vis (CH₂Cl₂, rt): λ (nm (M⁻¹ cm⁻¹)) = 561 (56).

4.5. Preparation of SBA⁵₆-x. Thiol-functionalized mesoporous silica supports (=SBA⁵₆-x) were prepared by a similar manner for the previously reported organoizide-functionalized SBA-15 by Nakazawa and Stack. Condensation ratio of mercaptopropyltrimethoxysilane (=MPTMS; x mol % of Si) and tetrachlorosilane (=TEOS; (100 − x) mol % of Si) were defined as x = 0.5 or 1. In a flask, 8.0 g of the surfactant Pluronic P123 [triblock copolymer EO₃₀PO₇₀EO₃₀] where EO = poly(ethylene glycol) and PO = poly(propylene glycol)] was placed and then dissolved in 260 mL of water with 40 mL of conc. HCl solution (35 wt %) by stirring at 313 K for 4 h. To the resultant solution, 18.4 mL (81.3 mmol) of TEOS and appropriate amounts of MPTMS (76.0 µL when x = 0.5 or 155 µL when x = 1.0) were added. The mixture was stirred at 323 K for 24 h and subsequently heated at 363 K for 24 h. Once cooled, the solid product was filtered and washed with deionized H₂O and EtOH. The P123 surfactant was removed using Soxhlet extraction with a mixture of 200 mL of H₂O and 200 mL of EtOH over 24 h. The resultant white solid was dried under vacuum. Then the remaining silanol groups on the as-prepared thiol-functionalized SBA-15 were end-capped by the trimethylsilyl group. A suspension of the dried solid of the precursor of SBA⁵₆-x (5.4 g) and 1,1,1,3,3,3-hexamethyldisilazane (=HMDS; 10 mL) in toluene (100 mL) was stirred at 323 K for 1 h. The resultant solid was collected by filtration then washed with toluene and CH₂Cl₂. Dryness under evacuation yielded 5.3 g of end-capped support, namely, SBA⁵₆-x. Loading amounts of the thiol groups were determined using ¹H NMR spectrometry as follows: 10 mg of SBA⁵₆-x (x) was dissolved in 2 mL of D₂O solution containing a small amount of NaOH under heating. To this solution, 10 mg (0.072 mmol) of p-nitrophenol was added as an internal standard. The loading amounts of the thiol groups were estimated by a comparison of the integration values of ¹H NMR signals of ethylene and phenyl groups.

4.6. Preparation of SBA⁵₆-x·Tp⁻ (x). To a suspension of SBA⁵₆-x (2.0 g) in CHCl₃ (30 mL), [K(allyl-TpCF₃)] (180 mg, 0.38 mmol) and AIBN (10 mg) were added. The resultant mixture was refluxed for 6 h. The white solid of SBA⁵₆-x·Tp⁻ was obtained by filtration. The resultant solid was washed with CHCl₃ and then dried under evacuation. The loading amounts of Tp⁻ were estimated from the contents of nitrogen (wt % of N) using CHN elemental analysis (data are shown in Table S2).

4.7. Preparation of SBA⁵₆-x·Ac⁻·Tp⁻ (x). In 30 mL of toluene, an appropriate amount of SBA⁵₆-x·Tp⁻ (x) was suspended. To this suspension, acetyl chloride (2.0 equiv with respect to the loading amounts of thiol) and DBU (2.5 equiv) were added, and the resultant mixture was refluxed for 6 h. The white filtrates of SBA⁵₆-x·Ac⁻·Tp⁻ (x) were washed with toluene and then dried under evacuation.

4.8. Preparation of Catalysts. In 20 mL of CH₂Cl₂, 0.20 g of the support [SBA⁵₆-x·Tp⁻ (x)] or SBA⁵₆-x·Ac⁻·Tp⁻ (x)] was suspended. To this suspension, an acetonitrile (10 mL) solution of CoBr₂·6H₂O (13 mg, 0.039 mmol) was added, and the resultant mixture was stirred at room temperature for 2 h. Filtration, washing with MeCN and methanol, and then drying under evacuation yielded a pale blue solid of the catalysts Co/SBA⁵₆-x·Tp⁻ (x) (4 x = 0.5) and 5 (x = 1.0) or Co/SBA⁵₆-x·Ac⁻·Tp⁻ (x) (4' x = 0.5 and 5' (x = 1.0)). Loading amounts of cobalt on the catalysts were determined as follows. The catalyst (10 mg) was dissolved into 1 mL of aqueous solution of KOH (0.04 g/mL) under heating. Then, the solution was acidified with 20 mL of conc. aq. HNO₃ and diluted with H₂O to 50 mL volume.
The solution was passed through syringe filter before being introduced into an atomic absorption spectrometer.

### 4.9. Catalytic Reactions

Typical procedure for the heterogeneous reaction is as follows: In Schlenk flask, an appropriate amount of the catalyst (1 μmol cobalt on the immobilized catalyst) was suspended in 5 mL of MeCN. Cyclohexene (0.25 mL, 2.5 mmol), nitrobenzene (10 μL, 0.10 mmol; as internal standard), and 70 wt % aqueous tert-BuOOH (2.5 mmol) were added to this suspension. All reactions were carried under Ar, and the products were analyzed using GC with an internal standard.

#### ASSOCIATED CONTENT

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00022.

Characterizations of the SBA supports and the catalysts, comparison of the catalytic activities, spectroscopic data of \([K(\text{allyl-Tp}^{Cl})]_2\), UV–vis spectra of the solutions of 1−3, diffuse reflectance UV–vis spectra of the immobilized cobalt species derived from CoBr₂·6H₂O and Co(OAc)₂·4H₂O, and crystallographic files in CIF format for 1 and 2 (PDF)

Crystallographic data of cobalt(II) complexes (CIF)

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**Notes**
The authors declare no competing financial interest.

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