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Sheltering Mono-P-Ligated Metal Complexes in Porous Polystyrene Monolith: Effect of Aryl Pendant Stabilizers on Catalytic Durability

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Abstract: Metal centers that can generate coordinatively unsaturated metals in accessible and stable states have been developed using synthetic polymers with sophisticated ligand and scaffold designs, which required synthetic efforts. Herein, we report a simple and direct strategy for producing polymer-supported phosphine-metal complexes, which stabilizes mono-P-ligated metals by modulating the electronic properties of the aryl pendant groups in the polymer platform. A three-fold vinylated PPh3 was copolymerized with a styrene derivative and a cross-linker to produce a porous polystyrene-phosphine hybrid monolith. Based on the Hammett substituent constants, the electronic properties of styrene derivatives were modulated and incorporated into the polystyrene backbone to stabilize the mono-P-ligated Pd complex via Pd-arene interactions. Through NMR, TEM, and comparative catalytic studies, the polystyrene-phosphine hybrid, which induces selective mono-P-ligation and moderate Pd-arene interactions, demonstrated high catalytic durability for the cross-coupling of chloroarenes under continuous-flow conditions.

Introduction

Coordinatively unsaturated metal complexes play a central role in various molecular conversions via organometallic[1] and biocatalytic transformations.[2] Polymer-supported catalysts have been developed as efficient, durable, and easily recoverable transition metal catalysts, taking advantage of their high chemical stability and flexibility in functionalizing the polymer backbone.[3] Catalytically active sites that can generate coordinatively unsaturated metal centers have been supported on linear polymers,[4] hyper-cross-linked polymers,[5] porous coordination polymers,[6] and porous organic polymers[7] for efficient organic syntheses. The above-mentioned studies include the design of ligands and scaffolds for suppressing multi-ligation and/or self-aggregation pathways by site isolation strategies,[8] despite considerable synthetic efforts.

Noncovalent interactions between aromatic π-systems and arenes, cations, and anions have been extensively studied, emphasizing their importance in molecular recognition and conformational regulation in chemistry and biology.[9] For durable polymer-supported metal nanoparticles, Kobayashi et al. developed a series of polymer-incarcerated (PI) metal catalysts for organic transformations, in which the metal nanoclusters were stabilized via interactions between the π-systems of phenyl pendants on the polymer and metal nanoclusters.[10,11] The screening of electron-donating/withdrawing substituents on aromatic rings facilitates the modulation of the strength of noncovalent interactions, which can be described in terms of Hammett substituent constants.[12] The applications of this concept for the stabilization of polymer-supported metals are limited.[13] Michaelis et al. developed polystyrene-supported bimetallic nanoparticles, in which the electronic properties of the aryl pendant groups on polystyrene were optimized for high reactivity and selectivity in nitroarene reductions,[13b] although the quantitative analysis of such metal-arene interactions based on the Hammett substituent constants was omitted. These pioneering studies on metal nanoparticle catalysts motivated us to seek a polymer support for high catalytic durability of coordinatively unsaturated metal complexes via noncovalent interactions between the aryl pendant of the polymer and the metal, which has been overlooked in the design of polymer-supported organometallic complexes.

Recently, Sawamura et al. developed a series of multifold cross-linked phosphines with a polystyrene backbone via simple radical copolymerization. Because of the site isolation of the phosphine unit in the polymer platform, the polystyrene-phosphine hybrids efficiently formulated mono coordination toward transition metals and exhibited high activities in challenging cross-couplings and C-H activations.[14] However, polystyrene-supported phosphine-metal complexes could get deactivated due to the aggregation and/or leaching of metals. Herein, we present the design of polymer-supported metal complexes based on the modulation of the interactions between polystyrene pendants and metal catalysts for high catalytic durability. Styrene derivatives with different aromatic ring electronic properties were screened as stabilizers for phosphine-metal complexes and copolymerized with three-fold vinylated PPh3 and a cross-linker to afford a porous polystyrene-phosphine hybrid monolith (M-PS-TPP) (Figure 1). M-PS-TPPs with various pendant functionalities were applied to Pd-catalyzed continuous-flow reactions. Based on NMR analyses and comparative catalytic studies, the ligand performance of M-PS-TPPs for challenging C-Cl transformations via Suzuki–Miyaura cross-coupling reactions was evaluated. A proof-of-concept was demonstrated using M-PS-TPP, which allowed selective mono-P-ligation toward the metal and interactions between the aryl pendant stabilizer and the metal, which affect the catalytic durability.

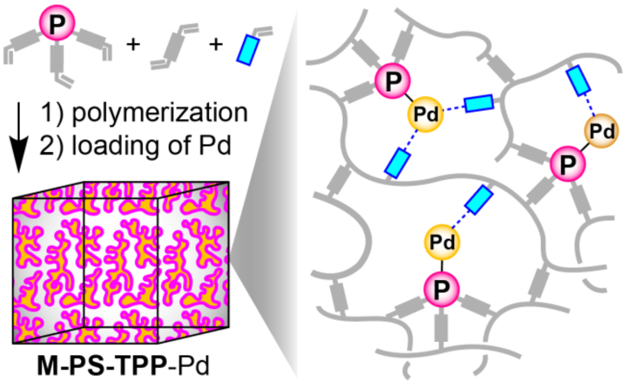


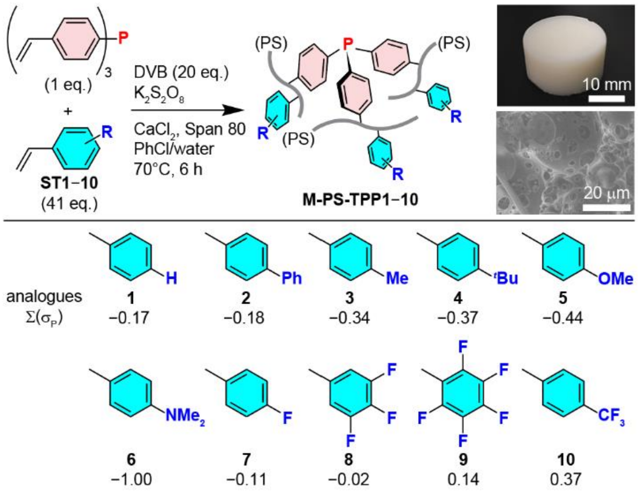
Figure 1. Schematic of mono-P-ligated Pd complex stabilized via aryl pendant stabilizers in porous polystyrene-phosphine hybrid monolith (M-PS-TPP). Blue rectangles and gray lines represent aryl pendant stabilizers and polystyrene chains.

Results and Discussion

We began our investigations by screening styrene monomers (ST1–10) with a wide range of electronic properties of aromatic rings: a parent styrene (ST1: R = H) and its derivatives containing neutral (ST2: R = 4-Ph), electron-donating (ST3–6: R = 4-Me, 4-tBu, 4-OMe, 4-NMe2), and electron-withdrawing substituents (ST7–10:4-F, 3,4,5-triF, 2,3,4,5,6-pentaF, 4-CF3) on the aromatic rings. Substituted toluene derivatives (1–10) were envisaged as analogues of the aryl pendant stabilizers derived from ST1–10 after the polymerization of M-PS-TPP1–10, and the sums of para-Hammett substituent constants ($\Sigma(\sigma\pi)$) for 1–10 were calculated (Scheme 1).[12,15] All M-PS-TPPs were prepared by radical copolymerization in the presence of a high internal phase emulsion (HIPE), as previously reported.[16] The HIPE was successfully obtained using a monomer mixture containing tris(4-vinylphenyl)phosphane (1 equiv.),[14a] divinylbenzene (DVB, 20 eq.), and ST1–10 (41 equiv.), and incubated at 50–70°C for 6 h to produce a self-standing material (M-PS-TPP1–10) with high yield (92−98%) (Supporting Scheme S1,S2, and Supporting Table S1). The FE-SEM observations of the dried M-PS-TPPs revealed their characteristic window and void structures (Supporting Figure S1), which were reflected in the pore size distributions determined by Hg intrusion porosimetry

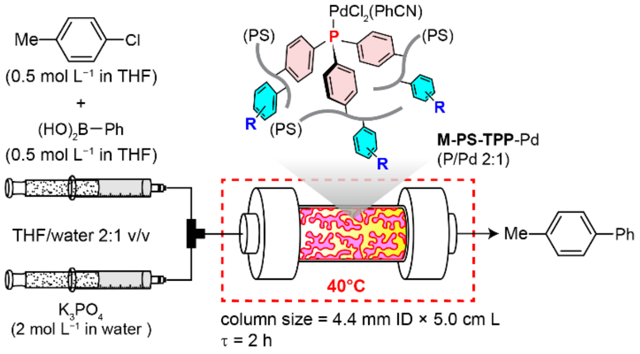
(Supporting Figure S2 and Supporting Table S2). The large flow-through pores and high porosity of M-PS-TPP were expected to provide continuous-flow catalysis in a column reactor. The P loading ([P]) in M-PS-TPPs was estimated based on the feed ratio of PPh3. The presence of coordinatively active PPh3 units was confirmed by 31P CP/MAS NMR spectra of M-PS-TPPs as well as some PPh3 oxide content because of the partial oxidation of the P atom during the synthesis of the monolith (Supporting Figures S3–S12). No significant differences among the 31P CP/MAS NMR chemical shifts (δP) of M-PS-TPP1–10 were observed (−7–−4 ppm), indicating that the incorporation of ST1–10 had little effect on the electronic nature of the supported PPh3 units in all M-PS-TPPs.

Scheme 1. Synthesis of M-PS-TPPs; Photographic image (upper) and SEM Image (lower) of M-PS-TPP-5; Analogues of Aryl Pendant Stabilizers with various sum of para-Hammett substituent constants (Σ(σp))



Next, we examined the coordination behavior and catalytic performance of M-PS-TPPs bearing aryl pendants with various electronic properties as stabilizers for metal catalysts. After the complexation between [PdCl$_2$(PhCN)$_2$] and M-PS-TPP (P/Pd 2:1), the resulting M-PS-TPP-Pd was analyzed using 31P CP/MAS NMR. All M-PS-TPP-Pd systems exhibited selective mono-P-ligation of Pd over bis-P-ligation (Supporting Figures S3–S12). The polystyrene-supported mono-P-ligated Pd was fabricated in a column reactor, and its catalytic performance was evaluated for the C-C cross-couplings between 4-chlorotoluene (0.5 mol L−1) and phenylboronic acid (0.5 mol L−1) employing K$_3$PO$_4$ aq. (2 mol L−1) and THF/water as the base and solvent, respectively (40°C, residence time (τ) = 2 h) (Scheme 2, Supporting Figure S13, and Supporting Table S3).[16a] Along with the permeation of the substrate solutions, a gradual decrease in the turnover frequency (TOF) of all M-PS-TPP-Pd were observed (Figure 2a). After 58 h on stream, the turnover numbers (TONs) of M-PS-TPP1–10-Pd were calculated and varied in the range of 646–2911 along with the corresponding Σ(σp) varying from −1.00 to +0.37 (Figure 2b, Supporting Figure S14). The electron-withdrawing groups (R = 3,4,5-triF, 2,3,4,5,6-pentaF, 4-CF3) with positivε Σ(σπ) (+0.02–+0.37) afforded relatively low TONs (1038–1210). Notably, the TONs gradually increased from 1325 to 2911 with decreasinγ Σ(σp) from +0.11 to −0.44, exhibiting the best catalytic performance of M-PS-TPP5-Pd (R = 4-OMe) in the challenging C-C cross-coupling reaction. Interestingly, a drastic decrease in TON was observed for M-PS-TPP6-Pd (R = 4-NMe2, Σ(σπ) = −1.00), which had the strongest electron-donating aryl pendant stabilizer in this study.

Scheme 2. Continuous-Flow Setup for Suzuki–Miyaura Cross-Coupling between 4-Chlorotoluene and Phenylboronic Acid using M-PS-TPP-Pd



The design of aryl pendant stabilizers based on their electronic properties successfully enhanced the catalytic durability of M-PS-TPP-Pd in the C-C cross-couplings. TEM observations revealed significant Pd aggregation in the spent M-PS-TPP8–10-Pd (R = 3,4,5-triF, 2,3,4,5,6-pentaF, 4-CF3), although less Pd aggregation was observed in the spent M-PS-TPP5-Pd (R = 4-OMe) (Figures 3a and c, Supporting Figure S15). For the monolith with the strongest electron-donating aryl pendants, M-PS-TPP-6-Pd (R = 4-NMe2), TEM images clearly indicated the absence of Pd clustering (Figure 3b). These observations suggest the stabilization effects of the aryl pendants on the supported phosphine-Pd complex, in which moderate stabilization resulted in the best catalytic durability of the M-PS-TPP-Pd system. When electron-withdrawing groups (R = 3,4,5-triF, 2,3,4,5,6-pentaF, 4-CF3) are present on the aryl pendants, Pd could not be effectively protected from aggregation via Pd-arene interactions during catalytic cycles, resulting in low catalytic durability. However, the strong electron-donating properties and/or existence of tertiary amino ligand (R = 4-NMe2) did not enhance the catalytic durability, probably because of the inhibition of active Pd0 formation and/or subsequent catalytic cycles by the considerably strong stabilization due to Pd-arene and/or Pd-N interactions (Figure 2b). Through the screening of polystyrene-phosphine hybrids, we found that M-PS-TPP5-Pd (R = 4-OMe) exhibited moderate Pd stabilization from the aryl pendants for considerably high catalytic durability. Notably, the origins of these different catalytic performance were not explained βψ τ distributions and porosity in the continuous-flow reactors (Supporting Figures S16–S18).

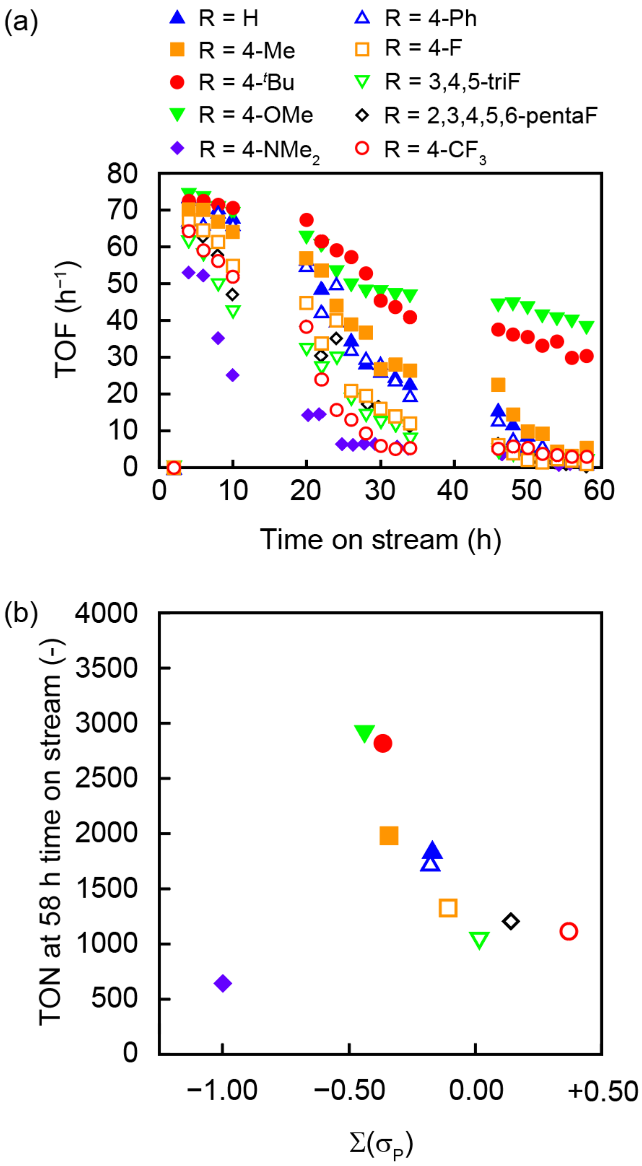


Figure 2. (a) Changes in TOFs and (b) relationship between TON of M-PS-TPP1–10-Pd with various substituents (R) on the aryl pendant stabilizers and their □(□p) in the C-C cross-coupling reactions (58 h on stream). Conditions: 4-chlorotoluene (0.5 mol L−1) and phenylboronic acid (0.5 mol L−1) in THF, K3PO4 (2 mol L−1) in water, M-PS-TPP1–10-Pd column (P/Pd 2:1), THF-phase/water-phase 2:1 v/v, □ = 2 h, 40°C.

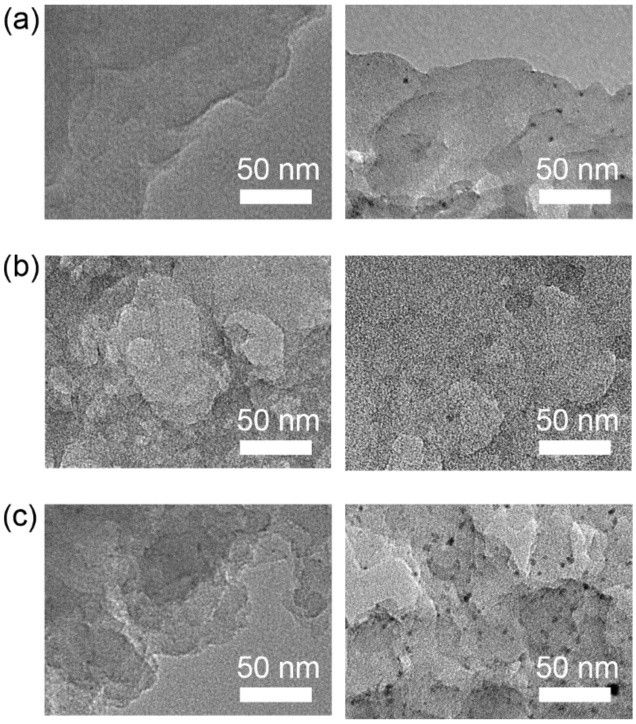


Figure 3. TEM images of (a) M-PS-TPP5-Pd (R = 4-OMe), (b) M-PS-TPP6-Pd (R = 4-NMe2), and (c) M-PS-TPP10-Pd (R = 4-CF3), before (left) and after (right) use in the continuous-flow C-C cross-couplings (time on stream = 58 h).

Buchwald et al. reported the unique ability of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) to stabilize both the Pd0 and PdII centers before and after oxidative addition via labile Pd-arene and Pd-O interactions during cross-coupling.[17] In our polystyrene-based system, the OMe groups on the aryl pendant could positively affect the TON of M-PS-TPP5-Pd (R = 4-OMe, TON = 2911) through Pd-O and Pd-arene interactions.

Scheme 3. (a) Synthesis of PPh3-Free Polystyrene Monolith and (b) Adsorption of Pd Species on the Monolith

To directly confirm the interactions between the aromatic rings of polystyrene and Pd, adsorption experiments with Pd sources (PdII or Pd0) on the PPh3-free polystyrene monolith were conducted (Scheme 3, Supporting Scheme S3). The adsorption rate of [PdCl2(PhCN)2] increased (from 15 to 75%) with decreasing □(□p) (from 0.37 to −1.00), implying that stronger electron-donating substituents on the aromatic rings promoted the higher adsorption rate (Figure 4a). In contrast, the adsorption of [PdCl2(PPh3)2] on all the polymers was negligible (Figure 4b) compared with that of [PdCl2(PhCN)2]. Pd0 sources such as [Pd(PPh3)4] and [Pd2(dba)3] did not show a significant adsorption rate on any of the polystyrene monoliths (~4%).

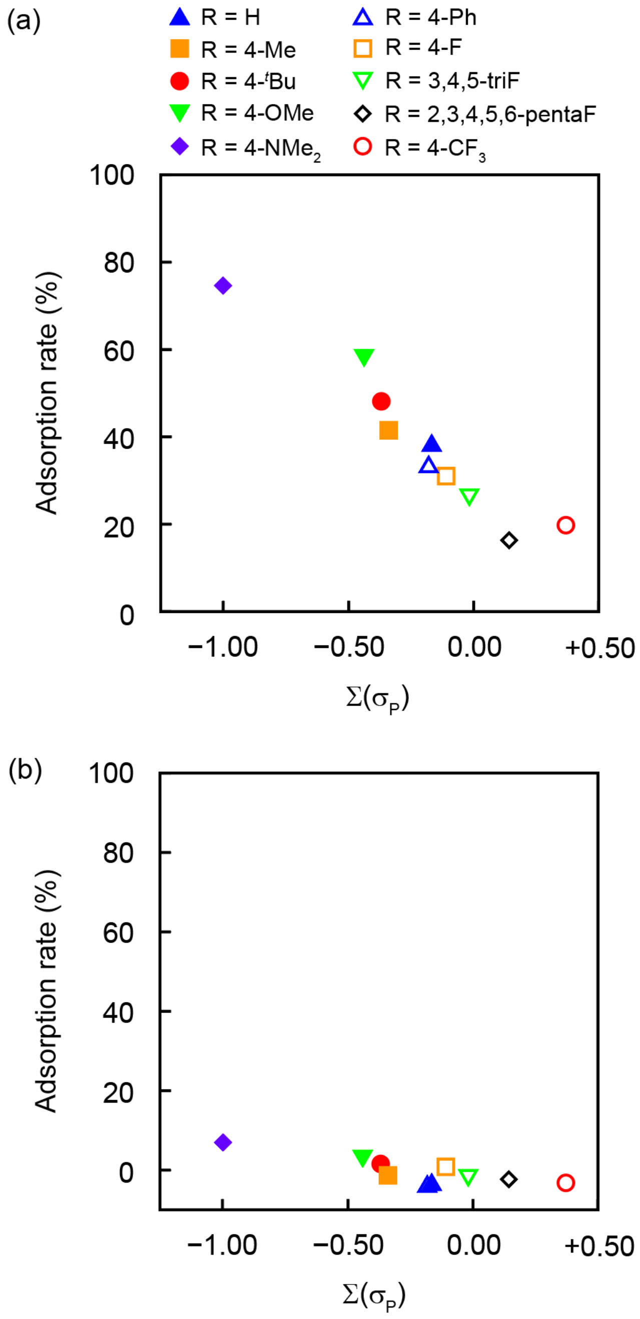


Figure 4. Adsorption rate of (a) [PdCl2(PhCN)2] and (b) [PdCl2(PPh3)2] on phosphine-free polystyrene monoliths with various aryl pendants.

The adsorption rate of [PdCl2(PhCN)2] on the monoliths increased with increasing electron-donating properties of the incorporated aryl pendants (lower □(□p)), although [PdCl2(PPh3)2], [Pd(PPh3)4], and [Pd2(dba)3] did not exhibit significant adsorption on the monoliths. It was suggested that the ligand exchange of the labile species (PhCN or solvent) with the aromatic rings in the polymer was promoted by the electron-donating properties of the aromatic rings at the Pd center. Additionally, the coordination of the aromatic ring on the polymer to PdII might be weaker than that of PPh3 and did not cleave the P-Pd bonds of the supported phosphine-Pd complexes in M-PS-TPP-Pd during the catalytic reactions.

Kobayashi et al. evaluated the catalytic durability of polystyrene-supported PPh3-Pd prepared from different Pd sources (PdII and Pd0) and demonstrated that the production rate of catalytically active Pd0 was strongly related to catalytic durability in continuous-flow Suzuki–Miyaura cross-couplings.[18] Based on these results, the speculated mechanism for the stabilization effect of Pd catalysts in the M-PS-TPPs is as follows: PdII coordinated to a labile ligand (PhCN or solvent, which are weaker than PPh3) is supported on polystyrene via the mono-P-ligation of three-fold cross-linking PPh3. Subsequently, the aryl pendants on the polystyrene stabilize the PPh3-Pd complex via aromatic □-electron donations and/or coordination of functional groups. The catalytic durability of the resulting M-PS-TPP-Pd is regulated by the degree of stabilization from the aryl pendants, that is, the production rate of catalytically active Pd0 species from the PdII pre-catalyst system.

Conclusion

In summary, a simple and direct strategy to efficiently generate and stabilize a highly active mono-P-ligated metal complex on a polystyrene-phosphine hybrid was developed based on the site isolation of phosphine and stabilization from the aryl pendants on the polymer. Various combinations of the electronic properties of the aryl pendants on polystyrene-phosphine hybrids were evaluated for their coordination abilities and catalytic performances. The applicability of the polystyrene-supported phosphine-Pd complex to the C-C cross-couplings of chloroarenes in continuous-flow systems was demonstrated, where the selective formation of mono-P-ligated Pd and moderate interactions between the aryl pendant stabilizers and metal centers were highlighted. We believe that this polymer-based concept can be expanded to explore unprecedented catalytic systems, including unstable catalytic centers.

Supporting Information

The authors have cited additional references within the Supporting Information.[19–22]

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Keywords: Heterogeneous catalysis • Transition metals • Phosphane ligands • Noncovalent interactions • Polymers

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