EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402735

Metallacrown Ether Catalysts Containing Phosphine–Phosphite Polyether Ligands for Rh-Catalyzed Asymmetric Hydrogenation – Enhancements in Activity and Enantioselectivity

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Keywords: Asymmetric catalysis / Hydrogenation / Supramolecular chemistry / Crown compounds / Rhodium

A new class of tunable metallacrown ether rhodium catalysts based on α,ω-(phosphine–phosphite) polyether ligands were prepared either by a template-induced method or by a non-template procedure. For the asymmetric hydrogenation of α-arylenamides with the addition of K^+ cations, the *ortho*-diphenylphosphine-substituted metallacrown ether catalyst showed high enantioselectivities (up to 99 % *ee*), which are comparable to or better than the results obtained for phosphine–phosphite ligands with two or more chiral elements. Remarkable enhancements in enantioselectivity and noticeably increased catalytic activity were achieved through the supramolecular recognition between K^+ cations and the metallacrown ether catalyst.

Introduction

Owing to their unique features of selective recognition and structural tunability upon supramolecular regulation, metallacrown ethers have received extensive attention in recent years.[1,2] Among them, monocyclic metallacrown ethers, which are often formed by the chelation of α,ω-(multidentate donor) polyether ligands to transition metal ions, are of great interest as catalysts owing to the potential bifunctionality of such hard–soft dimetallic complexes. The introduction of a macrocyclic crown ether skeleton with selective binding properties into the catalyst structure is expected to result in distinctive catalytic performance involving a host–guest recognition process.[3] However, to the best of our knowledge, the application of metallacrown ethers as catalysts has not been widely studied,[2d,2f–2l] especially the use of chiral metallacrown ethers in asymmetric catalysis.[2g,2l] Recently, we have developed a new class of readily available and tunable bis(phosphite) ligands with an oligo(ethylene glycol) backbone, and a pronounced enhancement of enantioselectivity was achieved in the rhodium-catalyzed asymmetric hydrogenation of α-dehydroamino acid esters by the addition of NaBArF {BArF = $[3,5\text{-}(CF_3)_2C_6H_3]_4B$}.[2g] Later, Vidal-Ferran and co-workers reported a similar chiral bis(phosphite)-containing metallacrown ether catalyst bearing a 1,1′-biphenyl unit in the oligo(ethylene glycol) backbone. This catalyst was successfully applied in the Rh-catalyzed asymmetric hydroformylation of terminal olefins with an increase of up to 62 % *ee* caused by the addition of CsBArF.[2l] On the basis of these successes, we anticipate that such a strategy could be extended to other bidentate ligands, including heterobidentate ligands containing a poly(ether) linkage. However, the preparation of metallacrown ethers bearing different coordinating groups is still challenging. To the best of our knowledge, no successful example has been reported.

The enantiopure phosphine–phosphite ligands represent a class of tunable and nonsymmetric chiral phosphorus ligands with binding groups that differ in their electronics and sterics, diverse carbon backbones with varied linkages of different distances, and a variety of stereogenic elements.[4] These ligands are accessible by standard covalent chemistry[5] or supramolecular interactions[6] and have been extensively studied in asymmetric catalysis such as hydroformylation, copper-mediated conjugate additions, palladium-mediated allylic substitutions and, particularly, the asymmetric hydrogenation of functionalized alkenes and prochiral imines. High efficiency and enantioselectivity have usually been achieved by utilizing such phosphine–phosphite ligands with more than one chiral element.[4a] However, for enamide substrates, rather few phosphine–phosphite/metal catalysts have been found to be highly enantioselective in the asymmetric hydrogenation.[5a,5b,5g,6c] Considering the widespread application of phosphine–phosphite ligands[4a] and as a continuation of our ongoing en-

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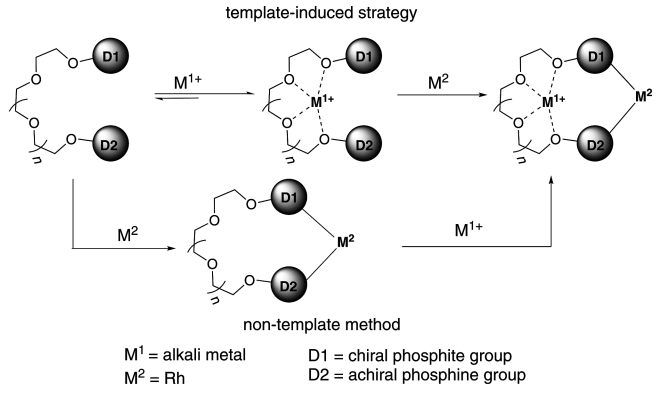
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402735.

deavor to develop effective chiral supramolecular catalysts based on crown ethers,[2g,6h,6i] herein, we report the preparation of a new class of metallacrown ether catalysts. The catalysts were prepared by the intramolecular coordination of achiral phosphine–chiral phosphite ligands with a Rh center in both the presence[7] and absence of a template (Scheme 1), and their application in the asymmetric hydrogenation of enamides was studied with an emphasis on the elucidation of the effects of host–guest recognition between alkali metal cations and metallacrown ether catalysts on the catalytic performance.



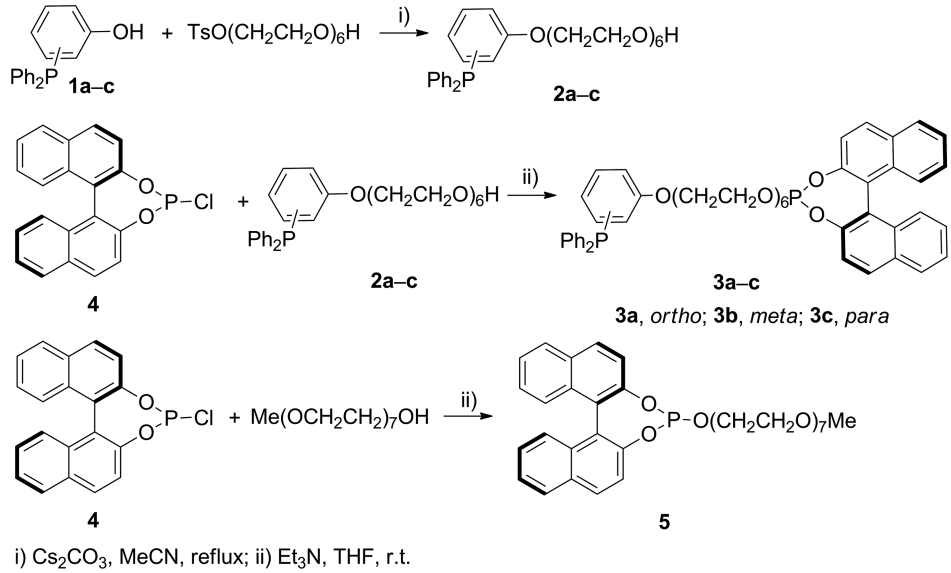
Scheme 1. Schematic representation of two synthetic routes to the chiral metallacrown ether catalysts.

Results and Discussion

1. Ligand Synthesis and Association Study with K^+ Cations

The designed α,ω-(phosphine–phosphite) polyether ligands were synthesized by the stepwise coupling of the respective phosphine or phosphite ligand with a hexa(ethylene glycol) building block, which was selected according to the results of our previous study.[2g] As shown in Scheme 2, the reactions of monohydroxy-substituted triphenylphosphines **1a**–**1c** with monotosylated hexa(ethylene glycol) in the presence of Cs_2CO_3 afforded **2a**–**2c** in excellent yields. The α,ω-(phosphine–phosphite) polyether ligands **3a**–**3c** were readily prepared from the corresponding **2a**–**2c** by the treatment with the binol-derived phosphorochloridite **4** and Et_3N as a base in moderate yields. All of these phosphine–phosphite ligands were unambiguously characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as HRMS spectrometry. The obtained results are in full agreement with the compounds synthesized. As a control experiment, the known monophosphite ligand **5** with a septa(ethylene glycol) monomethyl ether chain was prepared in high yield by the same method as that for ligands **3**.[2g]

With these polyether-linked phosphine–phosphite ligands in hand, we first investigated the association of K^+ cations with the ligands through ^1H and ^{31}P NMR spectroscopy studies by mixing the corresponding ligands **3a**–**3c** with KBArF in dry CD_2Cl_2 in a 1:1 molar ratio (concentration: 11.8 mM). In general, the ^1H NMR signals of the oxyethylene protons remarkably shifted upfield and widened owing to the strong shielding effect of the $BArF^-$ anion (see Supporting Information).[8] Specifically, the ^1H NMR spectrum of [K(**3a**)]BArF showed a dispersed array of relatively well-defined resonances that differenced greatly from those of **3a**; three sets of multiple peaks with the same integration were observed in the more upfield region of δ = 2.0–2.6 ppm compared to the ^1H NMR spectra of [K(**3b**)]BArF and [K(**3c**)]BArF. There were also distinct changes in the aromatic region upon the addition of KBArF. In the $^{31}P\{^1H\}$ NMR spectra, the addition of KBArF caused pronounced downfield shifts to the signals of the phosphite moiety for all ligands **3a**–**3c** (see Supporting Information). For instance, the phosphite signal for **3a** shifted from δ = 142.9 to 146.4 ppm upon the addition of KBArF. For the phosphine moiety, the signal changes for **3a**–**3c** were significantly different. For **3a**, the phosphine signal shifted upfield



Scheme 2. Synthesis of phosphine–phosphite ligands **3a**–**3c** and monophosphite ligand **5**.

from δ = –15.8 to –17.4 ppm upon the addition of KBArF; for **3b** and **3c**, however, negligible signal changes were observed upon the addition of KBArF. All of these results suggested that the distinct effect of alkali cation association with **3a** was possibly due to the different electronic and steric properties of the *ortho*-substituted phosphine ligand. Furthermore, with **3a** as an example, the association constant calculated from the ^{31}P NMR spectroscopy titration data by nonlinear data fitting[9] was 68 ± 7 M^{-1} at 25 °C in anhydrous acetone. Furthermore, a 1:1 guest–host ratio was supported by the Job plot analysis (see Figures S1–S3). The above results qualitatively and quantitatively demonstrated the supramolecular binding of K^+ cations to the hexa(ethylene glycol) moiety in the bidentate phosphine–phosphite ligands.

2. Preparation and Characterization of Metallacrown Ethers

Having demonstrated the supramolecular interactions between K^+ cations and the phosphine–phosphite polyether ligands, which have two terminal ligating groups close together, we started to investigate the preparation of rhodium metallacrown ether catalysts by selecting the template method[2g] as the initial procedure. As illustrated in Scheme 1, by the addition of an equal amount of KBArF into the ligand solutions (11.8 mM) before the coordination of the ligand to the transition metal ion, the rhodium complexes were generated in situ with an equal amount of the metal precursor $Rh(cod)_2BF_4$ (cod = cyclooctadiene). As expected, two sets of double doublet peaks were observed in the ^{31}P NMR spectra (Figure 1) of Rh/(**3b**+K) and Rh/(**3c**+K). Notably, for Rh/(**3a**+K), a set of broad double peaks in the downfield region was observed, probably because of the steric effect of the *ortho* substitution. Although the most intense signals in the ESI-HRMS spectrum were assigned to a Rh/**3a** species, the peaks for Rh/(**3a**+K) were also observed (Figure S4).

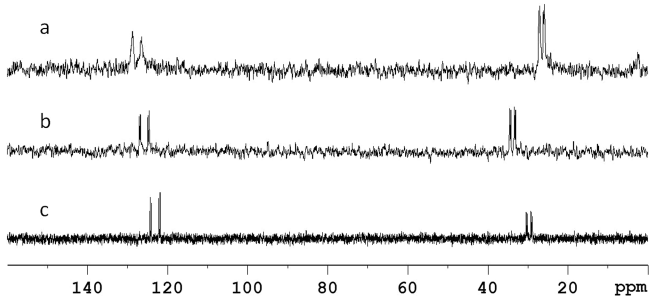


Figure 1. Stacked plot of the ^{31}P NMR spectra (121.5 MHz, 295 K, 11.8 mM in CD_2Cl_2) of (a) [**3a** + KBArF] + $Rh(cod)_2BF_4$, (b) [**3b** + KBArF] + $Rh(cod)_2BF_4$, and (c) [**3c** + KBArF] + $Rh(cod)_2BF_4$.

Table 1. Summary of the Rh coordination ^{31}P NMR spectroscopic data with and without KBArF.

Ligand + $Rh(cod)_2BF_4$	^{31}P NMR [ppm] without KBArF	^{31}P NMR [ppm] with KBArF
3a + $Rh(cod)_2BF_4$	126.8 (d, $J_{OP,Rh}$ = 269.1 Hz), 25.7 (dd, $J_{P,Rh}$ = 144.8 Hz, $J_{P,OP}$ = 37.2 Hz)	127.6 (d, $J_{OP,Rh}$ = 279.6 Hz), 26.6 (dd, $J_{P,Rh}$ = 143.5 Hz, $J_{P,OP}$ = 36.5 Hz)
3b + $Rh(cod)_2BF_4$	125.9 (dd, $J_{OP,Rh}$ = 265.7 Hz, $J_{OP,P}$ = 37.4 Hz), 33.8 (dd, $J_{P,Rh}$ = 145.2 Hz, $J_{P,OP}$ = 37.4 Hz)	125.8 (dd, $J_{OP,Rh}$ = 265.2 Hz, $J_{OP,P}$ = 37.6 Hz), 33.8 (dd, $J_{P,Rh}$ = 145.4 Hz, $J_{P,OP}$ = 37.6 Hz)
3c + $Rh(cod)_2BF_4$	123.2 (dd, $J_{OP,Rh}$ = 266.8 Hz, $J_{OP,P}$ = 38.0 Hz), 29.6 (dd, $J_{P,Rh}$ = 142.3 Hz, $J_{P,OP}$ = 38.0 Hz)	123.1 (dd, $J_{OP,Rh}$ = 267.0 Hz, $J_{OP,P}$ = 37.7 Hz), 29.7 (dd, $J_{P,Rh}$ = 143.2 Hz, $J_{P,OP}$ = 37.7 Hz)

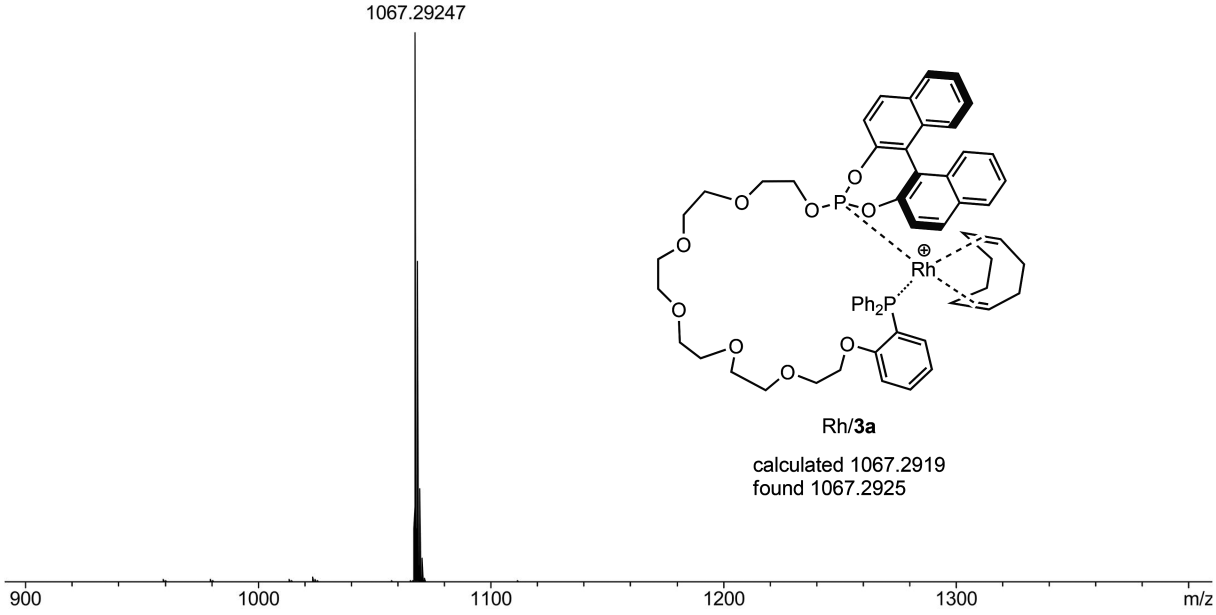


Figure 2. ESI-HRMS spectrum for **Rh/3a** complex.

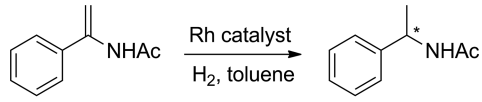
Alternatively, metallacrown ethers are often prepared under dilute conditions without the addition of a template.[2a–2e] Thus, we attempted to prepare the rhodium metallacrown ether catalysts through the direct coordination of the cationic $Rh(cod)_2BF_4$ and ligands **3a**–**3c** in an equimolar ratio (concentration: 11.8 mM) without the participation of an alkali metal cation as a template. Gratifyingly, the obtained ^{31}P NMR spectra were very similar to those acquired by the template-induced method, albeit with slight differences in both the chemical shifts and the coupling constants (Table 1). The formation of metallacrown ethers for Rh/**3a**–**3c** was also verified by ESI-HRMS (Figures 2 and S4). In contrast to the low efficiency and selectivity of previously reported nontemplate syntheses of metallacrown ethers,[2f] the success might be ascribed to the cationic nature of the metal precursor. When $[Rh(cod)Cl]_2$ was used, multiple Rh complex species were observed (Figure S5).

By comparing the chemical shifts in the ^{31}P NMR spectra of the in situ prepared metallacrown ethers with and without the binding of K^+ cations, differences shown by Rh/**3a** were noticed. Downfield shifts of 0.8 and 0.9 ppm for the phosphite and phosphine moieties were recorded, respectively, whereas the signal changes for Rh/**3b** and Rh/**3c** were negligible. These results implied that the catalytic performance for these metallacrown ether catalysts might be different.

3. Asymmetric Hydrogenation of Enamides

Having realized the effective formation of chiral rhodium metallacrown ether catalysts, we then evaluated their catalytic properties in the asymmetric hydrogenation of α-arylenamide derivatives. In general, rather few phosphine–phosphite/metal catalysts have been found to be highly enantioselective in the asymmetric hydrogenation of enamide substrates,[5a,5b] although such phosphorus ligands offer the advantages of easy preparation and derivatization as well as high air-stability. Gratifyingly, 100% conversions were achieved within 12 h for all of the reactions screened. By selecting nonpolar organic solvents that favor host–guest assembly between alkali cations and metallacrown ethers, ligand **3a** with the diphenylphosphine group at the *ortho* position provided a good enantioselectivity (84%*ee*) in the Rh-catalyzed hydrogenation of enamide **6a** in toluene (Table 2, Entry 1; also see Table S2 for solvent optimization); the *ee* with **3a** is much better than those obtained with **3b** and **3c** (Table 2, Entries 2–3). Although **5** itself afforded the reduced product with high enantioselectivity (Table 2, Entry 4), a racemic product was obtained by using a mixed ligand system with the monophosphite **5** and PPh_3 in a 1:1 molar ratio (Table 2, Entry 5). To our delight, in the presence of 1.0 mol-% KBArF and under otherwise the same reaction conditions, a higher enantioselectivity of 93%*ee* was obtained with ligand **3a** (Table 2, Entry 6). Ligands **3b** and **3c** also gave the product with a slight enhancement of enantioselectivity in the presence of KBArF (Table 2, Entries 7–8). The above results indicate that the performance of the Rh/**3a** metallacrown ether catalyst was positively improved by the addition of K^+ cations, as evidenced by the clear enhancement of catalytic enantioselectivity. Therefore, **3a** was selected as the optimal ligand. The addition of K^+ cations after the coordination between Rh and ligand **3a** gave the same enantioselectivity in the hydrogenation (Table 2, Entry 9); this suggests that the preparation method of the supramolecular Rh/ligand/K^+ metallacrown ether catalysts does not affect the enantioselective outcome of the hydrogenation.

Table 2. Asymmetric hydrogenation of enamide **6a** with Rh/**3a**–**3c**.[a]

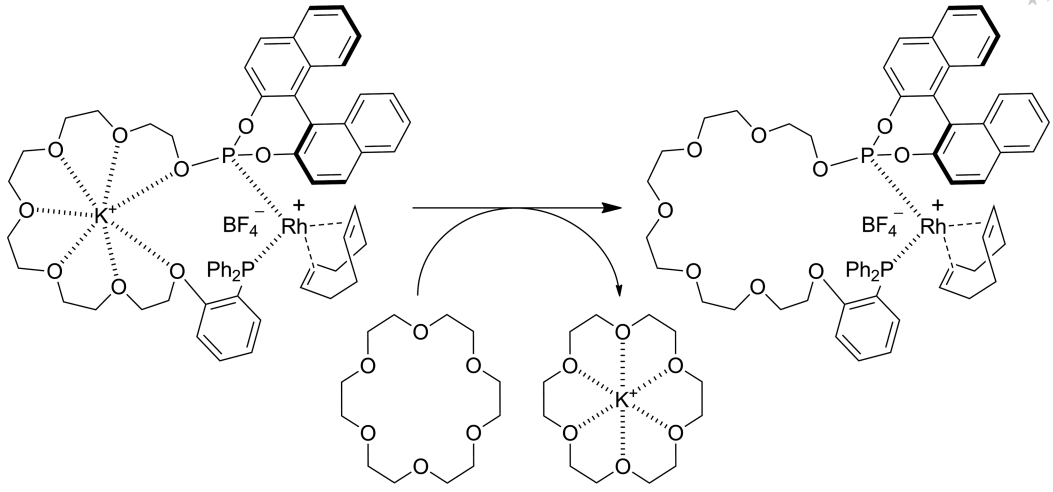


6a **7a**

Entry	Ligand	Additive (M^+/ligand)	*ee* [%][b]
1	**3a**	–	84
2	**3b**	–	5
3	**3c**	–	11
4	**5**	–	87
5	**5**/PPh_3 (1:1)	–	0
6	**3a**	KBArF (1:1)	93
7	**3b**	KBArF (1:1)	9
8	**3c**	KBArF (1:1)	13
9[c]	**3a**	KBArF (1:1)	93
10	**3a**	LiBArF (1:1)	89
11	**3a**	NaBArF (1:1)	91
12	**3a**	CsBArF (1:1)	92
13	**3a**	KBArF (0.5:1)	90
14	**3a**	KBArF (2:1)	87
15	**3a**	KBArF (5:1)	81
16[d]	**3a**	KBArF (1:1)	84
17[e]	**3a**	KBArF (1:1)	84

[a] Unless otherwise stated, the hydrogenations were performed with 0.1 mmol of **6a** in 1 mL of toluene under the following conditions: **6a**/**3a**–**3c**/$Rh(cod)_2BF_4$ (100:1.1:1), **6a**/**5**/$Rh(cod)_2BF_4$ (100:2.2:1), 20 atm of H_2, room temp. for 12 h. The Rh/ligand/K^+ catalysts were prepared by a template-induced method. [b] 100% conversions were observed in all cases, and the enantioselectivities were determined by chiral GC analysis. [c] KBArF was added after the formation of the metallacrown ether Rh/**3a**. [d] 18-Crown-6 was added during the preparation of the catalyst. [e] 18-Crown-6 was added directly into the mixed solution of the in situ prepared catalyst and the substrate.

To identify the effects of alkali cations on the catalytic performance, different alkali metal salts with the same counteranion were screened (Table 2, Entries 6, 10–12). The K^+ cation gave the best result, and lower enantioselectivities were observed for Na^+, Li^+, and Cs^+, possibly owing to the difference in the match with the metallacrown ether catalyst. When the amount of KBArF was increased or decreased, the enantioselectivity dropped (Table 2, Entries 13–15). In the above optimization experiments, the best result was obtained with the combination of **3a** and K^+ (1 equiv. to **3a**) to give the hydrogenation product in 93%*ee* (Table 2, Entry 6; 9% enhancement of *ee* value). Control experiments were also performed to ascertain the key role played by the



Scheme 3. Removal of K^+ cation from the metallacrown ether catalyst with 18-crown-6.

K^+ cations (Scheme 3). Owing to the stronger binding of 18-crown-6 to K^+ cations than Rh/**3a**, the addition of 18-crown-6 before or after the formation of the Rh/**3a**/K^+ metallacrown ether catalyst provided decreased enantioselectivities similar to that obtained without K^+ cations (Table 2, Entries 16–17 vs. Entry 1). These results clearly demonstrated that the addition of alkali metal cations could effectively improve the catalytic enantioselectivity of the rhodium metallacrown ether catalysts through a supramolecular recognition adjustment.

Subsequently, we investigated the influence of the addition of KBArF on the reaction rate for the asymmetric hydrogenation of **6a**. The reaction conditions were identical to the optimized conditions (Table 2, Entry 6) except that the hydrogen pressure was set to 5 atm. As explicitly shown in the time-conversion curves in Figure 3, the hydrogenation rate was accelerated with the addition of KBArF; this clearly indicates that the addition of alkali metal cations can effectively improve the catalytic activity of the rhodium metallacrown ether catalyst.

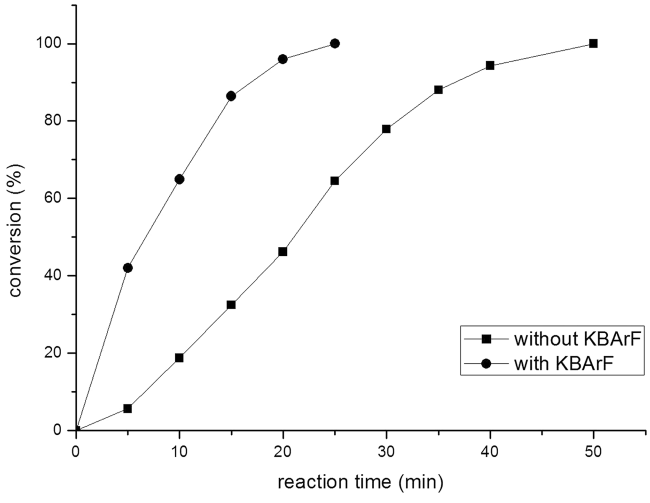
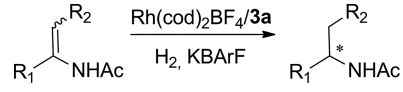


Figure 3. Conversion plotted against time for the asymmetric hydrogenation of **6a**.

To establish the positive effects of the supramolecular recognition between alkali cations and the metallacrown ether catalysts on both hydrogenation activity and enantioselectivity, a series of α-arylenamides were hydrogenated by employing the Rh/(**3a**+K) complex as the catalyst under the optimized conditions. As shown in Table 3, the hydrogenation of α-*para*-substituted phenylenamides **6a**–**6f** proceeded smoothly with full conversions and excellent enantioselectivities (93–99%*ee*), which are comparable to or even better than the best results obtained for phosphine–phosphite ligands with a chiral backbone.[5a,5b] For *meta*-chlorophenylenamide **6g**, fairly good enantioselectivity was observed (Table 3, Entry 7). For the more challenging *ortho*-chlorophenylenamide **6h**, only 39% conversion was achieved; this was still higher than the 12% conversion ob-

Table 3. Asymmetric hydrogenation of α-arylenamides catalyzed by Rh/(**3a**+K).[a]



6a–i **7a–i**

Entry	Substrate (R^1, R^2)	*ee* [%][b]
1	**6a** (Ph, H)	93 (84)
2	**6b** (4-Me-Ph, H)	96 (84)
3	**6c** (4-F-Ph, H)	94 (85)
4	**6d** (4-CF_3-Ph, H)	99 (92)
5	**6e** (4-Cl-Ph, H)	99 (94)
6	**6f** (4-Br-Ph, H)	98 (93)
7	**6g** (3-Cl-Ph, H)	87 (81)
8	**6h** (2-Cl-Ph, H)	70 (66)
9	**6i** (Ph, Me)	58 (50)

[a] The hydrogenations were performed with 0.1 mmol of **6** in 1 mL of toluene under the following conditions: **6**/**3a**/KBArF/Rh-$(cod)_2BF_4$ = 100:1.1:1.1:1, 20 atm of H_2, room temp. for 12 h. [b] 100% conversions were observed in all cases except Entry 8 (39% conversion vs. 12% conversion without KBArF). The enantioselectivities were determined by chiral GC analysis except for that of **7h** (determined by chiral HPLC). The configuration of the product is (*S*). The data in parentheses were obtained without an alkali metal.

tained in the absence of KBArF (Table 3, Entry 8). For trisubstituted α-phenylenamide **6i**, only moderate enantioselectivity was obtained (Table 3, Entry 9). Most importantly, a remarkable enhancement in enantioselectivity was observed in all cases in the presence of K^+ cations. For example, the (*S*)/(*R*) enantiomeric ratio of **7d** reached 199 in the presence of K^+ cations, which is greatly improved from that obtained [(*S*)/(*R*) = 24] without the cation regulation.

Conclusions

A new class of readily available and tunable metallacrown ether catalysts based on α,ω-(phosphine–phosphite) polyether ligands was successfully prepared and applied in the rhodium-catalyzed asymmetric hydrogenation of α-arylenamides. It has been demonstrated that the addition of alkali metal cations leads to positive enhancements of enantioselectivity and activity through the coordination of K^+ cations to the metallacrown ether. Studies of this supramolecular approach in the preparation of other chiral tunable catalysts are in progress.

Experimental Section

General: Unless otherwise noted, all experiments were performed under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques or in a nitrogen-filled glovebox. All of the solvents were treated before use according to the standard methods. Commercially available reagents were used without further purification. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at ambient temperature with a Bruker Advance DMX 300 Spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz, and ^{31}P 121 MHz) with samples in $CDCl_3$ or CD_2Cl_2. Chemical shifts (δ) are given in ppm and are referenced to the residual solvent peaks (^{1}H and ^{13}C NMR) or to an external standard (85% H_3PO_4 for ^{31}P NMR). Coupling constants (*J*) are reported in Hertz. The ESI-HRMS spectra were recorded with a Thermo Scientific® apparatus. The conversions and enantiomeric excesses of the reduced products were determined either by chiral GC with a Chrompack Chiralsil-DEX CB column and Chrompack Chirasil-L-Val column or by chiral HPLC with a Chiralcel OD column. Flash column chromatography was performed with silica gel of 200–300 mesh.

Compounds **1a**–**1c** and monotosylated hexa(ethylene glycol) were synthesized by modified literature procedures.[10,11] Compound **4** and all of the α-arylenamide substrates were prepared according to the published method.[12,13]

General Synthetic Procedure for 2a–2c: Under nitrogen atmosphere, cesium carbonate (0.75 g, 2.3 mmol) was added in one portion to a solution of 2-(diphenylphosphanyl)phenol (**1a**, 0.47 g, 1.7 mmmol) and monotosylated hexa(ethylene glycol) (0.66 g, 1.5 mmol) in deoxygenated CH_3CN (20 mL). The resulting mixture was heated to reflux overnight. After removal of the solvent, the residue was extracted with ethyl acetate (EA, 50 mL × 2). The combined organic layers were washed with brine, subsequently dried with anhydrous Na_2SO_4, and finally purified by flash chromatography to give **2a** (0.81 g, 1.5 mmol) as a white to pale yellow viscous oil in almost quantitative yield (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (br, 1 H), 3.45–3.73 (m, 22 H), 4.04 (t, *J* = 5.0 Hz, 2 H), 6.64–6.68 (m, 1 H), 6.83–6.90 (m, 2 H), 7.27–7.35 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.8, 68.5, 69.4, 70.5, 70.6, 70.7, 70.7, 70.9, 72.7, 111.4, 115.6, 121.3, 126.1, 126.3, 128.4, 128.5, 128.7, 130.3, 133.6, 133.9, 134.2, 136.8, 136.9, 160.2, 160.4 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –15.3 ppm. HRMS (ESI): calcd. for $C_{30}H_{40}O_7P$ $[M + H]^+$ 543.2506; found 543.2504.

Compound 2b: Prepared by the same procedure as that for **2a**; 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.69 (br, 1 H), 3.49–3.64 (m, 20 H), 3.70–3.73 (m, 2 H), 3.95 (t, *J* = 4.8 Hz, 2 H), 6.79 (t, *J* = 7.3 Hz, 3 H), 7.13–7.26 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.8, 67.4, 69.8, 70.4, 70.6, 70.7, 70.9, 72.7, 115.2, 119.5, 119.8, 126.2, 126.4, 128.5, 128.6, 128.8, 129.5, 129.6, 133.7, 134.0, 137.1, 137.2, 138.7, 138.9, 158.8, 158.9 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –4.8 ppm. HRMS (ESI): calcd. for $C_{30}H_{40}O_7P$ $[M + H]^+$ 543.2506; found 543.2505.

Compound 2c: Prepared by the same procedure as that for **2a**; 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (br, 1 H), 3.58–3.74 (m, 20 H), 3.85 (t, *J* = 4.9 Hz, 2 H), 4.13 (t, *J* = 4.8 Hz, 2 H), 6.90 (d, *J* = 8.1 Hz, 2 H), 7.23–7.34 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.9, 67.5, 69.8, 70.5, 70.7, 70.8, 72.7, 115.0, 115.1, 128.5, 128.6, 128.7, 133.5, 133.7, 135.6, 135.8, 137.7, 159.8 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = –7.1 ppm. HRMS (ESI): calcd. for $C_{30}H_{40}O_7P$ $[M + H]^+$ 543.2506; found 543.2506.

General Synthetic Procedure for 3a–3c: Under nitrogen atmosphere, a solution of (*R*)-[1,1′-binaphthyl-2,2′-diyl]chlorophosphite (**4**, 0.70 g, 2.44 mmol) in tetrahydrofuran (THF, 10 mL) was added to a solution of **2a** (1.10 g, 2.03 mmol) and Et_3N (1.7 mL, 6.0 mmol) in deoxygenated THF (30 mL) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 16 h. The precipitated Et_3NHCl was removed by filtration through a pad of Celite. After the solvent was removed under reduced pressure, the residue was purified by flash column chromatography to give **3a** (1.1 g, 1.26 mmol) as a colorless and viscous oil in 62% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.43–3.62 (m, 20 H), 3.92–4.08 (m, 4 H), 6.64–6.69 (m, 1 H), 6.83–6.92 (m, 2 H), 7.24–7.54 (m, 19 H), 7.93–8.02 (m, 4 H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 64.8, 64.9, 68.1, 68.8, 69.7, 70.9, 70.9, 71.0, 71.0, 71.1, 71.1, 111.9, 121.5, 122.2, 123.0, 124.4, 124.5, 125.3, 125.5, 126.6, 126.6, 126.7, 126.7, 127.1, 128.7, 128.8, 128.8, 129.0, 130.5, 130.6, 130.8, 131.5, 132.0, 132.9, 133.2, 133.7, 133.8, 134.2, 134.5, 137.3, 137.5, 148.0, 148.0, 149.0, 160.6, 160.8 ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 142.9, –15.8 ppm. HRMS (ESI): calcd. for $C_{50}H_{51}O_9P_2$ $[M + H]^+$ 857.3003; found 857.3005.

Compound 3b: Prepared by the same procedure as that for **3a**; 60% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.58–3.76 (m, 20 H), 3.93–4.12 (m, 4 H), 6.84–6.93 (m, 3 H), 7.25–7.56 (m, 19 H), 7.95–8.03 (m, 4 H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 64.8, 64.9, 67.7, 69.9, 70.9, 71.0, 71.0, 71.1, 115.2, 119.8, 120.0, 122.2, 123.1, 124.1, 124.4, 124.5, 125.3, 125.5, 126.3, 126.6, 126.7, 127.1, 127.5, 128.8, 128.8, 128.8, 128.9, 129.2, 129.9, 130.0, 130.5, 130.8, 131.3, 131.5, 132.0, 132.9, 133.2, 134.0, 134.2, 137.5, 137.7, 139.3, 139.4, 148.0, 148.9, 149.0, 159.2, 159.3 ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 144.0, –4.0 ppm. HRMS (ESI): calcd. for $C_{50}H_{51}O_9P_2$ $[M + H]^+$ 857.3003; found 857.3004.

Compound 3c: Prepared by the same procedure as that for **3a**; 52% yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 3.59–3.71 (m, 18 H), 3.80 (t, *J* = 6.9 Hz, 2 H), 3.91–3.96 (m, 1 H), 4.07–4.14 (m, 3 H), 6.92 (d, *J* = 6.3 Hz, 2 H), 7.26–7.55 (m, 20 H), 7.94–8.03 (m, 4 H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 64.8, 64.9, 67.9, 68.2, 69.9, 70.9, 71.0, 71.0, 71.0, 71.1, 71.2, 115.2, 115.3, 122.2, 123.1, 124.4, 124.7, 125.4, 125.5, 126.7, 126.7, 127.1, 127.5, 128.2, 128.3, 128.8, 128.9, 130.5, 130.8, 131.5, 132.0, 132.9, 133.2, 133.7, 133.9, 135.8, 136.1, 138.4, 138.5, 148.0, 149.0, 149.0, 160.2 ppm. ^{31}P NMR (121 MHz,

CD_2Cl_2): δ = 142.9, –7.4 ppm. HRMS (ESI): calcd. for $C_{50}H_{51}O_9P_2$ $[M + H]^+$ 857.3003; found 857.3005.

The monophosphite **5**, as a known compound, was synthesized in 86% yield by the same method as that for ligand **3**.[2g]

Typical Procedure for the in-situ-Preparation of the Metallacrown Catalysts for Identification: A mixture of the corresponding phosphine–phosphite ligand **3a**–**3c** (5.9×10^{-3} mmol) and $Rh(cod)_2BF_4$ (5.9×10^{-3} mmol) was dissolved in CD_2Cl_2 (0.5 mL), and the solution was stirred for 30 min in a glovebox. The in situ formed complexes were characterized by ^{31}P NMR spectroscopy and ESI-HRMS. For the template-induced strategy, the preparation was identical except that an equimolar amount of KBArF was added to the ligand **3a**–**3c** solution before the coordination with $Rh(cod)_2BF_4$.

Typical Procedure for the Asymmetric Hydrogenation of α-Arylenamides (Template-Induced Method): A mixture of the corresponding phosphine–phosphite ligand **3a**–**3c** (3.3×10^{-3} mmol) and KBArF (3.3×10^{-3} mmol) in dichloromethane (1.5 mL) was stirred at room temperature for 20 min under nitrogen atmosphere. To the resulting solution, $Rh(cod)_2BF_4$ (3.0×10^{-3} mmol) was added, and the solution was stirred for another 30 min. Then, the above in situ prepared catalyst (0.5 mL, 1.0×10^{-3} mmol) was added to a 50 mL glass-lined stainless steel reactor with a magnetic stirring bar, which was charged with enamide **6a** (16.1 mg, 0.1 mmol) in dichloromethane (0.5 mL). The reactor was closed and transferred outside the glovebox, and the solvent was evaporated under reduced pressure. The reactor was transferred into the glovebox again; toluene (1.0 mL) was added, and then the autoclave was closed and pressurized with hydrogen to 20 atm. The mixture was stirred at ambient temperature for 12 h. After careful venting of the hydrogen, the conversions and enantioselectivities of the reduced products were determined by chiral GC with a Chrompack Chiralsil-DEX CB column and Chrompack Chirasil-L-Val column or chiral HPLC with a Chiralcel OD column.

Supporting Information (see footnote on the first page of this article): Details of experimental procedures and characterization data, including spectra for binding studies, optimization of asymmetric hydrogenation reactions, and copies of ^1H, ^{13}C and ^{31}P NMR spectra.

Acknowledgments

Financial support from the National Natural Science Foundation of China (NSFC) (grant numbers 21232008 and 21373231), the National Basic Research Program of China (973 Programs, grant numbers 2010CB833300 and 2011CB808600), and the Chinese Academy of Sciences is gratefully acknowledged.

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Received: June 10, 2014
Published Online: September 8, 2014

