Tetrahedron: *Asymmetry* 21 (2010) 1411–1420

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Rh(I) coordination chemistry of hexacationic *Dendriphos* ligands and their application in hydroformylation catalysis

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ARTICLE INFO

Article history:
Received 1 March 2010
Accepted 19 April 2010
Available online 31 May 2010

Dedicated to Professor Henri Kagan on the occasion of his 80th birthday

ABSTRACT

The coordination chemistry of hexacationic *Dendriphos* ligands L* with respect to Rh(I), as well as their application in Rh-catalyzed hydroformylation reactions, is described. Complexes of the type $RhCl(CO)(L^*)_2$ were synthesized and characterized. The results show that *Dendriphos* ligands are weaker σ-donors and/or stronger π-acceptors compared to PPh_3. The reaction of L* with $[Rh(cod)_2]BF_4$ in MeCN afforded monophosphine-Rh(I) complexes of the type Rh(cod)(MeCN)(L*), which points to the tendency of these ligands to form coordinatively unsaturated metal complexes. The catalytic performance of *Dendriphos* ligands in the Rh-catalyzed hydroformylation appeared to be dominated by steric effects arising from the large dendritic shells of these ligands. Furthermore, the possibility of tuning the catalytic activity and selectivity of the catalytic species, by changing the six counteranions of the hexacationic *Dendriphos* ligand, has been investigated. Changing the anions from BF_4^- to the chiral anions camphorsulphonate or Δ-Trisphat did not render the hydroformylation reaction of styrene enantioselective, albeit small changes in its regioselectivity were observed.

1. Introduction

Hydroformylation of olefins is one of the most important, industrially applied processes in homogeneous catalysis.[1,2] Rh-catalyzed hydroformylation using catalysts modified with phosphine ligands was reported by Wilkinson in 1968.[3] In 1984, the industrial Ruhrchemie/Rhône-Poulenc process went into operation, which employs the water-soluble, trisulfonated phosphine TPPTS (3,3′,3″-phosphinidynetris(benzenesulfonic acid), trisodium salt) in an aqueous biphasic system for the Rh-catalyzed hydroformylation of propene, while allowing separation and recycling of the Rh/TPPTS catalyst.[4] Some recent developments in hydroformylation research include the development of suitable ligands for hydroformylation in supercritical CO_2, ionic liquids, or other unconventional media for multiphase homogeneous catalysis.[1,5] Furthermore, achieving control of the hydroformylation regioselectivity, leading to exclusive production of either the linear or branched aldehyde, has been an important issue. Major progress in this area has been made by, *e.g.*, Van Leeuwen et al. through the development of the *bite angle* concept for chelating diphosphines.[6] Several examples of dendritic catalysts containing phosphine functionalities have also been applied in hydroformylation reactions, and in some cases facilitated catalyst separation or increased product regioselectivities have been achieved.[7,8]

We have previously reported hexa-*meta*-ammoniomethyl-functionalized *Dendriphos* ligands $[\mathbf{1}]^{6+}$–$[\mathbf{4}]^{6+}$ (Fig. 1) and their application in the Suzuki–Miyaura cross-coupling reaction.[9] *Dendriphos* ligands behave as very bulky ligands and lead to a preferential formation of coordinatively unsaturated phosphine metal complexes, which explains the observed high catalytic activity in the Suzuki–Miyaura reaction of catalytic systems employing these ligands. The presence of six permanent cationic charges in the backbone of this class of ligands is proposed to result in a significant inter-ligand Coulombic repulsion, which plays a crucial role in their bulky behavior. In the case of $[\mathbf{1}]^{6+}$, $[\mathbf{2}]^{6+}$, and tri-*para*-ammoniomethyl substituted ligand $[\mathbf{5}]^{3+}$,[9d] Coulombic repulsion forces have been demonstrated by an investigation of their coordination chemistry with respect to Pt(II).[10] Recently, tricationic $[\mathbf{5}]^{3+}$ has been successfully applied in combination with an anionic latex in biphasic aqueous hydroformylation of higher olefins.[11] As a continuation of the investigation of this class of ligands in homogeneous catalysis, we have recently focussed on a study of their coordination behavior with respect to Rh(I), as well as the application of these ligands in monophasic Rh-catalyzed hydroformylation reactions. The effects of both increasing the steric demand of the phosphine and changing the nature of the charge balancing anions in the dendritic structure on the catalytic activity have been explored.

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doi:10.1016/j.tetasy.2010.04.037

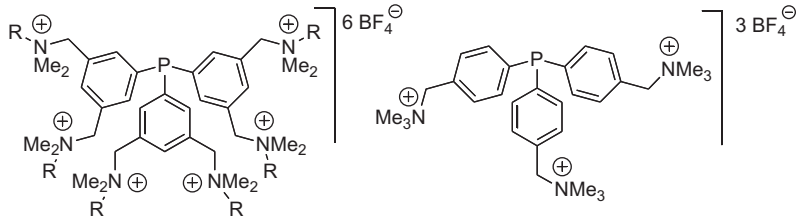


Figure 1. Hexacationic *Dendriphos* ligands [**1**][BF_4]$_6$–[**4**][BF_4]$_6$ and tricationic ligand [**5**][BF_4]$_3$. G1 and G2 represent first and second generation Fréchet-type dendrons, respectively.

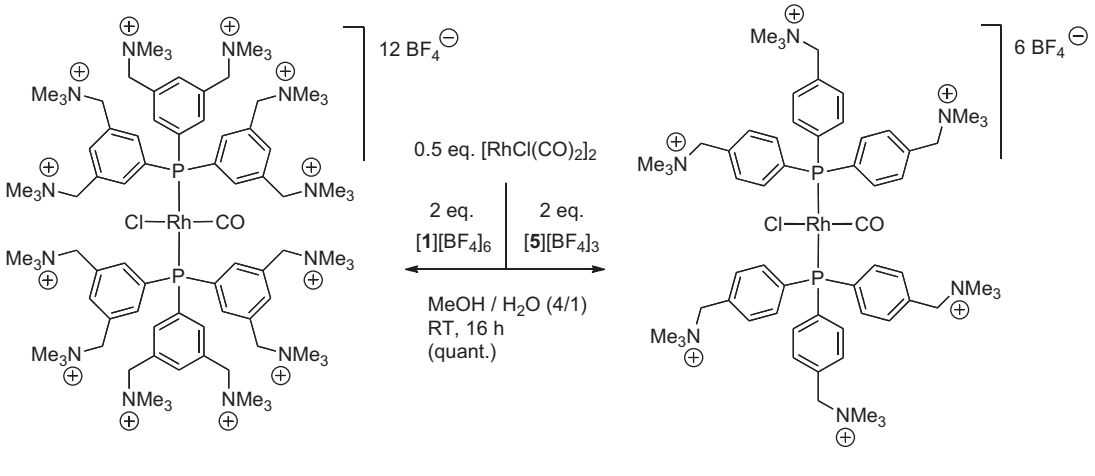
Asymmetric counterion-directed catalysis is a rapidly expanding area of research. This strategy employs chiral counterions as the only source of chiral information in reactions catalyzed by otherwise achiral transition metal complexes.[12] The potential of chiral anionic auxiliaries in asymmetric chemistry, including asymmetric catalysis, has been reviewed by Lacour et al.[12b,12f] For example, Toste et al. observed very high enantiomeric excess values in hydroalkoxylation and hydroamination reactions catalyzed by a cationic Au(I) complex in the presence of a chiral binaphthol-derived phosphate anion.[12e] Milstein et al. have employed anionic TPPTS as ligand in combination with chiral cations in Rh-catalyzed hydrogenation reactions. However, no enantiomeric excess was observed in this case.[13] As hexacationic *Dendriphos* ligands are surrounded by six counterions, we were interested to explore the potential of these systems for achieving chiral induction in Rh-catalyzed reactions, by using the anions as the only source of chirality. It was envisaged that association of the chiral anions with the ammonium groups in the coordinated *Dendriphos* ligands could lead to chiral induction at the Rh center. The influence of the polarity of the solvent, which may lead to solvent-separated or contact ion pairing,[14] and the influence of sterically demanding dendrons on the *Dendriphos* structure have been investigated.

2. Results

2.1. Rh(I) coordination chemistry

The tetrafluoroborate salts of the hexacationic phosphine ligands [**1**]$^{6+}$ and [**3**]$^{6+}$ and the tricationic ligand [**5**]$^{3+}$, as well as benchmark ligand PPh_3, were reacted with $[RhCl(CO)_2]_2$ at room temperature in MeOH/H_2O (4/1 (v/v)) ([**1**][BF_4]$_6$, [**5**][BF_4]$_3$), or CH_2Cl_2 (PPh_3, [**3**][BF_4]$_6$) in a phosphine to Rh molar ratio of 2. Analysis of the products by ^{31}P NMR indicated quantitative formation of the complexes *trans*-RhCl(CO)L_2 for L = PPh_3, [**1**][BF_4]$_6$, and [**5**][BF_4]$_3$, respectively (Scheme 1). The observed chemical shifts as well as the coupling constants $^1J_{P,Rh}$ of the complexes derived from [**1**]$^{6+}$ and [**5**]$^{3+}$ are close to those of *trans*-RhCl(CO)(PPh_3)$_2$ (Table 1). The values observed for the latter complex correspond well with those reported in the literature for the authentic complex.[15] The complexes *trans*-[RhCl(CO)(**1**)$_2$][BF_4]$_{12}$ **6** and *trans*-[RhCl(CO)(**5**)$_2$][BF_4]$_6$ **7** were isolated and fully characterized. In their ^{13}C NMR spectra, the *ipso*-, *ortho*- (and for **7**, the *meta*-) carbons of the aryl rings were observed as *pseudo* triplets due to the presence of AA′X systems (A = ^{31}P, X = ^{13}C),[16] which is consistent with the coordination of two phosphine ligands to the Rh center. Further confirmation of these structures was provided by high resolution ESI-MS measurements (Table 2, entries 1 and 2), which showed the presence of cations formed by dissociation of two or three BF_4^- ions. The value of the CO stretching vibration in the IR spectrum of *trans*-[RhCl(CO)(**1**)$_2$][BF_4]$_{12}$ **6** (1981 cm^{-1}) is significantly larger than that of the complex derived from PPh_3 (1963 cm^{-1}, Table 1),[17] indicating that this oligocationic phosphine is a weaker σ-donor and/or stronger π-acceptor than PPh_3 itself (see Section 3). For *trans*-[RhCl(CO)(**5**)$_2$][BF_4]$_6$ **7**, an intermediate value of 1971 cm^{-1} was observed.

The ^{31}P NMR spectrum of the mixture obtained upon reaction of $[RhCl(CO)_2]_2$ with [**3**]$^{6+}$ showed a very broad peak around 35 ppm, as well as a signal for free [**3**]$^{6+}$ and the signal for its phosphine



Scheme 1. The respective reactions of [**1**][BF_4]$_6$ and [**5**][BF_4]$_3$ with $[RhCl(CO)_2]_2$.

Table 1
^{31}P NMR and IR spectral data for complexes **6**, **7**, and *trans*-RhCl(CO)(PPh_3)$_2$

Entry	Complex	^{31}P NMR		IR
		δ (ppm)	$^1J_{P,Rh}$ (Hz)	ν(CO) (cm^{-1})
1	*trans*-RhCl(CO)(PPh_3)$_2$	30.1[a]	127	1963
2	*trans*-[RhCl(CO)(**1**)$_2$][BF_4]$_{12}$ **6**	34.7[b]	131	1981
3	*trans*-[RhCl(CO)(**5**)$_2$][BF_4]$_6$ **7**	30.7[c]	126	1971

[a] Measured in $CDCl_3$.
[b] Measured in D_2O.
[c] Measured in CD_3OD/D_2O (2/1).

oxide, even though the reaction was carried out under a dinitrogen atmosphere. This suggests the presence of an equilibrium between [RhCl(CO)(**3**)$_2$][BF_4]$_{12}$ and another complex in which the molar ratio of [**3**]$^{6+}$:Rh is 1. The latter could be a dimeric chloride- or CO-bridged complex, formed upon dissociation of [**3**]$^{6+}$.

Titrations of [Rh(cod)$_2$][BF_4] (cod = 1,5-cyclooctadiene) with [**1**][BF_4]$_6$, [**3**][BF_4]$_6$, [**5**][BF_4]$_3$, and PPh_3, respectively, were performed in CH_3CN/CD_3CN (8/2 (v/v)). At a phosphine to Rh molar ratio of 1, ^{31}P NMR showed a very broad signal at 29–32 ppm in all cases. In the case of PPh_3, addition of larger amounts of ligand led to the observation of a double triplet and a double doublet in an integration ratio of 1:2 (Table 3). This pattern is typical of an A_2BX system (A = the two mutually *trans* positioned phosphines, B = the phosphine *trans* to MeCN, X = Rh) and corresponds to the square planar complex [Rh(MeCN)(PPh_3)$_3$][BF_4].[18] At PPh_3:Rh = 4, a broad signal was observed at −4 ppm in the ^{31}P NMR spectrum, corresponding to free PPh_3. In the ^{1}H NMR spectra of these mixtures, distinct signals were generally observed for the cod ligand coordinated to Rh and uncoordinated cod. At PPh_3:Rh = 4, the signals for coordinated cod had been completely replaced by those for free cod, indicating that quantitative displacement of the cod ligands had occurred. Thus, the maximum number of molecules of PPh_3 that coordinate to Rh(I) is three under these circumstances. A similar behavior was observed for [**5**]$^{3+}$. In this case, however, the ^{31}P NMR signals were broad. As the [**5**]$^{3+}$:Rh ratio was increased, the ratio between the signals corresponding to free and coordinated cod in the ^{1}H NMR spectrum shifted toward the free cod. However, at [**5**]$^{3+}$:Rh = 4, a small amount of coordinated cod was still observed. At this ratio, the ^{31}P NMR spectrum at 0 °C clearly showed a characteristic A_2BX system, indicating the presence of the complex [Rh(MeCN)(**5**)$_3$][BF_4]$_{10}$ (Table 3, entry 4). At room temperature, most likely a fast ligand exchange equilibrium at the Rh(I) center exists between [**5**]$^{3+}$ and cod.

For both [**1**]$^{6+}$ and [**3**]$^{6+}$, addition of larger amounts of phosphine ligand than 1 equiv with respect to Rh immediately led to the observation of a broad signal corresponding to free phosphine while the broad signal at 32 ppm remained unchanged.[19] Lowering the temperature to −20 °C led to a sharpening of the signals and the observation of a doublet in both cases (Table 3). The chemical shift and the magnitude of $^1J_{P,Rh}$ of these species correspond well to those of *cis*-RhCl(cod)(PPh_3).[20] This indicates that the maximum number of phosphine ligands coordinated to Rh(I) under these circumstances is one for both [**1**]$^{6+}$ and [**3**]$^{6+}$. The complex derived from [**1**]$^{6+}$ was isolated and fully characterized. The ^{1}H NMR spectrum in D_2O showed signals for coordinated cod and MeCN. The room temperature ^{31}P NMR spectrum in D_2O consisted of a sharp doublet (32.1 ppm, $^1J_{P,Rh}$ = 156 Hz), suggesting that the broadness of the signal in CD_3CN is due to a ligand exchange equilibrium with solvent molecules, which does not occur in D_2O. In the ^{13}C NMR spectrum, the *ortho*-carbon signal of the aryl rings in the phosphine was observed as a doublet, which is consistent with the coordination of only one [**1**]$^{6+}$ ligand to the Rh center. Based on these data, the species formed were assigned to *cis*-[Rh(cod)(MeCN)(L)][BF_4]$_7$ (L = **1** or **3**) (Scheme 2). By ESI-MS, the cations [Rh(cod)(**1**)][BF_4]$_{7-n}^{n+}$ (n = 2, 3) were observed (Table 2, entry 3). The MeCN ligand most likely dissociates from the Rh(I) center during the ESI-MS measurement. Thus, the respective reactions of both [**1**]$^{6+}$ and [**3**]$^{6+}$ with [Rh(cod)$_2$]BF_4 lead to complexes in which a maximum of one phosphine ligand is coordinated to the Rh(I) center. This behavior is dramatically different from that of PPh_3, which gave rise to the formation of a trisphosphine Rh(I) species. The similarity of the reactivity of relatively small [**1**]$^{6+}$ and that of dendritic [**3**]$^{6+}$ suggests that the presence of six ammoniomethyl substituents, rather than the large dendritic shell in [**3**]$^{6+}$, is responsible for the observed coordination behavior.

Table 2
ESI-MS data for complexes **6**, **7**, and **8**

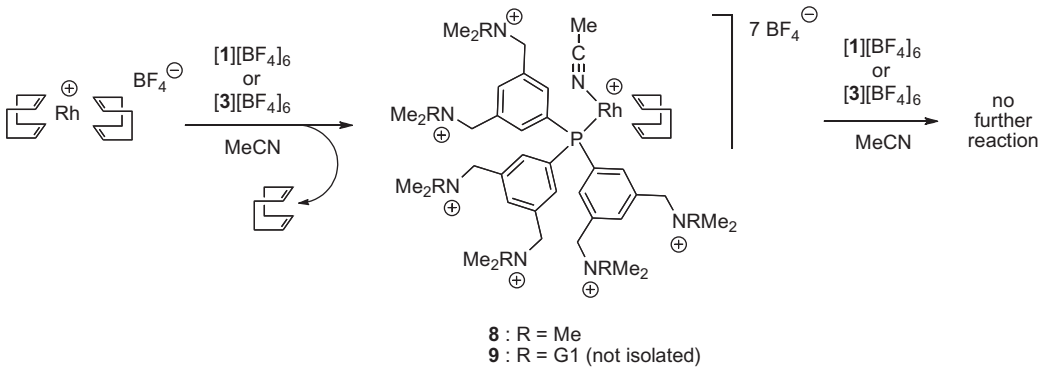
Entry	Complex	Major ions observed	Calcd (m/z)	Found (m/z)
1[a]	*trans*-[RhCl(CO)(**1**)$_2$][BF_4]$_{12}$ **6**	[RhCl(CO)(**1**)$_2$][BF_4]$_9^{3+}$	779.351	779.352
2[a]	*trans*-[RhCl(CO)(**5**)$_2$][BF_4]$_6$ **7**	[RhCl(CO)(**5**)$_2$][BF_4]$_4^{2+}$	735.276	735.284
		[RhCl(CO)(**5**)$_2$][BF_4]$_3^{3+}$	461.183	461.179
3	*cis*-[Rh(cod)(MeCN)(**1**)][BF_4]$_7$ **8**	[Rh(cod)(**1**)][BF_4]$_5^{2+}$	670.30	670.28
		[Rh(cod)(**1**)][BF_4]$_4^{3+}$	417.86	417.85

[a] High resolution measurement.

Table 3
^{31}P NMR spectral data for several phosphine–Rh(I) complexes[a]

Entry	Rh–P Complex	δ (ppm)	$^1J_{P,Rh}$ (Hz)	$^2J_{P,P}$ (Hz)	Reference
1	[Rh(MeCN)(PPh_3)$_3$][BF_4]	45.5 (dt)	174	41	This work, 18
		32.8 (dd)	137	41	
2[b]	*cis*-[Rh(cod)(MeCN)(**1**)][BF_4]$_7$ **8**	32.4 (d)	152	–	This work
3[b,c]	*cis*-[Rh(cod)(MeCN)(**3**)][BF_4]$_7$ **9**	32.6 (d)	150	–	This work
4[c,d]	[Rh(MeCN)(**5**)$_3$][BF_4]$_{10}$ **10**	45.7 (dt)	176	41	This work
		32.0 (dd)	138	40	
5	*cis*-RhCl(cod)(PPh_3)	31.5 (d)	152	–	20

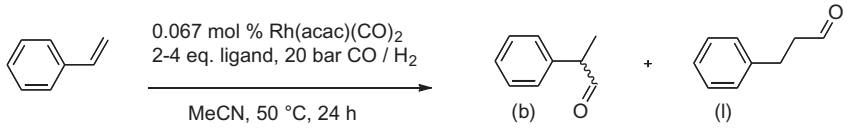
[a] Measured in CH_3CN/CD_3CN (8/2), except for entry 5, in THF/C_6D_6.
[b] Measured at -20 °C.
[c] Not isolated.
[d] Measured at 0 °C.



Scheme 2. The respective reactions of $[\mathbf{1}][BF_4]_6$ and $[\mathbf{3}][BF_4]_6$ with $[Rh(cod)_2][BF_4]$.

2.2. Application of Dendriphos ligands in Rh-catalyzed hydroformylation

Dendriphos ligands $[\mathbf{1}][BF_4]_6$–$[\mathbf{4}][BF_4]_6$ were applied in the Rh-catalyzed hydroformylation of styrene (reaction 1). $Rh(acac)(CO)_2$ was used as Rh precursor and L:Rh ratios of 2 and 4 were tested at an Rh loading of 0.067 mol %, using 20 bar of syngas at 50 °C. For comparison, triphenylphosphine was tested under identical conditions. Acetonitrile was chosen as solvent for the reaction, as it is the only solvent in which all five ligands are soluble. The reaction mixtures were clear, homogeneous solutions in all cases. The reactions were performed in an AMTEC SPR16 parallel reactor, allowing simultaneous screening of up to four reactions. During the reaction, the gas uptake was monitored and used to calculate the turnover frequency (TOF) values. After a reaction time of 24 h, the product mixtures were analyzed by GC.



(1)

For all reactions, analysis of the product mixtures by GC after 24 h indicated complete conversion and chemoselectivity toward aldehydes. The use of *Dendriphos* ligands leads to lower rates and branched to linear (*b*:*l*) selectivities compared to PPh_3. Furthermore, the results show a clear decrease in the observed TOF values within the *Dendriphos* family upon increase of the ligand size (higher generation) (Fig. 2). The application of $[\mathbf{3}][BF_4]_6$ in the hydroformylation of 1-octene was also studied (Table 4). Again, a lower reaction rate compared to PPh_3 was observed. For this substrate, PPh_3 and $[\mathbf{3}][BF_4]_6$ give similar regioselectivities.

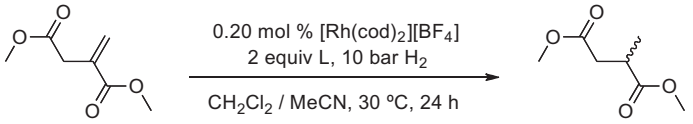
2.3. Synthesis of assemblies of $[\mathbf{1}]^{6+}$and $[\mathbf{3}]^{6+}$ with chiral anions and their application in Rh-catalyzed hydroformylation and hydrogenation

Next, [Na][Δ-Trisphat] **11** was prepared by reaction of [cinchonidinium][Δ-Trisphat][21,22] with NaH. The enantiomeric purity of the product was confirmed by comparison of its circular dichroism spectrum to that of the starting compound [cinchonidinium][Δ-Trisphat], which at the same concentration gave identical ellipticity values within experimental error (see Section 5). Subsequent exchange of the halide counteranions in $[\mathbf{1}]^{6+}$ and $[\mathbf{3}]^{6+}$ for Δ-Trisphat was accomplished by treatment of $[\mathbf{1}]Cl_6$ and $[\mathbf{3}]Br_6$, respectively, with 6 equiv of [Na][Δ-Trisphat] (Scheme 3).

Upon combining solutions of the *Dendriphos* and Trisphat salts in CH_2Cl_2/MeCN, precipitation of insoluble sodium halide salts occurred, which could be separated by filtration. Drying of the remaining solutions in vacuo then conveniently gave *Dendriphos*/Δ-Trisphat assemblies **12** and **13**. The assembly $[\mathbf{3}]$[camphorsulfonate]$_6$ **14** was prepared by ion exchange of $[\mathbf{3}][BF_4]_6$ with an excess of $[NH_4]$[camphorsulfonate] in a biphasic CH_2Cl_2/H_2O mixture. Quantitative ion exchange was ensured by elemental analysis for all three cases. Analysis by ESI-MS for **12** and **14** led to detection of the expected masses for the ions $[\mathbf{1}][Trisphat]_{(6-n)}^{n+}$ (n = 2, 3) and $[\mathbf{3}][camphorsulfonate]_{(6-n)}^{n+}$ (n = 2, 3, 4), which were formed by dissociation of several anions from the assemblies during the mass measurements. The assemblies **12** and **13** were further characterized by optical rotation measurements as well as circular dichroism spectroscopy. In both cases, the results were identical to those obtained for [Na][Δ-Trisphat] **11** (see Section 5).

The effect of changing the counteranions in the ligands $[\mathbf{1}]^{6+}$ and $[\mathbf{3}]^{6+}$ on the regio- and enantioselectivity in the hydroformylation of styrene was investigated (Table 5). In all cases, an L:Rh ratio of 2 was used and the conversion and chemoselectivity toward aldehydes were quantitative after 24 h. Changing the counterions of $[\mathbf{3}]^{6+}$ from BF_4 to camphorsulfonate or Δ-Trisphat (entries 3–7) gave a small decrease in selectivity, while a small increase was seen for $[\mathbf{1}]^{6+}$ (entries 1 and 2). For $[\mathbf{3}][BF_4]_6$ and $[\mathbf{3}]$[camphorsulfonate]$_6$, changing the solvent from MeCN to CH_2Cl_2 led to slightly lower selectivities. Unfortunately, no enantioselectivity was observed in these reactions.

Ligands $[\mathbf{1}]^{6+}$ and $[\mathbf{3}]^{6+}$ were also applied in the hydrogenation of dimethyl itaconate (reaction 2, Table 6). In the reactions using $[\mathbf{3}]^{6+}$, low conversions were obtained when CH_2Cl_2 was used as the solvent (entries 3, 5, and 7), suggesting that $[\mathbf{3}]^{6+}$ does not efficiently stabilize the Rh center under these conditions. The presence of a small amount of MeCN dramatically increased the catalytic activity in some cases (entries 4 and 6). Changing the counterion from BF_4 to camphorsulfonate or Δ-Trisphat did not lead to significant enantiomeric excess.



(2)

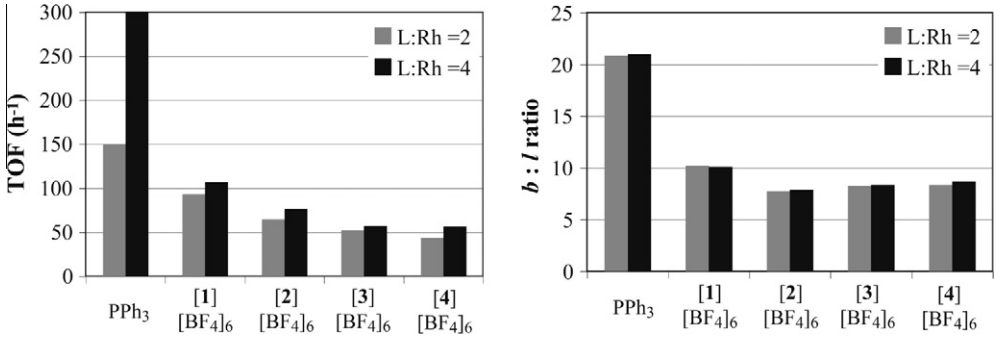


Figure 2. TOF values (left) and *b*:*l* ratios (right) for hydroformylation of styrene using $Rh(acac)(CO)_2$ in combination with PPh_3 and [**1**][BF_4]$_6$–[**4**][BF_4]$_6$ (reaction 1). TOF values were calculated at 20% conversion.

Table 4
Application of [**3**][BF_4]$_6$ in the hydroformylation of 1-octene[a]

Entry	L	L:Rh	*l*:*b*	TOF (h^{-1})
1	PPh_3	4	2.7	857
2	[**3**][BF_4]$_6$	2	2.4	300
3	[**3**][BF_4]$_6$	4	2.8	273

[a] Reaction conditions: 0.067 mol % Rh, MeCN, 80 °C, 20 bar CO/H_2, 24 h. Conversion and chemoselectivity toward aldehydes are quantitative in each case.

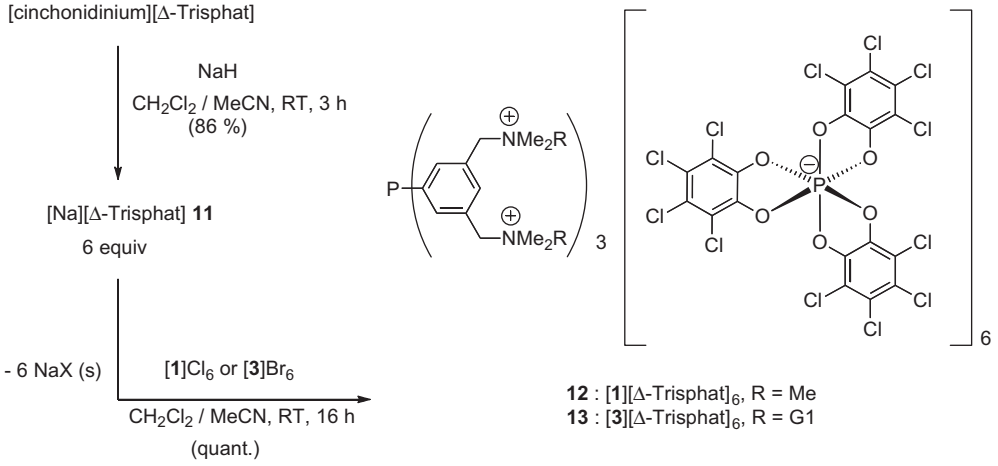
Table 5
Application of [**1**]$^{6+}$ and [**3**]$^{6+}$ with chiral anions in the hydroformylation of styrene (reaction 1)

Entry	Ligand	Solvent	$p(H_2+CO)$ (bar)	*b*:*l*	ee (%)
1	[**1**][BF_4]$_6$	MeCN	20	10.2	0
2	[**1**][Δ-Trisphat]$_6$ **12**	MeCN	20	11.0	2
3	[**3**][BF_4]$_6$	MeCN	20	8.3	0
4	[**3**][camphorsulfonate]$_6$ **14**	MeCN	20	6.9	0
5	[**3**][BF_4]$_6$	CH_2Cl_2	35	7.2	0
6	[**3**][camphorsulfonate]$_6$ **14**	CH_2Cl_2	35	6.6	0
7	[**3**][Δ-Trisphat]$_6$ **13**	CH_2Cl_2	35	5.4	0

3. Discussion

The frequency of the CO stretching vibration (ν(CO)) in the IR spectrum of complexes of the type *trans*-$RhCl(CO)L_2$ (L = monodentate phosphine ligand) is often used as a measure of the combination of σ-donating and π-accepting characteristics of L with respect to a transition metal.[23] In these complexes, electron density donated by L enhances back-donation from the metal center into the LUMO orbital of the CO ligand, which leads to a decrease of ν(CO). A higher donating strength of the phosphine thus corresponds to a lower carbonyl stretching frequency. The higher ν(CO) in the IR spectrum of complex *trans*-[$RhCl(CO)(\mathbf{1})_2$][BF_4]$_{12}$ (**6**) compared to *trans*-$RhCl(CO)(PPh_3)_2$ (Table 1) indicates that [**1**]$^{6+}$ is a weaker σ-donor and/or a stronger π-acceptor than PPh_3. This result is consistent with the magnitude of the $^1J_{P,Se}$ coupling constant in ^{31}P NMR of the phosphine selenide of [**1**]$^{6+}$.[9d] A significantly larger $^1J_{P,Se}$ coupling constant was observed for [**1**(Se)]$^{6+}$ compared to PPh_3(Se), indicating the lower σ-donating strength of the former. Although the corresponding *trans*-$RhCl(CO)(L)_2$ complexes for L = [**2**][BF_4]$_6$–[**4**][BF_4]$_6$ have not been prepared, we believe that all four *Dendriphos* ligands have similar electronic characteristics on the basis of measurements of the corresponding phosphine selenides.[9d] The lower donating strength of *Dendriphos* ligands can be explained by the electron-withdrawing effect of the six $-(CH_2)NRMe_2^+$ substituents.[24]

It has been well established that triarylphosphine ligands substituted with electron-withdrawing groups lead to faster catalysts compared to PPh_3 in Rh-catalyzed hydroformylation.[25] The lower rates observed for [**1**][BF_4]$_6$–[**4**][BF_4]$_6$ compared to PPh_3 in the hydroformylation of both styrene and 1-octene are thus unexpected. A possible explanation for this trend is the increase in ligand size within the *Dendriphos* ligand series. The rate-limiting step in hydroformylation reactions is assumed to be either CO dissociation or alkene coordination.[1] The presence of a large dendritic ligand might limit the accessibility of the catalytic center



Scheme 3. Ion exchange from halide to Δ-Trisphat for [**1**]$^{6+}$ and [**3**]$^{6+}$.

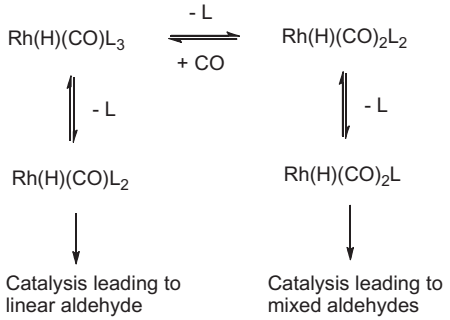
Table 6
Application of $[\mathbf{1}]^{6+}$ and $[\mathbf{3}]^{6+}$ with chiral anions in hydrogenation of dimethyl itaconate (reaction 2)

Entry	Ligand	Solvent	Conversion (%)	ee (%)
1	$[\mathbf{1}][BF_4]_6$	MeCN	>99	0
2	$[\mathbf{1}][\Delta\text{-Trisphat}]_6$ **12**	CH_2Cl_2/MeCN (7/1)	99	0
3	$[\mathbf{3}][BF_4]_6$	CH_2Cl_2	13	0
4	$[\mathbf{3}][BF_4]_6$	MeCN	>99	0
5	$[\mathbf{3}][\text{camphorsulfonate}]_6$ **14**	CH_2Cl_2	4	0
6	$[\mathbf{3}][\text{camphorsulfonate}]_6$ **14**	CH_2Cl_2/MeCN (7/1)	73	0
7	$[\mathbf{3}][\Delta\text{-Trisphat}]_6$ **13**	CH_2Cl_2	60	4
8	$[\mathbf{3}][\Delta\text{-Trisphat}]_6$ **13**	CH_2Cl_2/MeCN (7/1)	60	2
9	$[\mathbf{3}][\Delta\text{-Trisphat}]_6$ **13**	CH_2Cl_2/MeCN (1/7)	75	0

for substrate molecules, thereby slowing down the alkene coordination step and thus the overall reaction. A similar effect has been observed for dendritic carbosilane-substituted phosphines.[7d,e]

The use of 4 versus 2 equiv of ligand with respect to Rh leads to a doubling of the hydroformylation TOF in the case of PPh_3. This effect has been observed before in polar solvents.[26] In contrast, only a small increase is observed for $[\mathbf{1}][BF_4]_6$–$[\mathbf{4}][BF_4]_6$ upon doubling the phosphine concentration. This difference might suggest that the combination of $Rh(acac)(CO)_2$ and *Dendriphos* ligands leads to incomplete formation of the catalytically active species (Scheme 4). The decrease in rate would then be caused by a decrease in the effective concentration of active species due to formation of other catalytically inactive species. It is not clear which species are present under catalytic conditions and to what extent these species lead to catalytically active or inactive species. Plausible candidates for a type of species which can diminish the observed activity are the dimeric CO-bridged complexes.[7d]

Several different (pre)catalytic species are known to be in equilibrium with each other when monodentate phosphines are used in hydroformylation reactions.[1] The equilibria lead to the two key catalytic species $RhH(CO)L_2$ and $RhH(CO)_2L$, which are formed via one or two subsequent phosphine dissociation steps (Scheme 4). For aliphatic substrates such as 1-octene, it is widely acknowledged that the linear/branched regioselectivity ratio of the product aldehydes is largely controlled by the competitive reactions of the olefin substrate with these catalytic species. The bisphosphine intermediate $RhH(CO)L_2$ leads to selective formation of the sterically least hindered substrate, that is, the linear isomer, while the monophosphine intermediate $RhH(CO)_2L$ is far less selective.[1]



Scheme 4. Precatalytic and catalytic species playing a role in product regioselectivities in hydroformylation of 1-octene.

In the hydroformylation of 1-octene, the use of $[\mathbf{3}][BF_4]$ gave a nearly identical *l*:*b* regioselectivity compared to PPh_3. This suggests that the ratio between the monophosphine and bisphosphine-Rh catalytically active species formed in situ is not significantly different for $[\mathbf{3}][BF_4]_6$ ligands compared to PPh_3. This is corroborated by the fact that no significant isomerization of the alkene starting material was observed, which is known to be enhanced when a relatively high concentration of monophosphine-Rh species is present.[27] The behavior of $[\mathbf{3}][BF_4]$ in the hydroformylation of 1-octene thus contrasts to previous results obtained in the application of *Dendriphos* ligands in the Pd-catalyzed Suzuki–Miyaura reaction. In these studies, the tendency of *Dendriphos* ligands toward the formation of coordinatively unsaturated, monophosphine-metal complexes was clearly reflected by their performance as ligands in this catalytic reaction.[9b–d]

Phosphine-free Rh complexes or Rh nanoparticles formed in situ during the reaction are not believed to play a significant role in the catalytic hydroformylation reactions using *Dendriphos* ligands. The use of phosphine-free Rh species or Rh nanoparticles are reported to give *l*:*b* ratios between 1.0 and 1.8 for hydroformylation of 1-octene,[25c,28] which clearly do not correspond to the observed ratio of 2.8 using $[\mathbf{3}][BF_4]_6$.

In the hydroformylation of styrene, all *Dendriphos* ligands lead to lower branched to linear (*b*:*l*) regioselectivities compared to PPh_3 (Fig. 2, right), with no apparent trend. Possibly, the dendritic shell of *Dendriphos* ligands might favor to some extent the formation of the linear aldehyde, for steric reasons.[29] The main product, however, is still the branched aldehyde in all cases. This is generally observed for hydroformylation of styrene under the applied conditions, even for phosphine-free Rh catalysts, due to the formation of η^3-benzyl intermediates, which lead to the branched product.[1,30]

We speculated that association of chiral anions with the ammonium groups in *Dendriphos* ligands could lead to chiral induction at the catalytic Rh center in the hydroformylation or hydrogenation reactions. The cationic phosphine ligands were envisaged as a way to bring the anionic chiral auxiliaries in proximity with the catalytic center. Depending on the polarity of the solvent, either solvent-separated ion pairing or contact ion pairing[14] can occur between the anions and the ammonium cations. We therefore included the use of CH_2Cl_2 as a solvent of low polarity in these investigations, in order to enhance the association of the chiral anions with the catalytic species, through contact ion pairing with the ammonium cations in the hexacationic *Dendriphos* ligands. Unfortunately, significant enantioselectivity was not observed in any of the reactions, using either MeCN or CH_2Cl_2 as solvent. This indicates that no transfer of chiral information occurs from the anions to the catalytic center. It is plausible that the chiral anions are located too far away from the catalytic center, even when contact ion pairing occurs. Furthermore, the anions are probably still free to rotate, which further hampers any transfer of chiral information.

In terms of *b*:*l* product regioselectivity in the hydroformylation of styrene, using CH_2Cl_2 as solvent, changing the counterions of $[\mathbf{3}]^{6+}$ from BF_4^- to camphorsulfonate or Δ-Trisphat led to small changes. A slightly higher preference for the formation of the linear isomer was observed (Table 5, entries 5–7). This could be due to an increase in the effective size of the phosphine ligand with the larger anions, which is expected to favor formation of the sterically least hindered, linear product. This suggests that in CH_2Cl_2, the anions are indeed closely associated with the ammonium cations in the *Dendriphos* structure through contact ion pairing.

4. Conclusions

Measurement of the CO stretching vibration by IR spectroscopy of the complex $[RhCl(CO)(\mathbf{1})_2][BF_4]_{12}$ indicates that $[\mathbf{1}]^{6+}$ is a weaker σ-donor and/or a stronger π-acceptor compared to PPh_3. Furthermore, the reactivity of $[\mathbf{1}][BF_4]_6$ and $[\mathbf{3}][BF_4]_6$ with respect to $[Rh(cod)_2][BF_4]$ shows a tendency toward the formation of Rh(I) complexes with a low phosphine coordination number, which is most likely caused by inter-ligand Coulombic repulsion forces. The combination of *Dendriphos* ligands $[\mathbf{1}][BF_4]_6$–$[\mathbf{4}][BF_4]_6$ with $Rh(acac)(CO)_2$ leads to active hydroformylation catalysts. Complete conversion and chemoselectivity toward aldehydes were observed for both styrene and 1-octene as substrates. Within the *Dendriphos* ligand family, decreases in both the rate and the product regioselectivity were seen with higher ligand generations, as well as in comparison to the benchmark ligand triphenylphosphine. These observations cannot be directly related to the coordination behavior of *Dendriphos* ligands with respect to Rh(I). Instead, their performance as ligands in the hydroformylation reaction seems to be dominated by the steric effects that arise from the large dendritic shells of these ligands, rather than by their reduced σ-donating strength or the presence of Coulombic inter-ligand repulsion forces. Finally, the possibility of inducing chirality by changing the anions in the *Dendriphos* structure from BF_4^- to the chiral anions camphorsulfonate or Δ-Trisphat was explored. Unfortunately, this did not lead to enantioselectivity, in either MeCN or CH_2Cl_2 as solvents, indicating that under catalytic conditions, the chiral anions are not located in a well-defined orientation that is close enough to the catalytic Rh center for transfer of chiral information to occur.

5. Experimental

5.1. General remarks

Experiments involving sensitive reagents were performed under an inert N_2 atmosphere using standard Schlenk techniques. Manipulations involving free phosphines were carried out in deoxygenated solvents. Prior to use, MeCN was distilled from Na and CH_2Cl_2 from CaH_2. $[RhCl(CO)_2]_2$, $Rh(acac)(CO)_2$ and ammonium camphorsulfonate were purchased from Aldrich. Amberlite IRA-900 resin was purchased from Acros Chimica. $[\mathbf{1}]I_6$,[9a] $[\mathbf{2}]Br_6$–$[\mathbf{4}]Br_6$,[9a] $[\mathbf{5}]I_3$,[9d] [cinchonidinium][Δ-Trisphat],[21] and $[Rh(cod)_2][BF_4]$[31] were synthesized according to literature procedures. NMR spectra were measured on a Varian Inova 300 or a Varian AS 400 spectrometer at 25 °C unless stated otherwise. ^1H and $^{13}C\{^1H\}$ spectra were referenced to residual solvent signals. IR spectra (ATR) were measured with a Perkin–Elmer Spectrum One FT-IR instrument. Elemental analyses were carried out by Dornis & Kolbe, Mikroanalytisches Laboratorium, Müllheim a/d Ruhr, Germany. Synthesis gas [CO (99.997%)/H_2 (99.997%) 1:1] and hydrogen were purchased from Linde gas. Catalytic samples were analyzed by GC using a Shimadzu GC 17A, equipped with an HP Pona column (crosslinked Me Siloxane) and chiral GC using a Shimadzu GC 2010, equipped with a Lipodex-E column. Time-of-flight electrospray ionization mass spectra (ESI-MS) were measured by the Biomolecular Mass Spectrometry and Proteomics Group, Utrecht University, on a Micromass LC-T mass spectrometer (Waters, Manchester, UK), operating in positive ion mode. Samples were introduced at concentrations of 20–50 μM. The nanospray needle potential was typically set to 1300 V and the cone voltage to 20–60 V. The source block temperature was set to 80 °C.

5.2. Synthesis of $[\mathbf{1}][BF_4]_6$–$[\mathbf{5}][BF_4]_3$

Hexacationic phosphines $[\mathbf{1}]I_6$ and $[\mathbf{2}]Br_6$ and tricationic phosphine $[\mathbf{5}]I_3$ were subjected to anion exchange using an Amberlite IRA-900 resin. Before use, the resin (50 g, Cl form) was rinsed with a solution of HBF_4 in demineralized water (1 M, 500 mL), followed by demineralized water (250 mL), a solution of $NaBF_4$ in MeOH/MeCN (1/1 (v/v), 0.3 M, 250 mL),[32] demineralized water (500 mL), and MeOH/MeCN (1/1 (v/v), 100 mL). The ion exchange was performed under a N_2 atmosphere using MeOH/MeCN (1/1 (v/v)) as the eluent (150 mL), followed by evaporation of the solvent in vacuo. A column with dimensions 20–25 cm (length) and 2 cm (width) was used. For $[\mathbf{3}]^{6+}$ and $[\mathbf{4}]^{6+}$, the exchange was performed by mixing a solution of the ligands in CH_2Cl_2 (100 mL) with a solution of $NaBF_4$ in demineralized water (1 M, 4 × 100 mL), under a N_2 atmosphere. After separation of the layers, the organic layer was washed with demineralized water (5 × 100 mL) and evaporated to dryness.

5.2.1. $[\mathbf{1}][BF_4]_6$

Starting from 1.1 g $[\mathbf{1}]I_6$, the product was obtained as an off-white powder. Yield: 0.92 g (quant.). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.75 (d, $^3J_{P,H}$ = 7.2 Hz, 6H, *o*-Ar), 7.69 (s, 3H, *p*-Ar), 4.41 (s, 12H, NCH_2), 3.01 (s, 54H, $N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ (ppm) = 140.9 (d, $^2J_{P,C}$ = 20.7 Hz, *o*-Ar), 140.4 (d, $^1J_{P,C}$ = 14.9 Hz, *i*-Ar), 139.3 (s, *p*-Ar), 130.7 (d, $^3J_{P,C}$ = 7.0 Hz, *m*-Ar), 68.8 (s, NCH_2), 53.3 (s, $N(CH_3)_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = −3.2. ESI MS: (*m*/*z*) 1129.4 {$[M-BF_4]^+$, calcd 1129.6}, 521.16 {$[M-2BF_4]^{2+}$, calcd 521.30}, 318.41 {$[M-3BF_4]^{3+}$, calcd 318.53}. Elem. Anal. Calcd for $C_{42}H_{75}B_6F_{24}N_6P$ (1215.88): C, 41.49; H, 6.22; N, 6.91; P, 2.55. Found: C, 41.42; H, 6.20; N, 7.06; P, 2.63.

5.2.2. $[\mathbf{2}][BF_4]_6$

Starting from 1.0 g $[\mathbf{2}]Br_6$, the product was obtained as an off-white powder. Yield: 0.82 g (80%). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.85 (d, $^3J_{P,H}$ = 7.2 Hz, 6H, *o*-Ar), 7.65 (s, 3H, *p*-Ar), 7.55 (m, 30H, Ph), 4.43 (24H, NCH_2), 2.83 (s, 36H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ (ppm) = 141.3 (d, $^2J_{P,C}$ = 20.3 Hz, *o*-Ar), 140.6 (d, $^1J_{P,C}$ = 14.9 Hz, *i*-Ar), 139.7 (s, *p*-Ar), 134.2 (s, Ph), 131.7 (s, Ph), 130.4 (d, $^3J_{P,C}$ = 7.0 Hz, *m*-Ar), 130.2 (s, Ph), 128.3 (s, Ph), 69.1 (s, NCH_2), 68.2 (s, NCH_2), 49.3 (s, $N(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = −2.6. ESI MS: (*m*/*z*) 1585.4 {$[M-BF_4]^+$, calcd 1585.8}, 749.13 {$[M-2BF_4]^{2+}$, calcd 749.39}, 470.11 {$[M-3BF_4]^{3+}$, calcd 470.26}. Elem. Anal. Calcd for $C_{78}H_{99}B_6F_{24}N_6P$ (1672.46): C, 56.02; H, 5.97; Br, 0.0; N, 5.02; P, 1.85. Found: C, 55.88; H, 5.93; Br, 0.0; N, 4.96; P, 1.91.

5.2.3. $[\mathbf{3}][BF_4]_6$

Starting from 1.5 g $[\mathbf{3}]Br_6$, the product was obtained as an off-white powder. Yield: 1.2 g (80%). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.89 (d, $^3J_{P,H}$ = 6.8 Hz, 6H, *o*-Ar), 7.65 (s, 3H, *p*-Ar), 7.40–7.26 (m, 60H, Ph), 6.75 (18H, Ar′), 5.07 (s, 24H, OCH_2), 4.40 (s, 12H, NCH_2Ar'), 4.31 (s, 12H, NCH_2Ar), 2.82 (s, 36H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ (ppm) = 161.1 (s, *m*-Ar′), 141.3 (d, $^2J_{P,C}$ = 20.1 Hz, *o*-Ar), 140.6 (d, $^1J_{P,C}$ = 14.9 Hz, *i*-Ar), 139.6 (s, *p*-Ar), 137.7 (s, *o*-Ar′), 130.3 (d, $^3J_{P,C}$ = 7.0 Hz, *m*-Ar), 130.1 (s, Ph), 129.5 (s, Ph), 129.0 (s, Ph), 128.7 (s, Ph), 113.1 (s, *p*-Ar′), 105.3 (s, *i*-Ar′), 70.9 (s, OCH_2), 68.5 (NCH_2), 49.5 (s, $N(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = -2.2. ESI MS: (*m*/*z*) 1385.8 {$[M-2BF_4]^{2+}$, calcd 1385.6}, 894.52 {$[M-3BF_4]^{3+}$, calcd 894.76}, 649.42 {$[M-4BF_4]^{4+}$, calcd 649.32}. Elem. Anal. Calcd for $C_{162}H_{171}B_6F_{24}N_6O_{12}P$ (2945.92): C, 66.05; H, 5.85; Br, 0.0; N, 2.85; P, 1.05. Found: C, 65.78; H, 5.72; Br, 0.0, N, 2.84; P, 1.10.

5.2.4. $[\mathbf{4}][BF_4]_6$

Starting from 1.1 g $[\mathbf{4}]Br_6$, the product was obtained as an off-white powder. Yield: 0.88 g (85%). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.92 (br s, 6H, *o*-Ar), 7.64 (br s, 3H, *p*-Ar), 7.3–7.2 (br m, 120H, Ph), 6.7–6.6 (br m, 42H, overlapping Ar′, Ar″), 6.46 (s, 12H,

o-Ar′), 4.91 (s, 72H, OCH_2), 4.35 (br s, 12H, NCH_2Ar'), 4.25 (br s, 12H, NCH_2Ar), 2.75 (br s, 36H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ (ppm) = 161.0, (s, *m*-Ar″), 160.9 (s, *m*-Ar′), 141.3 (br s, Ar), 140.5 (br s, Ar), 140.3 (s, *o*-Ar′), 139.5 (br s, Ar), 138.0 (s, *o*-Ar″), 130.2 (br s, Ar), 129.9 (s, Ph), 129.5 (s, Ph), 128.9 (s, Ph), 128.7 (s, Ph), 113.0 (s, *p*-Ar′), 107.5 (s, *p*-Ar″), 105.5 (s, *i*-Ar′), 102.3 (s, *i*-Ar″), 70.7 (s, OCH_2), 69.0 (br., NCH_2), 49.5 (s, $N(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = -2.2. ESI MS: (*m*/*z*) 2659.3 $\{[M\text{-}2BF_4]^{2+}$, calcd 2659.7}, 1743.3 $\{[M-3BF_4]^{3+}$, calcd 1743.4}, 1286.0 $\{[M-4BF_4]^{4+}$, calcd 1286.1}. Elem. Anal. Calcd for $C_{330}H_{315}B_6F_{24}N_6O_{36}P$ (5492.85): C, 72.16; H, 5.78; Br, 0.0; N, 1.53; P, 0.56. Found: C, 72.08; H, 5.71; Br, 0.0; N, 1.54; P, 0.52.

5.2.5. $[5][BF_4]_3$

Starting from 1.9 g [**5**]I_3, the product was obtained as an off-white powder. Yield: 1.3 g (84%). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 7.57 (d, $^3J_{H,H}$ = 7.2 Hz, 6H, *m*-Ar), 7.45 (dd, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,P}$ = 7.8 Hz, 6H, *o*-Ar), 4.46 (s, 6H, CH_2), 3.06 (s, 27H, $N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) = 140.2 (d, $^1J_{C,P}$ = 13.2 Hz, *i*-Ar), 135.2 (d, $^2J_{C,P}$ = 19.9 Hz, *o*-Ar), 134.2 (d, $^3J_{C,P}$ = 7.3 Hz, *m*-Ar), 129.8 (s, *p*-Ar), 69.6 (s, CH_2), 53.3 (s, $N(CH_3)_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = -5.6 (s). ESI MS: (*m*/*z*) 282.66 $\{[M-2BF_4]^{2+}$, calcd 282.67}. Elem. Anal. Calcd for $C_{30}H_{45}B_3F_{12}N_3P$ (739.09): C, 48.75; H, 6.14; N, 5.69; P, 4.19. Found: C, 48.85; H, 6.13; N, 5.66; P, 4.26.

5.3. $[RhCl(CO)(\mathbf{1})_2][BF_4]_{12}$ 6

To a solution of [**1**]$[BF_4]_6$ (50.5 mg, 41.5 μmol) in MeOH/H_2O (4/1 (v/v), 5.0 mL) was added a solution of $[RhCl(CO)_2]_2$ (4.0 mg, 10 μmol, i.e., 21 μmol Rh) in MeOH (1.0 mL), upon which a precipitate formed. The mixture was stirred for 16 h at room temperature and subsequently dried in vacuo, yielding a brown oil (59 mg). NMR analysis of this crude product showed quantitative formation of **6**. Further purification was performed by washing with MeOH (2 × 20 mL), affording the product as an off-white powder. Yield: 28 mg (51%). ^1H NMR (400 MHz, D_2O): δ (ppm) = 8.13 (m, 12H, *o*-Ar), 8.00 (s, 6H, *p*-Ar), 4.57 (s, 24H, CH_2), 3.02 (s, 108H, $N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, D_2O): δ (ppm) = 140.8 (s, *m*-Ar), 140.6 (s, *p*-Ar), 133.9 (*pseudo* t, $J_{C,P}$ = 22.0 Hz, *i*-Ar), 129.9 (*pseudo* t, $J_{C,P}$ = 4.5 Hz, *o*-Ar), 67.9 (s, CH_2), 52.4 (s, $N(CH_3)_3$). $^{31}P\{^1H\}$ NMR (121 MHz, D_2O): δ (ppm) = 34.7 (d, $^1J_{P,Rh}$ = 131 Hz). IR: (cm^{-1}) 1981 (C-O). HR-ESI MS: (*m*/*z*) 779.352 $\{[M-3BF_4]^{3+}$, calcd 779.351}.

5.4. $[RhCl(CO)(\mathbf{5})_2][BF_4]_6$ 7

To a solution of [**5**]$[BF_4]_3$ (31.8 mg, 0.0430 mmol) in MeOH/H_2O (4/1 (v/v), 5.0 mL) was added a solution of $[RhCl(CO)_2]_2$ (4.0 mg, 10 mmol, i.e., 21 mmol Rh) in MeOH (1.0 mL). The mixture was stirred for 16 h at room temperature and subsequently dried in vacuo, affording the product as a yellow powder. Yield: 36 mg (quant.). ^1H NMR (300 MHz, CD_3OD/D_2O, 2/1 (v/v)): δ (ppm) = 7.92 (m, 12H, *o*-Ar), 7.72 (d, $^3J_{H,H}$ = 7.0 Hz, 12H, *m*-Ar), 4.58 (s, 12H, CH_2), 3.13 (s, 54H, $N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD/D_2O, 2/1 (v/v)): δ (ppm) = 136.2 (*pseudo* t, $J_{C,P}$ = 6.6 Hz, *m*-Ar), 135.3 (*pseudo* t, $J_{C,P}$ = 22.6 Hz, *i*-Ar), 134.0 (*pseudo* t, $J_{C,P}$ = 5.2 Hz, *o*-Ar), 131.6 (s, *p*-Ar), 69.7 (s, CH_2), 53.5 (s, $N(CH_3)_3$). $^{31}P\{^1H\}$ NMR (121 MHz, CD_3OD/D_2O, 2/1 (v/v)): δ (ppm) = 30.7 (d, $^1J_{P,Rh}$ = 126 Hz). IR: (cm^{-1}) 1971 (C–O). HR-ESI MS: (*m*/*z*) 735.284 $\{[M-2BF_4]^{2+}$, calcd 735.276}, 461.179 $\{[M-3BF_4]^{3+}$, calcd 461.183}.

5.5. $[Rh(cod)(MeCN)(\mathbf{1})][BF_4]_7$ 8

To a solution of $[Rh(cod)_2][BF_4]$ (15.0 mg, 0.0369 mmol) in MeCN (5.0 mL) was added [**1**]$[BF_4]_6$ (47.3 mg, 0.0389 mmol). The solution was stirred at room temperature for 2 h and subsequently dried in vacuo, yielding the product as a dark yellow powder. Yield: 57 mg (quant.). ^1H NMR (300 MHz, D_2O): δ (ppm) = 8.06 (d, 6H, $^3J_{H,P}$ = 10.8 Hz, *o*-Ar), 8.04 (s, 3H, *p*-Ar), 5.5 (br s, 4H, cod CH), 4.60 (s, 12H, CH_2), 3.12 (s, 54H, $N(CH_3)_3$), 2.45 (br s, 4H, cod CH_2), 2.15 (br s, 4H, cod CH_2), 2.01 (s, 3H, MeCN-Rh). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ (ppm) = 141.4 (s, Ar), 141.3 (s, Ar), 138.9 (m, *i*-Ar), 131.0 (d, $^2J_{C,P}$ = 10.8 Hz, *o*-Ar), 68.5 (s, CH_2), 53.3 (s, $N(CH_3)_3$), 31.3 (br s, cod CH_2) (cod CH and MeCN-Rh signals not resolved). $^{31}P\{^1H\}$ NMR (121 MHz, D_2O): δ (ppm) = 32.1 (d, $^1J_{P,Rh}$ = 156 Hz). ESI MS: (*m*/*z*) 670.28 $\{[M-MeCN\text{-}2BF_4]^{2+}$, calcd 670.30}, 417.85 $\{[M-MeCN\text{-}3BF_4]^{3+}$, calcd 417.86}. Elem. Anal. Calcd for $C_{52}H_{90}B_7F_{28}N_7PRh$ (1554.83): C, 40.17; H, 5.83; N, 6.31; P, 1.99. Found: C, 40.72; H, 6.43; N, 6.07; P, 1.91.

5.6. [Na][Δ-Trisphat] 11

At first, NaH (3.0 g, 65% dispersion in mineral oil, 81 mmol) was washed with hexane (3 × 50 mL) and subsequently suspended in CH_2Cl_2 (50 mL). To this suspension, a solution of enantiomerically pure [cinchonidinium][Δ-Trisphat] (1.42 g, 1.33 mmol) in CH_2Cl_2/MeCN (2/1 (v/v), 150 mL) was added dropwise in 30 min at room temperature. The white suspension was stirred at room temperature for 3 h and then the reaction was quenched by subsequent addition of EtOH and demineralized water. The mixture was dried in vacuo and washed with demineralized water (5 × 30 mL) and CH_2Cl_2 (3 × 30 mL). The crude product was then purified by silica column chromatography using CH_2Cl_2/acetone as eluent (gradient from 9/1 to 7/3 (v/v)), affording the product as a white powder. Yield: 0.91 g (86%) (R_f = 0.18, CH_2Cl_2/acetone, 7/3 (v/v)). $^{13}C\{^1H\}$ NMR (101 MHz, $(CD_3)_2CO$): δ (ppm) = 142.8 (d, $^2J_{P,C}$ = 6.6 Hz), 122.9 (s), 114.3 (d, $^3J_{P,C}$ = 19.9 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ (ppm) = -79.5. ESI MS: (*m*/*z*) 814.54 $\{[M+Na]^+$, calcd 814.54}. Elem. Anal. Calcd for $C_{18}Cl_{12}NaO_6P$ (791.59): C, 27.31; H, 0.0; Cl, 53.74. Found: C, 27.38; H, 0.14; Cl, 53.58. $[\alpha]_D^{20} = -332$ (*c* 1.0 mM in MeCN), −363 (*c* 1.0 mM in CH_2Cl_2), −413 (*c* 0.10 g/100 mL in EtOH, i.e. 1.26 mM). CD (MeCN, 5.0×10^{-5} M, 2 mm quartz cuvette, 20 °C) λ ($\Delta\varepsilon$) = 244 (−70), 220 (−297), 211 (+243).

5.7. $[\mathbf{1}][\Delta\text{-Trisphat}]_6$ 12

To a solution of [Na][Δ-Trisphat] (0.280 g, 0.354 mmol) in dry MeCN (10 mL) was added solid [**1**]Cl_6 (53 mg, 0.059 mmol) and the mixture was stirred for 16 h. The suspension was filtered over Celite and the filtrate was dried in vacuo, yielding the product as a white powder. Yield: 281 mg (quant.). ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 8.07 (d, $^3J_{P,H}$ = 7.2 Hz, 6H, *o*-Ar), 7.57 (s, 3H, *p*-Ar), 4.56 (s, 12H, CH_2), 3.09 (s, 54H, $N(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ (ppm) = 142.6 (d, $^2J_{P,C}$ = 7.0 Hz, Trisphat), 141.7 (d, $^2J_{P,C}$ = 21.1 Hz, *o*-Ar), 141.4 (d, $^1J_{P,C}$ = 14.2 Hz, *i*-Ar), 138.8 (s, *p*-Ar), 130.7 (d, $^3J_{P,C}$ = 7.0 Hz, *m*-Ar), 123.7 (s, Trisphat), 114.7 (d, $^3J_{P,C}$ = 19.8 Hz, Trisphat), 68.4 (s, CH_2), 53.6 (s, $N(CH_3)_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = −3.6 (PAr_3), −80.1 (Trisphat). ESI MS: (*m*/*z*) 1886.1 $\{[M-2Trisphat]^{2+}$, calcd 1884.7}, 1000.0 $\{[M-3Trisphat]^{3+}$, calcd 1000.3}. Elem. Anal. Calcd for $C_{150}H_{75}Cl_{72}N_6O_{36}P_7$ (5306.65): C, 33.95; H, 1.42; Cl, 48.10; N, 1.58; P, 4.09. Found: C, 34.10; H, 1.38; Cl, 47.89; N, 1.62; P, 3.92. $[\alpha]_D^{20} = -339$ (*c* 0.17 mM in MeCN, i.e. 1.0 mM Δ-Trisphat). CD (*c* 0.83×10^{-5} M in MeCN, i.e., 5.0×10^{-5} M Δ-Trisphat, 2 mm quartz cuvette, 20 °C) λ ($\Delta\varepsilon$) = 244 (−72), 220 (−307), 211 (+253).

5.8. $[\mathbf{3}][\Delta\text{-Trisphat}]_6$ 13

To a solution of [**3**]Br_6 (170 mg, 0.0587 mmol) in dry CH_2Cl_2 (10 mL) was added a solution of [Na][Δ-Trisphat] (0.280 g, 0.354 mmol) in dry MeCN (2 mL) and the mixture was stirred for

16 h. The suspension was filtered over Celite and the filtrate was dried in vacuo, redissolved in CH_2Cl_2, and filtered again over Celite. The filtrate was dried in vacuo, yielding the product as a light yellow powder. Yield: 404 mg (quant.). ^{1}H NMR (400 MHz, CD_3CN/$CDCl_3$, 1/1 (v/v)): δ (ppm) = 8.1–7.9 (br m, 9H, *o*- and *p*-Ar), 7.4–7.1 (br m, 60H, Ph), 6.8–6.6 (br m, 18H, Ar′), 4.95 (br s, 24H, OCH_2), 4.41 (br., 24H, NCH_2), 2.93 (br s, 36H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN/$CDCl_3$, 1/1 (v/v)): δ (ppm) = 160.7 (s, *m*-Ar′), 142.1 (d, $^2J_{P,C}$ = 6.6 Hz, Trisphat), 136.6 (s, *o*-Ar′), 128.9 (s, Ph), 128.5 (s, Ph), 128.0 (s, Ph), 123.0 (s, Trisphat), 114.2 (d, $^3J_{P,C}$ = 19.5 Hz, Trisphat), 112.8 (s, *p*-Ar'), 104.1 (s, *i*-Ar′), 70.6 (s, OCH_2), 68.0 (br s, NCH_2), 49.8 (s, $N(CH_3)_2$) (signals of Ar and *i*-Ph not resolved). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN/$CDCl_3$, 1/1 (v/v)): δ (ppm) = −2.0 (PAr_3), −80.0 (Trisphat). Elem. Anal. Calcd for $C_{270}H_{171}Cl_{72}N_6O_{48}P_7$ (7036.69): C, 46.09; H, 2.45; Cl, 36.28; N, 1.19; P, 3.08. Found: C, 45.65; H, 2.40; Cl, 36.25; N, 1.28; P, 2.85. $[\alpha]_D^{20} = -361$ (*c* 0.17 mM in CH_2Cl_2, i.e., 1.0 mM Δ-Trisphat). CD (*c* 0.83×10^{-5} M in MeCN, i.e., 5.0×10^{-5} M Δ-Trisphat, 2 mm quartz cuvette, 20 °C) λ ($\Delta\varepsilon$) = 244 (−62), 220 (−262), 211 (+214).

5.9. [3][camphorsulfonate]$_6$ 14

To a solution of [**3**][BF_4]$_6$ (0.55 g, 0.19 mmol) in CH_2Cl_2 (100 mL) was added a solution of ammonium camphorsulphonate (0.8 M in demineralized water, 25 mL). The mixture was vigorously stirred for 20 min. The layers were allowed to separate, the aqueous layer was removed, and the procedure was repeated twice with a fresh solution of ammonium camphorsulphonate. The organic layer was subsequently washed with demineralized water (4×50 mL) and dried in vacuo, yielding the product as an off-white powder. Yield: 0.58 g (82%). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 8.12 (d, $^3J_{P,H}$ = 6.8 Hz, 6H, *o*-Ar), 7.97 (s, 3H, *p*-Ar), 7.38–7.23 (m, 60H, Ph), 6.89 (s, 12H, *o*-Ar′), 6.68 (s, 6H, *p*-Ar′), 5.03 (s, 24H, OCH_2), 4.63 (s, 12H, NCH_2Ar'), 4.53 (s, 12H, NCH_2Ar), 3.01 (d, 6H, $^2J_{H,H}$ = 14.8 Hz, camph., CH_2SO_3), 2.92 (s, 36H, $N(CH_3)_2$), 2.63 (m, 6H, camph.), 2.51 (d, 6H, $^2J_{H,H}$ = 14.4 Hz, camph., CH_2SO_3), 2.13 (m, 6H, camph.), 1.89 (m, 6H, camph.), 1.79 (m, 6H, camph.), 1.68 (d, 6H, $J_{H,H}$ = 18.0 Hz, camph.), 1.46 (m, 6H, camph.), 1.16 (m, 6H, camph.), 0.93 (s, 18H, camph., CH_3), 0.66 (s, 18H, camph., CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) = 217.5 (s, camph., C=O), 160.9 (s, *m*-Ar′), 141.3 (m, overlapping Ar), 140.0 (br s, Ar), 137.8 (s, *o*-Ar′), 131.0 (s, *i*-Ph), 130.3 (d, $^3J_{P,C}$ = 7.0 Hz, *m*-Ar), 129.4 (s, Ph), 128.9 (s, Ph), 128.8 (s, Ph), 113.4 (s, *p*-Ar′), 104.7 (s, *i*-Ar′), 70.9 (s, OCH_2), 68.4 (s, NCH_2), 68.1 (s, NCH_2), 59.3 (s, camph.), 49.4 (s, $N(CH_3)_2$), 48.3 (s, camph.), 48.1 (s, camph.), 43.3 (s, camph.), 27.4 (s, camph.), 25.6 (s, camph.), 20.4 (s, camph.), 20.2 (s, camph.). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ (ppm) = -2.2. ESI MS: (*m*/*z*) 1674.3 {[M−2camph.]$^{2+}$, calcd 1674.3}, 1039.2 {[M−3camph.]$^{3+}$, calcd 1039.5}, 721.66 {[M−4camph.]$^{4+}$, calcd 721.85}. Elem. Anal. Calcd for $C_{222}H_{261}N_6O_{36}PS_6$ (3812.83): C, 69.93; H, 6.90; N, 2.20; P, 0.81. Found: C, 70.10; H, 6.97; N, 2.23; P, 0.80.

5.10. Procedure for titration of [Rh(cod)$_2$][BF_4] with [1][BF_4]$_6$, [3][BF_4]$_6$ and [5][BF_4]$_3$

A solution of [Rh(cod)$_2$][BF_4] (5–10 mg) in CD_3CN/CH_3CN (2/8 (v/v), 0.5 mL) was placed in an NMR tube. To this solution, portions of 0.1 mL of a stock solution of phosphine ligand (1.0 equiv with respect to Rh per 0.1 mL) were added via syringe, shaken at room temperature for 1 min, and analyzed.

5.11. General procedure for catalytic experiments in AMTEC

Catalytic experiments were performed in the parallel reactor system AMTEC SPR16, equipped with pressure sensors and a mass-flow controller suitable for monitoring and recording gas uptakes throughout the reactions. The stainless steel autoclaves of the AMTEC SPR16 were flushed automatically with argon 6 times to remove oxygen traces. The reactors were charged with a solution of the precatalyst under argon. The atmosphere was further exchanged with a 1/1 mixture of CO/H_2 (gas exchange cycle 1) and the reactors were heated and pressurized. In case of hydroformylation, the preformation of the catalyst under the applied conditions (vide infra) was performed for 2 h. Subsequently, the substrate was injected and the desired temperature and the final pressure were adjusted and kept constant throughout the experiment (V_{tot} = 8 mL). The uptake of synthesis gas was monitored and recorded automatically. At the end of the catalysis experiments, the reactors were cooled to room temperature and the autoclave contents were analyzed by means of GC and chiral GC.

5.12. Procedure for catalytic hydroformylation reactions

Rh(acac)(CO)$_2$ (3.0 mg, 0.012 mmol) and phosphine ligand (0.023–0.047 mmol) were dissolved in MeCN or CH_2Cl_2 (6.0 mL for hydroformylation of styrene, 5.3 mL for hydroformylation of 1-octene) and stirred for 5 min at room temperature. The clear, light green solutions were then transferred via syringe into the AMTEC parallel autoclaves. Catalyst preformation was carried out for 2 h at 50 °C under 20 bar CO/H_2. The substrate (for styrene, 2.0 mL (17 mmol), for 1-octene, 2.7 mL (17 mmol)) was subsequently added via syringe and the hydroformylation was carried out for 24 h at 20 bar CO/H_2 at 50 °C (styrene) or 80 °C (1-octene).

5.13. Procedure for catalytic hydrogenation reactions

[Rh(cod)$_2$][BF_4] (3.2 mg, 0.0079 mmol), phosphine ligand (0.016 mmol), and dimethyl itaconate (0.63 g, 4.0 mmol) were dissolved in MeCN or CH_2Cl_2 (8.0 mL) and stirred for 5 min at room temperature. The clear, light green solutions were subsequently transferred via syringe into the AMTEC parallel autoclaves. The hydrogenation was then carried out for 24 h at 10 bar H_2 at 30 °C.

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