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Synthesis and tetra-pincer nickel(II) and palladium(II) complexes of resorcin[4]arene-octophosphinite [Res(OPR$_2$)$_8$] and rhodium-catalyzed regioselective hydroformylation reaction†

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Abstract. The condensation reaction of resorcinol with pentanal yielded resorcin[4]arene **1** which on bromination using *N*-bromosuccinimide at room temperature produced tetra-bromide derivative **2**. The reactions of **2** with chlorodiphenylphosphine and *o*-phenylenephosphoro-chloridite yielded octaphosphinite **3** (here after referred as *octaphos*) and octaphosphite **4**, respectively. The reactions of **3** with Ni(COD)$_2$ or Pd$_2$(dba)$_3$·CHCl$_3$ in appropriate molar ratios yielded tetra-pincer complexes **5** and **6**, respectively. The structures of both the complexes were established by single crystal X-ray diffraction studies. The resorcin[4]arene backbone adopts a boat structure in these complexes. Typically, the Rh-catalyzed hydroformylation of styrene prevalently delivers branched (b) chiral aldehyde. A unique resorcin[4]arene skeleton based octaphos **3** was employed in the Rh-catalyzed hydroformylation of styrene. Hydroformylation of styrene with metal to ligand ratio of 1:1 (M:L) was found to be regioselective producing linear (l) aldehyde as major product with 100% conversion in 3h. The l:b ratio surprisingly increased when the *ortho* positions of styrene were populated by methyl and chloro substituents. In the hydroformylation of *p*-nitro styrene, despite electron withdrawing nature, triggered a remarkably high linear:branced aldehyde ratio of 2.4 (71% linear aldehyde). Highest linear selectivity of 97% (l:b ratio 27.8) was achieved in the case of 2,4,6-trimethylstyrene.

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† Electronic supplementary information (ESI): Tables of selected structural data and selected spectroscopic data. CCDC 1917466 and 1917467. For ESI and crystallographic data in CIF or other electronic format see DOI:

Introduction

Resorcin[4]arenes are a class of macrocyclic compounds used as a platform for the synthesis of functionalized receptors in the field of supramolecular chemistry.[1-3] The resorcin[4]arenes are structurally similar to calix[4]arenes and can easily be prepared by the condensation of resorcinol with aldehydes.[1] These bowl shaped compounds are used in molecular recognition where they can serve as hosts for small guest molecules and cations.[4] The interactions responsible for the molecular recognition are H-bonding, π-stacking, and dipole-dipole interactions.[5-8] These macrocycles are used as HPLC stationary phases,[11,12] in the selective extraction of lanthanides and actinides[9,10] and also as NMR chiral shift agents.[6,13] The macrocyclic ring in resorcin[4]arenes can adopt four symmetrical arrangements, *viz*, crown, chair, boat, and saddle (Chart 1). However, boat and chair are the two preferred conformations depending on the substituents on the cavitands.[14,15]

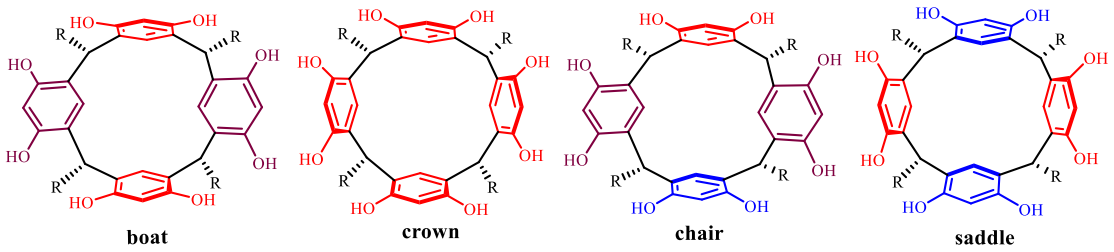

Chart 1 Possible stereoisomers of resorcin[4]arene.

The adjacent phenolic units of the resorcin[4]arene backbone can be bridged using methylene, dialkylsilicate, phosphoryl, and heterophenylene linkers to make the skeleton more rigid (Chart 2).[1,5,7,9,14,16-18] The length and nature of the bridge are known to affect the cavity size of these cavitands.[5,19-21] The resorcin[4]arenes have two zones that could be accessed for functionalization namely the upper and the lower rims of the molecule. Functionalization of the lower rim usually begins from an already functionalized aldehyde. The upper rim of the molecule possesses two possible sites for chemical modifications, the phenolic groups and the

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ortho positions of the resorcinol moieties.[16,22,23] The derivatization of phenolic –OH groups by phosphine moieties results in the formation of pincer-capable polyphosphorus ligands (Chart 2).[24-28] Such ligands can be used to make either conventional polynuclear complexes[29-35] or aromatic *ortho*-C—H bond activated multi-pincer complexes and also in host-guest chemistry[17,18,36,37] to trap small molecules. Puddephatt and co-workers have synthesized Pd^{II}, Cu^{I} and Ag^{I} complexes of resorcin[4]arene-based octa- and tetraphosphinites and also mixed tetracarboxylate-tetraphosphonite derivatives (Chart 2).[24-26,28] However, reports on pincer complexes based on these cavitands or their applications in catalytic reactions are scant in the literature.[38-43]

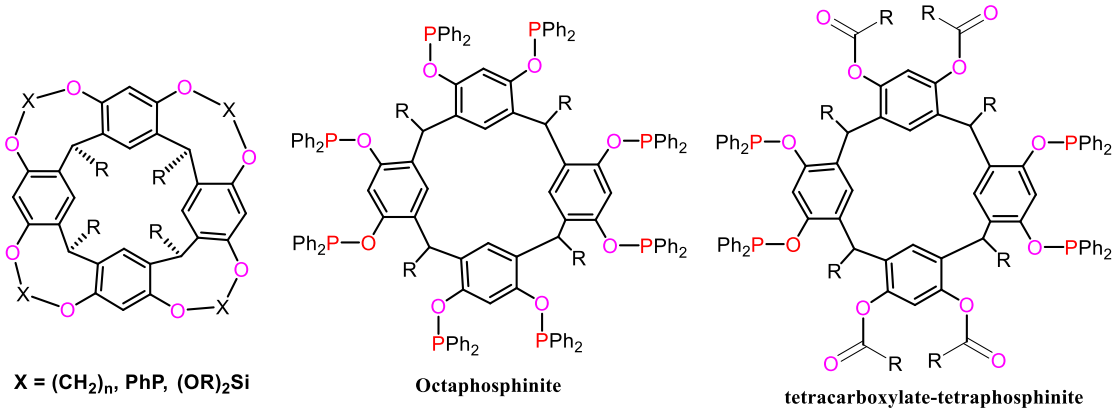

Chart 2 Substituted resorcin[4]arenes.

Hydroformylation of olefins is one of the most significant reactions in homogeneous catalysis because of their important industrial significance,[44] for example, in pharmaceuticals, agrochemicals, and other fine chemicals.[45-47] Numerous hydroformylation catalysts have been developed over the years[48-52] to improve the catalyst stability, activity and regioselectivity. Most efficient hydroformylation processes utilize rhodium catalysts with monophosphines or bisphosphines to achieve regioselectivity as well as stereoselectivity.[53] Since styrenes are excellent substrates to produce branched aldehydes, most of the investigations have been centered around the advancement of chiral ligands or procedures to make ideal branched

enantioisomer in high optical purity.[54] Nevertheless, ongoing research on Rh-catalyzed hydroformylation of styrene has uncovered that, opposite selectivity for linear aldehyde may likewise be conceivable through the choice of solvent,[55] biphasic system[56] or fine-tuned ligand[57] that assist in achieving highest linear regioselectivity.

A couple of models regarding hydroformylation of styrene concerning the linear product can be found in the literature. Reek and co-workers utilized a library of SUPRAPhos phosphine-phosphoroamidite ligands and achieved 72% (l:b ratio 2.6) and 70%(l:b ratio 2.4) of the linear aldehyde from styrene and 1-octene, respectively.[51] Zhang *et al*. reported highest selectivity towards the formation of linear aldehyde up to 96% (l:b ratio 22) in the case of 3-phenylpropanal involving a substituted tetraphosphorus/Rh system.[58] Sémeril *et al.* have reported the synthesis and application of a class of new diphosphites with a conical calixarene skeleton, which demonstrated high regioselectivity for the linear products in the hydroformylation of styrene (up to 75% linear aldehyde, l:b ratio 3.0) and allyl benzyl ether (l:b ratio up to 20).[59] These results encouraged us to explore octaphos **3** in the hydroformylation of styrene and its derivatives.

Herein, we describe the synthesis, tetranickel(II), and tetrapalladium(II) pincer complexes and catalytic investigation of octaphos/Rh system in hydroformylation reactions.

Results and discussion

The resorcin[4]arene derivative (**1**) was synthesized by the acid catalyzed condensation of resorcinol and pentanal in 89% yield.[60] The resorcin[4]arenes derived from aromatic aldehydes are soluble only in polar organic solvents. In order to enhance the solubility of the resorcin[4]arene, aliphatic aldehyde, pentanal was used.[61] The aromatic bromination of **1** using *N*-bromosuccinimide in 2-butanone resulted in tetrabromide **2** in good yield. The mass spectrum of **2** showed the base peak at 1094.9937 which corresponds to $[M+3Na–2H]^+$.

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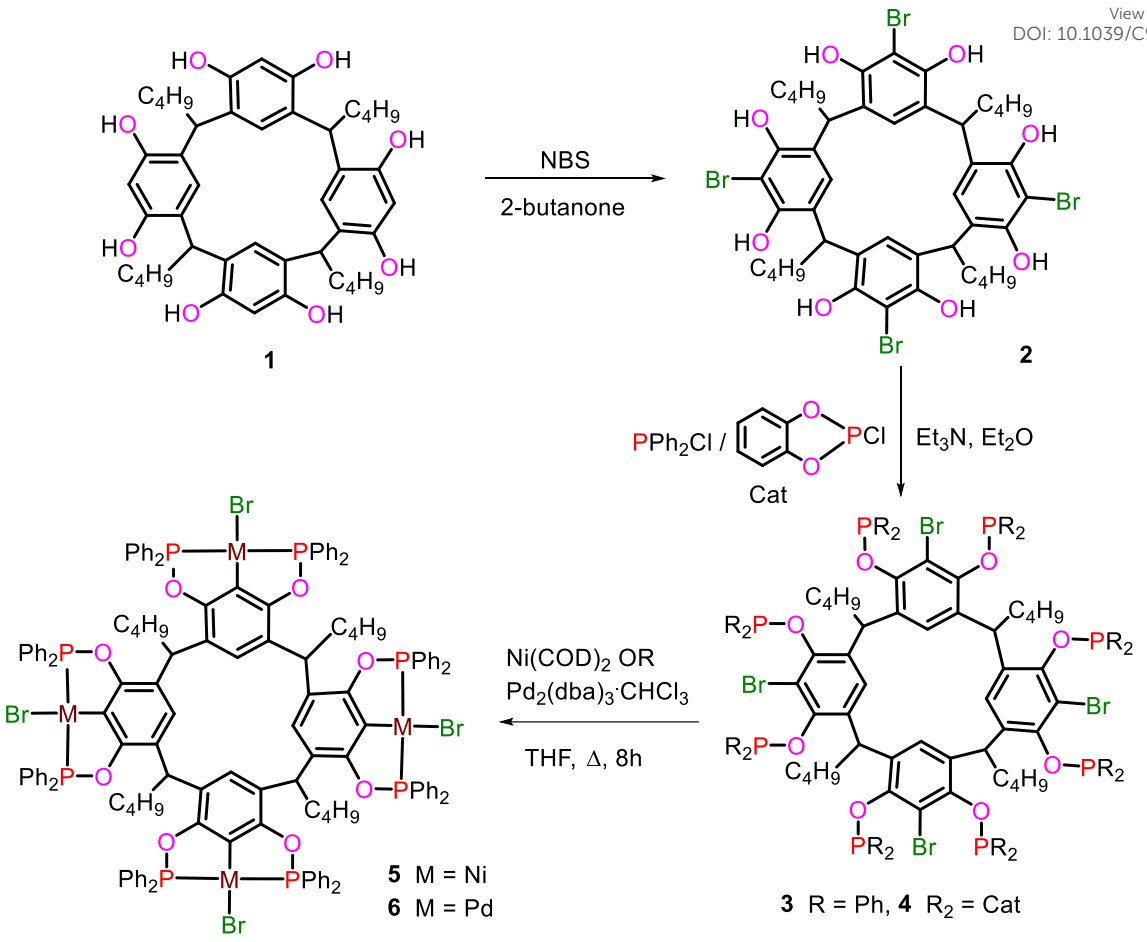

Scheme 1 Synthesis of octaphos ligands **2** and **3** and Ni^{II} and Pd^{II} complexes of octophos **3**.

The reaction of tetrabromoresorcin[4]arene (**2**) with chlorodiphenylphosphine in the presence of triethylamine yielded octaphos **3** in good yield. The $^{31}P\{^{1}H\}$ NMR spectrum of **3** showed two single resonances of equal intensities at 122.6 ppm and 116.4 ppm indicating the presence of two different types of phosphorus environments or possibility of having two different compounds. Other spectroscopic and analytic data confirmed the presence of only one product probably with boat conformation (Chart 1) having two phosphorus environments. For further confirmation, similar reaction of *o*-phenylenephosphorochloridite with **2** was performed to obtain octaphosphite **4**. The $^{31}P\{^{1}H\}$ NMR spectrum of **4** also displayed two singlets of equal intensities at 137.9 ppm and 137.4 ppm. The resorcin[4]arene backbone in both the ligands **3** and **4** found to prefer boat conformation that leads to two $^{31}P\{^{1}H\}$ resonances one each for the outward, and the upward directed –OPR_2 groups.[28]

The reaction of octaphos **3** with four equivalents of $Ni(COD)_2$ or two equivalents of $Pd_2(dba)_3{\cdot}CHCl_3$ in THF under refluxing conditions afforded pincer complexes **5** and **6**, respectively, as outlined in Scheme 1. The $^{31}P\{^1H\}$ NMR spectrum of nickel complex **5** showed a single resonance at 141.6 ppm, whereas that of palladium complex **6** consists of two sharp singlets at 142.6 and 141.8 ppm. This may be due to the rapid interconversion of boat conformations in the case of nickel complex. As expected, the low temperature (–20 °C) $^{31}P\{^1H\}$ NMR spectrum of nickel complex **5** also displayed two single resonances at 139.7 and 147.1 ppm. The two signals were observed because of the boat conformation of the resorcin[4]arene backbone in both the pincer complexes. At room temperature boat interconversion appears to be faster in nickel complexes compared to palladium analogue. The structures of both nickel and palladium complexes were established by single crystal X-ray diffraction studies.[62]

Molecular structures of pincers 5 and 6

The perspective views of the molecular structures of complexes **5** and **6** along with atom labeling scheme are shown in Figs. 1 and 2. The X-ray quality crystals of **5** and **6** were obtained by slow evaporation of dichloromethane solution at room temperature. The X-ray crystal structures of **5** and **6** confirm the oxidative addition of all the four C–Br bonds to the metal centers.

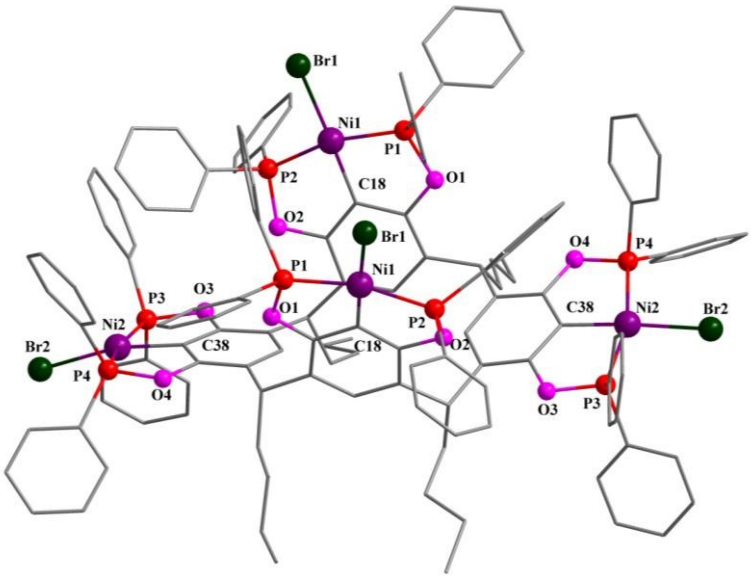

Fig. 1 The molecular structure of **5**. All hydrogen atoms and lattice solvents are omitted for clarity. Selected bond length (Å) and bond angles (°): Ni1–Br1 2.3146(8), Ni2–Br2 2.294(3), Ni1–P1 2.1471(15), Ni1–P2 2.1553(14), Ni2–P3 2.1495(18), Ni2–P4 2.1444(18), Ni1–C18 1.892(4), Ni2–C38 1.881(5), P1–O1 1.643(4), P2–O2 1.632(3), P3–O3 1.637(4), P4–O4 1.635(4), Br1–Ni1–P1 99.66(4), Br1–Ni1–P2 96.97(4), Br2–Ni2–P3 101.74(10), Br2–Ni2–P4 94.09(9), Br1–Ni1–C18 178.13(14), Br2–Ni2–C38 166.9(2), P1–Ni1–C18 81.89(15), P2–Ni1–C18 81.58(14), P3–Ni2–C38 82.79(16), P4–Ni2–C38 81.70(16), P1–Ni1–P2 162.63(6), P3–Ni2–P4 164.17(6).

The resorcin[4]arene skeleton adopts the boat conformation in both the complexes **5** and **6**, in which the two opposite aryl rings along with phosphinite substituents are flattened keeping the other two aryl rings upright and nearly parallel (^{31}P NMR data supported this conformation). The adjacent aryl rings with phosphinite substituents are nearly perpendicular to each other. The metallocycles and the corresponding benzene rings are coplanar. The Ni1–C18 and Ni2–C38 bond distances in **5** are 1.892(4) Å and 1.881(5) Å, respectively. The average M–C bond distance in nickel complex **5** [1.884 Å] is slightly shorter than that in palladium complex **6** [2.011 Å], which is expected due to the smaller atomic radius of nickel compared to palladium. The average M–P bond distances in complexes **5** [2.149 Å] and **6** [2.274 Å] are comparable with those of the reported pincer compounds, [NiCl{C_6H_3-2,6-($OPPh_2$)$_2$}] [2.157 Å], [NiI{C_6H_3-2,6-($OPPh_2$)$_2$}] [2.158 Å][39, 63-65] and [PdI{2,6-C_6H_3(OPR_2)$_2$}] [Pd–P, 2.261 to 2.294 Å].[66, 67] The C18–Ni1–Br1 bond angle [178.13(14)°] is almost linear, whereas the C38–Ni2–Br2 bond angle [166.9(2)°] deviates appreciably from linearity. In the case of palladium complex **6**, all the C–Pd–Br bond angles are nearly linear.

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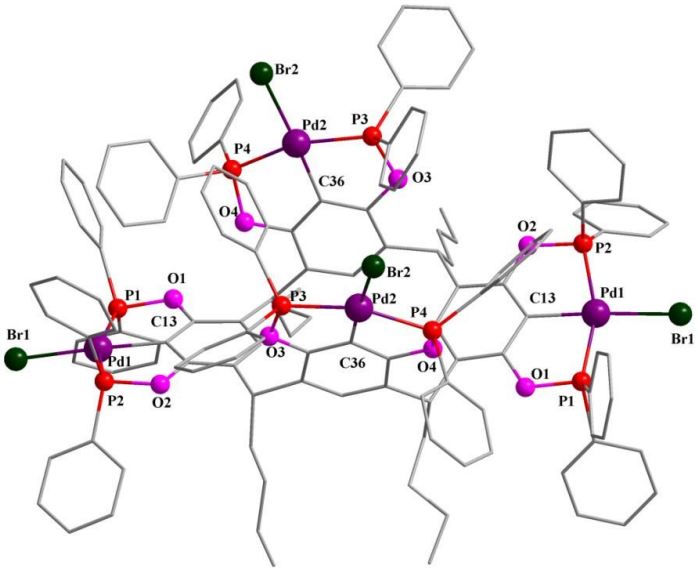
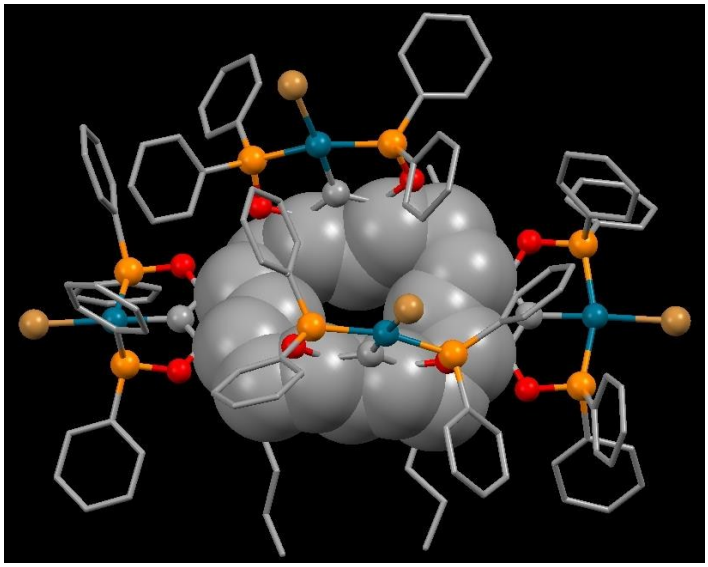


View 1

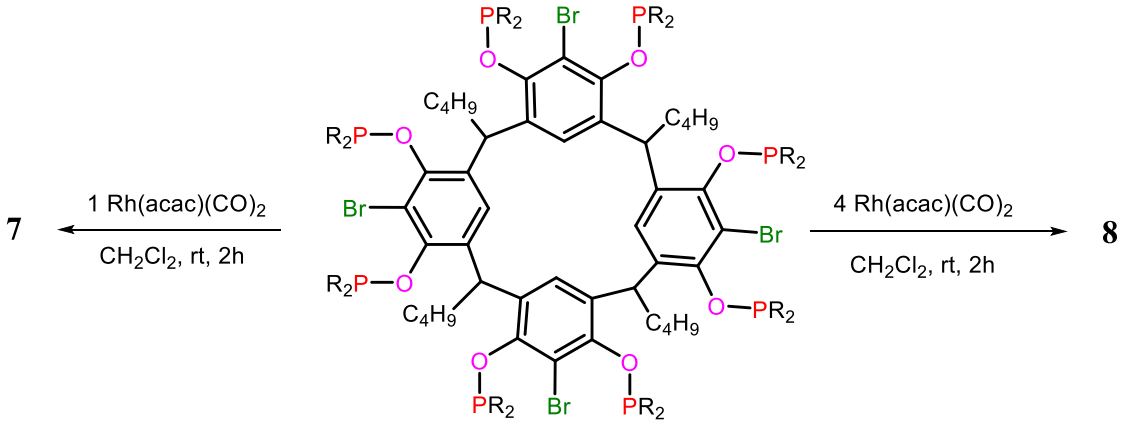


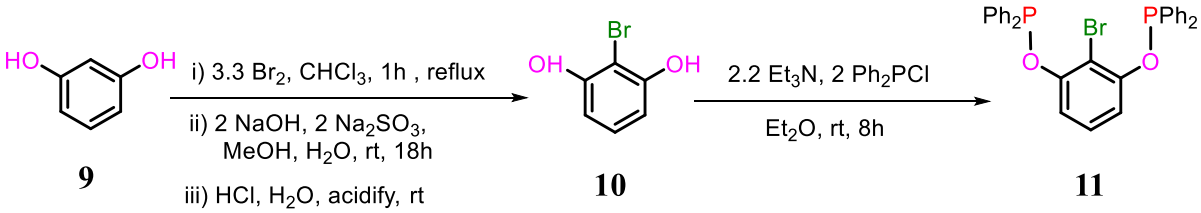
View 2

Fig. 2 The molecular structure of **6**. All the hydrogen atoms are omitted for clarity. View 1: Ball and Stick Model View 2: Partial Space Filling Model. Selected bond length (Å) and bond angles (°): Pd1–Br1 2.463(2), Pd2–Br2 2.4845(12), Pd1–P1 2.277(4), Pd1–P2 2.288(4), Pd2–P3 2.266(3), Pd2–P4 2.266(3), Pd1–C13 2.009(11), Pd2–C36 2.015(8), P1–O1 1.640(8), P2–O2 1.648(8), P3–O3 1.642(6), P4–O4 1.634(6), Br1–Pd1–P1 98.54(12), Br1–Pd1–P2 101.40(13), Br2–Pd2–P3 103.54(7), Br2–Pd2–P4 97.13(7), Br1–Pd1–C13 176.2(3), Br2–Pd2–C36 177.0(3), P1–Pd1–C13 79.9(3), P2–Pd1–C13 80.4(3), P3–Pd2–C36 79.5(3), P4–Pd2–C36 79.9(3), P1–Pd1–P2 159.86(13), P3–Pd2–P4 158.55(9).

Hydroformylation reactions of styrene derivatives

The literature report on hydroformylation of styrenes using rhodium-phosphorus donor systems suggest that the strong π-acceptor ligands are more effective and produce linear and/or branched derivatives.[51, 58, 59] Further, in hydroformylation reaction, active catalyst generated *in situ* from a mixture of ligand ($2PR_3$ or a bisphosphine (PP)) and $[Rh(acac)(CO)_2]$ yielded better results with higher conversion rates compared to isolated complexes of the type [Rh(acac)(κ,κ-PP)][68] or $[Rh(PR_3)(CO)(acac)]$[69]. In the present study, octaphos **3** was reacted with one and

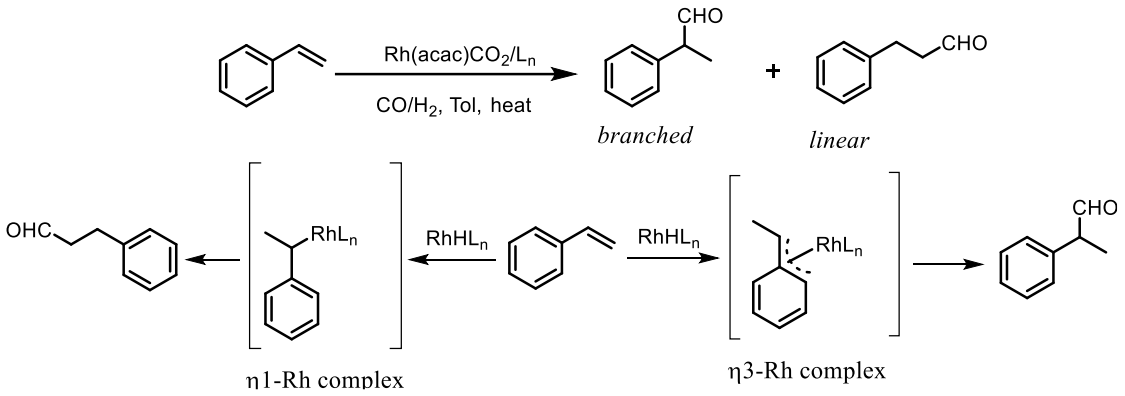




Scheme 2 Synthesis of Rh complex **7**, **8** and resorcinol based bisphosphine ligand $[C_6H_3Br(OPPh_2)_2]$(**11**)

four equivalents of $[Rh(acac)(CO)_2]$ in CH_2Cl_2 to form mono- and tetrarhodium complexes **7** and **8**, respectively (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of 1:1 product, complex **7**, showed two singlets for uncoordinated phosphorus atoms of two types due to boat conformation and a set of multiplets due to coordinated PPh_2 moieties showing $^1J_{RhP}$ coupling

(ESI, Fig. S5). $^{31}P\{^{1}H\}$ NMR spectrum of 1:4 product, complex **8**, showed three sets of resonances probably due to boat conformation with rhodium binding to PPh_2 moieties from adjacent aromatic groups to minimize steric congestion arising from bromine atom for chelating mode of coordination (ESI, Fig. S7). To compare the catalytic performance of octaphos, its monomeric analogue, bisphosphinite, $[C_6H_3Br(OPPh_2)_2]$ (**11**) was prepared and spectroscopically characterized by NMR and HRMS data and its *in situ* generated complex with $[Rh(acac)(CO)_2]$ was directly used in catalysis.



Scheme 3 Hydroformylation of styrene

The octaphos **3**, bisphosphinite **11** and two isolated complexes **7** and **8** were employed in the Rh-catalyzed hydroformylation of styrene derivatives. The catalytic activity and regioselectivity towards the linear product were investigated initially with PPh_3 and bisphosphinite $[C_6H_3Br(OPPh_2)_2]$ (**11**). Later, the reaction conditions were optimised (Table 1) for octaphos **3**/Rh system with respect to parameters such as: CO/H_2 pressure, temperature and ligand-to-rhodium (L/Rh) ratio. After initial screening at different temperatures and syngas pressure, the difference in effectiveness was rather pronounced. Change in the CO/H_2 pressure induced changes in the regioselectivity, but the catalytic activity was slightly affected. For example, on increasing the pressure from 10 to 20 bar, the selectivity for linear aldehyde went up from 50% to 62% (Table 1, entries 1 and 2). The decrease in reaction temperature resulted

in less conversion and hence higher pressure was applied with increase in the reaction time (entries 5 and 6). A slight decrease of l:b ratio and slight increase in isomerization were noticed when the L/Rh ratio was changed from 1:1 to 2:1 (entries 3 and 4). Surprisingly, changing the L/Rh ratio from 4:1 to 6:1 resulted in least conversion with least linear selectivity (Table 1, entries 9 and 10). Based on this data, most appropriate L/Rh ratio of 1:1 was employed. Increase in the temperature from 80 to 110 °C resulted in improved activity and regioselectivity (Table 1, entries 1, 3, and 4). Optimised reaction condition: solvent as toluene, 110 °C, 20 atm H_2/CO, substrate/L/Rh = 1000/1/1, was employed, which showed highest linear selectivity (entry 8). The catalytic ability of PPh_3, under these optimised conditions showed very low selectivity (entry 7). Low catalyst loading (substrate/L/Rh = 2000/1/1) also resulted in lower selectivity as well as low conversion (entries 13 and 14). The hydroformylation reactions with two isolated complexes **7** and **8** showed good linear selectivity but with poor conversions (entries 15 and 16). Similar catalytic reaction using $[C_6H_3Br(OPPh_2)_2]$(**11**)/Rh resulted in more branched isomer with 56% conversion (entry 17). The *in situ* generated 1:1 precatalyst with octaphos **3** was found to be superior in its regio selectivity and also conversion rates. Therefore, *in situ* generated complex was utilized for further investigation towards the hydroformylation of different styrene subsidiaries.

Using the optimised reaction conditions, a series of styrene derivatives were hydroformylated using the Rh/octaphos **3** catalyst. The substrate to catalyst ratio was 1000, and the catalyst concentration was 1.0 mM. The reaction was terminated after 3 h (Table 2). It was found that styrene substituted with electron-withdrawing group showed lower linear selectivity than that of styrene with electron-donating groups (Table 2). The steric hindrance of the substrates on the regioselectivity of the hydroformylation is likewise noteworthy. On introducing methyl group at *ortho* position of the styrene, the reactivity and the regioselectivity were improved significantly (entry 8). On adding methyl group at the other *ortho* position, the

reactivity was enhanced to form linear product in almost quantitative yield (entry 2). Unexpectedly, in the hydroformylation of *p*-nitro styrene, despite the presence of electron withdrawing substituent, highlighted the higher linear aldehyde selectivity (entry 5). Earlier report correlated the lower conversion of 2,4,6-trimethylstyrene, due to the bulkiness of substrate, that prevents the substrate from coordinating to the metal centre during the transformation.[58] Nonetheless, octaphos **3** showed remarkably high conversion along with almost quantitative linear selectivity of 97% (l:b ratio up to 27.8) with the same styrene derivative (entry 2)

Table 1 Hydroformylation of styrene using ligand **3** under different reaction conditions[a]

Entry	L/[Rh]	CO/H_2 (Bar)	Temp. (° C)	Time (h)	Conversion[e] (%)	l:b ratio[f]	l/b (%)[g]	TON
1	1:1	10	80	2	43	1.0	50/50	430
2	1:1	20	90	2	68	1.6	62/38	680
3	2:1	20	90	3	69	1.4	58/42	690
4	2:1	30	110	3	84	1.5	60/40	840
5	1:1	20	80	2	42	1.4	58/42	420
6	1:1	40	90	4	90	1.2	55/45	900
7	PPh_3	20	110	4	28	0.9	47/53	280
8	1:1	20	110	3	100	1.6	62/38	1000
9	6:1	20	110	3	traces (2)	0.9	47/53	20
10	4:1	30	110	4	74	0.8	44/56	740
11	1:4	20	110	3	84	1.4	58/42	840
12	1:4	20	85	3	79	1.3	57/43	790
13[b]	1:1	20	85	3	23	1.7	63/37	460
14[b]	1:1	20	110	3	69	1.4	58/42	1380
15[c]	**7**	20	110	3	60	1.5	60/40	600
16[c]	**8**	20	110	3	52	1.4	58/42	520
17[d]	1:1	20	110	3	56	0.7	45/55	560

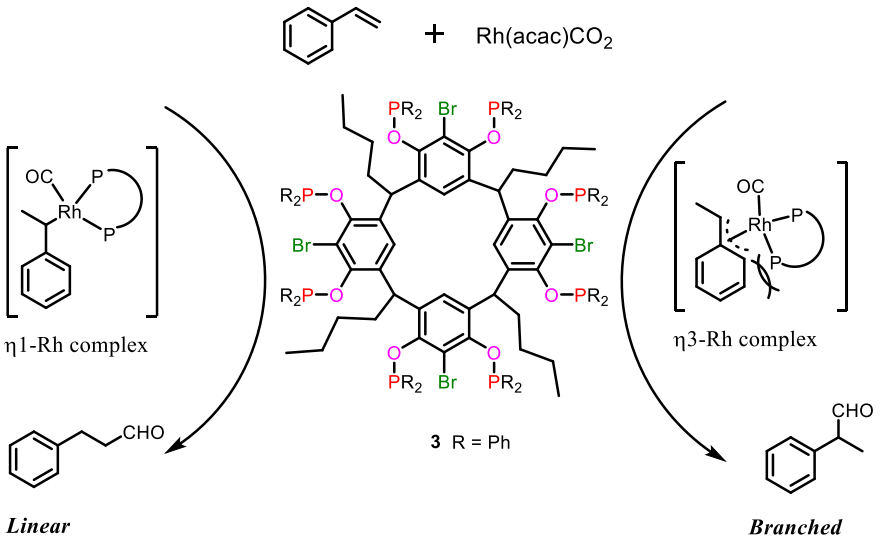
[a] S/C=1,000, $Rh(acac)(CO)_2$ = [Rh] = 1.0 mM, toluene as solvent, [b] S/C=2,000. [c] using metal complexes **7** and **8**, [d] L= $[C_6H_3Br(OPPh_2)_2]$(**11**), [e] Conversion of the styrenes determined on

the basis of GC. [f] l:b = linear:branched ratio, determined on the basis of GC analysis. [g] Percentage of linear aldehyde and branched aldehyde in all aldehydes.

Table 2 Hydroformylation of styrene derivatives[a]

Entry	Substrate	Conversion[b] (%)	l:b ratio[c]	l/b (%)[d]	TON
1	4-Bromostyrene	99	1.5	60/40	940
2	2,4,6-Trimethylstyrene	98	27.8	97/3	980
3	3-Methylstyrene	98	1.6	62/38	980
4	4-Chlorostyrene	98	1.6	62/38	980
5	3-Nitrostyrene	99	2.4	71/29	990
6	2-Chlorostyrene	99	5	83/17	990
7	2-Fluorostyrene	53	0.7	41/59	530
8	2-Methylstyrene	98	4.4	81/19	980
9	α-Methylstyrene	29	34.9	97/3	290
10	4-Vinylanisole	98	1.5	60/40	980

[a] S/C = 1000, Temp. = 110°C, Pressure = 20 bar (1:1=CO:H_2), time = 3 h, solvent = toluene. [b] Conversion of the substituted styrenes determined on the basis of GC. [c] l/b = linear:branched ratio determined on the basis of GC analysis. [d]Percentage of linear aldehyde and branched aldehyde in all aldehydes.



Scheme 4 Generally accepted reason behind the formation of linear and branch aldehyde.

It is interesting to analyse the data presented in Table 2. Although, hydroformylation reactions have been studied extensively, a very few studies concerning the mechanism of the hydroformylation of styrene to yield linear product are available in the literature.[70-72] The high regioselectivity for the hydroformylation of styrene towards linear aldehyde can be symbolized through steric cooperation between the ligands and the substrate. One of the most reasonable justification of this regioselectivity is the ready formation of a η^3-Rh complex as shown in Scheme 3. Previously, for the hydroformylation of styrene catalyzed by Rh complex, it was opined that the significant difference in the steric environment between the ligand and the substrate provide remarkable regioselectivity to form linear aldehyde.[58, 59, 68] In the present study, the dependency of the selectivity on the steric nature of the ligand is comparable as it incorporates bulky resorcin[4]arene skeleton. The steric hindrance furnished by octaphos **3** prevents the formation of η^3-Rh-complex over η^1-Rh complex (Scheme 4) and hence the preferential formation linear aldehyde with higher regioselectivity takes place.

Conclusions

In summary, resorcin[4]arene-based pincer-capable octaphos ligands and their tetra-pincer complexes were synthesized. The resorcin[4]arene backbone in both the ligands and in the pincer complexes adopts the boat conformation.

The Rh-catalyzed hydroformylation of styrene affords selectively the branched aldehyde, however, one can reverse the selectivity towards linear product by choosing an appropriate ligand framework as demonstrated by octaphos **3**. Octaphos effected moderate regeoselectivity for styrene, whereas in the case of substituted styrenes very high regeoselectivity towards linear aldehyde (97% linear aldehyde) was achieved. These resulted have demonstrated an excellent steric cooperation between the ligands and the substrate.

These pincer complexes with potential catalytic applications can also act as hosts for small molecules because of their large surface area for intermolecular interactions. This may also

help in tuning the catalytic activity of these cavitands for various other organic transformations. Work in this direction is in progress in our laboratory.

Experimental section

General procedures. All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional methods[73] and distilled prior to use. The precursor, $Pd_2(dba)_3 \cdot CHCl_3$ was prepared according to the published procedure.[74] $Ni(COD)_2$ was purchased from Aldrich chemicals and used as such without further purification. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were recorded using either Bruker AV 400 or AV 500 spectrometers operating at appropriate frequencies. The ^{31}P NMR spectra were acquired using broad band proton decoupling. The spectra were recorded in $CDCl_3$ (DMSO-d_6) solutions with $CDCl_3$ (DMSO-d_6) as internal lock. TMS and H_3PO_4 (85% in D_2O) were used as internal and external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. The signals are quoted as s (singlet), t (triplet), m (multiplet) and br (broad). The microanalyses were performed using Carlo Erba Model 1112 elemental analyzer. The mass spectra were recorded using Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes.

Synthesis of resorcin[4]arene (1). Resorcinol (20.0 g, 0.1816 mol) was dissolved in a mixture of water (20 mL), ethanol (95%, 60 mL) and aqueous HCl (37%, 18 mL). To this clear stirred solution was added slowly pentanal (15.7 g). The reaction was exothermic and temperature was maintained below 50 °C using a cold water bath. After the completion of addition, the reaction mixture was heated to 80 °C for 16 h. The yellow needles that separated were collected and washed with 30 mL of cold 1:1 ethanol-water mixture. A light yellow material thus obtained was dried at 80 °C for 12 h and used for the next step without further

purification. Yield: 89% (29 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.85 (s, 8H, OH), 7.12 (s, 4H, ArH), 4.18 (t, $^{3}J_{HH}$ = 7.8 Hz, 4H, CH), 2.01 (m, 8H, CH_2), 1.30–1.12 (m, 16H, CH_2), 0.81 (t, $^{3}J_{HH}$ = 7.4 Hz, 12H, CH_3).

Synthesis of tetrabromoresorcin[4]arene (2). To a well-stirred solution of **1** (20 g, 0.028 mmol) in 2-butanone (350 mL) was added N-bromosuccinimide (30 g, 0.168 mol) in portions. After 10 min, the product started to precipitate and the mixture was stirred for another 4 h. The precipitate was collected by filtration, washed with cold 2-butanone and dried under vacuum, to obtain **2** as an off-white solid. Yield: 71% (20.6 g). Mp >270 °C. Anal. Calcd. for $C_{44}H_{52}Br_4O_8$: C, 51.38; H, 5.10%. Found: C, 51.65; H, 5.14%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.11 (s, 8H, OH), 7.35 (s, 4H, ArH), 4.33 (t, $^{3}J_{HH}$ = 7.7 Hz, 4H, CH), 2.16 (m, 8H, CH_2), 1.32 (m, 8H, CH_2), 1.17 (m, 8H, CH_2), 0.84 (t, $^{3}J_{HH}$ = 7.3 Hz, 12H, CH_3). MS (EI): m/z = 1094.99 $[M+3Na–2H]^{+}$

Synthesis of (tetrabromo)resorcin[4]arene octaphosphinite (3). To an ice-cold solution of tetrabromoresorcin[4]arene (**2**) (2 g, 1.945 mmol) and triethylamine (2.19 g, 3.0 mL, 21.64 mmol) in diethyl ether (50 mL) was added dropwise a solution of chlorodiphenylphosphine (3.69 g, 3.0 mL, 16.72 mmol) in the same solvent (30 mL). After the completion of addition, the reaction mixture was stirred for 12 h at room temperature and then filtered through Celite to remove the amine hydrochloride salt. The solvent was removed under vacuum to obtain the product as a white solid. The crude product was recrystallized from toluene to obtain analytically pure **3**. Yield: 70% (3.4 g). Mp: >268 °C. Anal. Calcd. for $C_{140}H_{124}Br_4O_8P_8$: C, 67.21; H, 5.00%. Found: C, 67.23; H, 5.13%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-6.52 (m, 84H, ArH), 4.32 (m, 4H, CH,), 2.16 (m, 8H, CH_2), 1.37 (m, 8H, CH_2), 1.21 (m, 8H, CH_2), 0.81 (m, 12H, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 122.6 (s), 116.4 (s).

Synthesis of (tetrabromo)resorcin[4]arene octaphosphite (4). To an ice-cold solution of tetrabromoresorcin[4]arene (**2**) (1.0 g, 0.9725 mmol and triethylamine (1.09 g, 1.5 mL, 10.76

mmol) in diethyl ether (50 mL) was added dropwise a solution of *o*-phenylenephosphorochloridite (1.4 g, 8.02 mmol) in the same solvent (30 mL). After the completion of addition, the reaction mixture was stirred for 12 h at room temperature and then filtered through Celite to remove the amine hydrochloride salt. The solvent was removed under vacuum to obtain the product as a white solid. The crude solid was recrystallized from toluene to obtain analytically pure **4**. Yield: 60% (1.4 g). Mp: >270 °C. Anal. Calcd. for $C_{92}H_{76}Br_4O_{24}P_8$: C, 51.80; H, 3.59%. Found: C, 51.63; H, 3.27%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-6.52 (m, 84H, ArH), 4.32 (m, 4H, CH), 2.16 (m, 8H, CH_2), 1.37 (m, 8H, CH_2), 1.21 (m, 8H, CH_2), 0.81 (m, 12H, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 137.9 (s), 137.4 (s).

Synthesis of (tetrakisnickel)resorcin[4]arene (5). A mixture of octaphosphinite (**3**) (0.036 g, 0.0144 mmol) and $Ni(COD)_2$(0.016 g, 0.0578 mmol) was refluxed in THF (15 mL) for 6 h. Then the reaction mixture was allowed to cool to room temperature, filtered through Celite and all the volatilities were removed under vacuum. The yellow mass thus obtained was washed with hot petroleum ether to afford pale yellow powder, which was further recrystalized from a 1:1 mixture of dichloromethane/petroleum ether to obtain analytically pure **5**. Yield: 86% (0.034 g). Mp: >270 °C. Anal. Calcd. for $C_{140}H_{124}Br_4Ni_4O_8P_8$: C, 61.44; H, 4.57%. Found: C, 61.47; H, 4.22%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-6.61 (m, 84H, ArH), 4.73 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CH), 3.75 (t, $^3J_{HH}$ = 6.4 Hz, 2H, CH),1.92 (m, 8H, CH_2), 1.31 (m, 8H, CH_2), 0.91 (m, 8H, CH_2), 0.81 (m, 12H, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 141.6 (s). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, –20 °C): δ 139.7 (s), 147.1 (s).

Synthesis of (tetrakispalladium)resorcin[4]arene (6). A mixture of octaphosphinite (**3**) (0.09 g, 0.036 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (0.075 g, 0.072 mmol) was refluxed in THF (15 mL) for 6 h. Then the reaction mixture was allowed cooled to room temperature, filtered through Celite and all the volatilities were removed under reduced pressure. The yellow mass thus obtained was washed several time with hot petroleum ether to afford a pale yellow

crystalline product. Yield: 79% (0.084 g). Mp: >270 °C. Anal. Calcd. for $C_{140}H_{124}Br_4O_8P_8Pd_4\cdot(C_4H_8O)_2$: C, 57.87; H, 4.59%. Found: C, 57.84; H, 4.42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-6.48 (m, 84H, ArH), 4.79 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CH), 3.74 (m, 2H, CH), 1.94 (m, 8H, CH_2), 1.57 (m, 8H, CH_2), 1.32 (m, 8H, CH_2), 0.78 (m, 12H, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ142.6 (s), 141.8 (s).

X-Ray crystallography. A crystal of each of the compounds **5** and **6** suitable for X-ray crystal analysis was mounted on a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at φ = 0, 120 and 240° using the SMART[75] software package, or the APEX2[76] program suite. The raw data were reduced to F^2 values using the SAINT+ software[76]. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS[76]). Both the structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package[76]. The poor quality of the refinement in case of nickel(II) complex can be attributed to the extensive disorder. Hydrogen atoms attached to carbon were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Since the crystals were not diffracting well, X-ray crystallography data showed high R_1 values for both the compounds **5** and **6**. There were some significant disorder in the phenyl and ^{n}Bu groups in both the compounds which were modelled to their correct positions. However, in compound **5** significant peaks appeared around the methyl region of the disordered ^{n}Bu groups were left as such. In compounds **5** and **6** small regions of electron density peaks well-separated from the main molecule were present after the final refinement, indicating partially occupied and/or disordered solvent sites. Since the disorder could not be resolved and the nature and number of solvent molecules could not be

determined, all-electron density associated with the solvent molecule(s) were removed using the SQUEEZE procedure in PLATON.[77] The results indicated 59 electrons, and a volume of 905 $Å^3$ for **5**, whereas 374 electrons, and the volume of 1619 $Å^3$ for **6**. The given chemical formula and other crystal data do not take into account the unknown solvent molecule(s). Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1917466 (compound **5**), 1917467 (compound **6**).

General Procedure for the Hydroformylation of styrene

In a glovebox filled with nitrogen, octaphos **3** (0.1 mol %) and [Rh(acac)$(CO)_2$] (0.1 mol%) in 1 mL toluene were added to a 2 mL vial and after stirring for 5 min, styrene (0.48 mmol) and additional solvent were added in the above solution to make up the total volume of the reaction mixture to 10 mL. The solution was then transferred into an autoclave fitted with a mechanical stirrer. Once closed, the autoclave was flushed twice with syngas (CO/H_2 1:1 v/v), pressurised with a CO/H_2 mixture and heated. The reaction was terminated after 3 h. Octaphos **3** was first applied to optimize the hydroformylation conditions of styrene with respect to parameter changes of CO/H_2 pressure, temperature and ligand-to-rhodium (L/Rh) ratio. The effect of CO/H_2 pressure was verified with CO/H_2 pressure ranging from 10 to 30 psi atm. The reactions were performed with various L/Rh ratio and reactor was heated to desired temperature (a range of 80 to 110 °C) with a stirring speed of 340 rpm. After completion of the reaction, the reactor was cooled to room temperature and the remaining synthesis gas was carefully released in a well-ventilated fume hood. The reaction mixture was quantitatively analysed by gas chromatography. Catalytic conversions were determined by gas chromatography (GC) on a Rtx®-1 capilary column (inner diameter 0.25 mm, film thickness 0.25 µm, length 30.0 m). Retention times were compared with authentic samples.

Conflicts of interest

There are no conflicts to declare.

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62 *M.* Crystal data for **5**: $C_{140}H_{124}Br_4Ni_4O_8P_8 \cdot 2CH_2Cl_2$, monoclinic (C2/c), a = 28.0679(15) Å, b = 21.8228(12) Å, c = 25.4931(14) Å, α = 90°, β = 114.048(10)°, γ = 90°, V = 14259.7(13) Å^3, Z = 4, Dc = 1.353 g cm^{-3}, μ(Mo-Kα) = 1.858 mm^{-1}, F(000) = 5928, T = 100 K, GoF = 1.091, final R_1 = 0.0800 and wR_2 = 0.2393 for $I>2\sigma$ (I), R_1 = 0.0992 and wR_2 = 0.2558 for all data. CCDC 1917466. Crystal data for **6**: $C_{140}H_{124}Br_4O_8P_8Pd_4$, M = 2927.38, monoclinic (C2/c), a = 27.9334(7) Å, b = 21.8518(4) Å, c = 26.0254(5) Å, α = 90°, β = 114.212(10) °, γ = 90°, V = 14488.4(5) Å^3, Z = 4, D_c = 1.342 g cm^{-3}, μ(Mo-Kα) = 6.464 mm^{-1}, F(000) = 5888, T =150 K, GoF = 1.048, final R_1 = 0.0889 and wR_2 = 0.2276 for $I>2\sigma$ (I), R_1 = 0.1502 and wR_2 = 0.2740 for all data. CCDC 1917467.

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Synthesis and tetra-pincer nickel(II) and palladium(II) complexes of resorcin[4]arene-octophosphinite [Res(OPR$_2$)$_8$] and rhodium-catalyzed regioselective hydroformylation reaction

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This paper describes the synthesis of resorcin[4]arene based octaphosphinite ligands, tetra-pincer complexes of Ni^{II} and Pd^{II} and rhodium-octaphosphinite catalyzed hydroformylation of styrene and its derivatives.