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Synthesis, Structural Analysis, and Catalytic Properties of Tetrakis(binaphthyl or octahydrobinaphthyl phosphate) Dirhodium(II,II) Complexes

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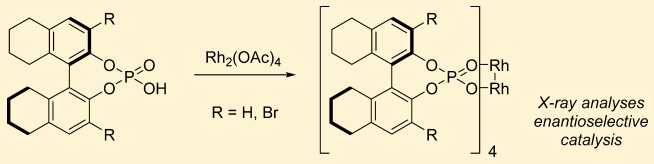
Supporting Information

ABSTRACT: The X-ray structural analyses of homoleptic Rh(II) complexes made of enantiopure (*R*)-1,1′-binaphthyl and (*R*)-(5,5′,6,6′,7,7′,8,8′-octahydro)binaphthyl phosphate ligands are for the first time presented. The possibility to introduce halogen atoms at the 3,3′-positions is also reported. The isolated dirhodium complexes were further tested as catalysts (1 mol %) in enantioselective cyclopropanations and Si−H insertion reactions, affording chiral cyclopropanes and silanes in good yield but moderate enantioselectivity (ee max 63%).



INTRODUCTION

Decomposition of diazo compounds in the presence of chiral dirhodium complexes constitutes an important field of enantioselective catalysis.[1] Such complexes are usually prepared by surrounding the central Rh−Rh core with four enantiopure bridging ligands, carboxylates and imidates in particular. The reactivity of these homoleptic complexes has been extensively examined.[2] Dirhodium complexes made of chiral biaryl phosphate ligands can also be prepared (Figure 1). In 1992, Pirrung and Zhang demonstrated that the treatment of $Rh_2(OAc)_4$ with an excess of 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate, BNP-H, formed the homoleptic $Rh_2(BNP)_4$ complex **1a**.[3] In the same year, McKervey et al. prepared a heteroleptic Rh(II) complex in which two homochiral BNP anions and two hydrogen carbonates surrounded the Rh−Rh backbone.[4] Later, a series of homoleptic 3,3′-, 4,4′-, or 7,7′-substituted binaphthyl phosphate dirhodium complexes were developed by Müller and Hodgson.[5−7] These phosphate dirhodium complexes were used as chiral catalysts by these authors and the community.[8−25]

Remarkably, despite the important synthetic activity in this field, only one dirhodium complex was reported with substituents at the 3,3′-positions of the binol moiety (Figure 1, R^1 = methyl, **1b**).[26] In view of the actual importance of such a substitution pattern in modern chiral phosphoric acid catalysis,[27−31] it seemed important to introduce atoms or groups other than methyl at the R^1 positions of $Rh_2(BNP)_4$ complexes. However, it was a challenge to predict whether the formation of such complexes would be possible since the structural determination of complex **1a** and derivatives had never been reported. Estimating which substituents R^1 would fit within the crowded environment around the dirhodium backbone was thus difficult, and assessing their influence on subsequent enantioselective transformations impossible. Herein, we describe the first X-ray structural analyses of dirhodium phosphate complexes. We also report that halogen atoms are not easily accommodated as 3,3′-substituents unless a partial hydrogenation of the binaphthyl backbone is performed. New dirhodium complexes of type **2** were formed and characterized (Figure 2). Results on the use of these complexes as catalysts for the enantioselective cyclopropanation of styrene and the Si−H insertion of aryldiazoacetates are reported. Unfortunately, erosion in yields and enantioselectivity is observed upon the addition of the 3,3′-substituents.

RESULTS AND DISCUSSION

At the start of this study, there was a lack of precise structural information for complexes **1a** and **1b**, these complexes being essentially characterized through NMR spectroscopy. Care was thus taken to repeat the synthesis of $Rh_2(BNP)_4$ **1a** and attempt to determine its structure through X-ray analysis. Compound **1a** was prepared according to the original protocol by refluxing eight equivalents of enantiopure (*R*)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate **3a** with $Rh_2(OAc)_4$ in chlorobenzene for 18 h (Scheme 1).[3] The desired complex was separated from the excess of acid **3a** by column chromatography (SiO_2, CH_2Cl_2) and isolated in 79% yield. Taking advantage of its moderate solubility in 1,4-dioxane, X-ray quality crystals of **1a** were obtained and subjected to structural analysis (Figure 3, Table S1 in the Supporting Information).

The X-ray analysis revealed a pseudo-C_4-symmetrical distribution of four bridging phosphate ligands around a Rh−Rh core (Rh−Rh bond distance 2.521(1) Å) and a coordination of the remaining Lewis acidic sites of the rhodium

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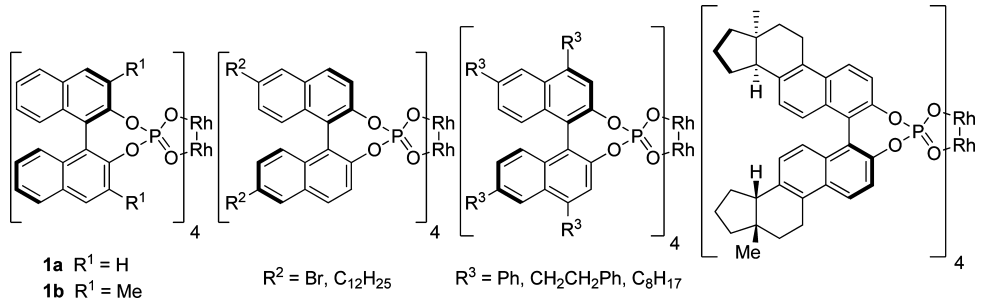


Figure 1. Known chiral homoleptic phosphate dirhodium complexes.

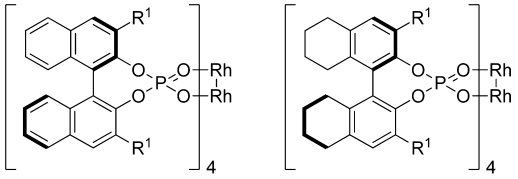
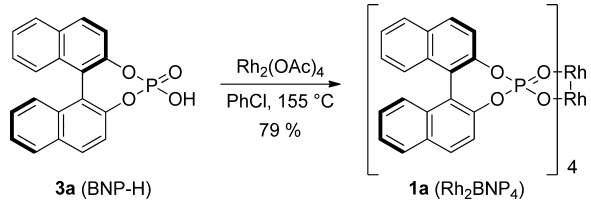


Figure 2. Targeted dirhodium complexes.

Scheme 1. Synthesis of Pirrung's Complex 1a Starting from Enantiopure (*R*)-BNP-H



atoms by one molecule of water and one molecule of 1,4-dioxane. The four bridging oxygen atoms of opposite phosphate ligands are quite perfectly aligned in a plane (maximum atomic deviation <0.1 Å and torsion angles O–Rh–Rh–O ~3.6°; see Tables S4–S5, Supporting Information). Neighboring O–Rh–Rh planes are essentially perpendicular to each other (angle 90.2(1)°). Phosphorus atoms lie out of this plane, forming a five-membered (P–O–Rh–Rh–O) envelope-like conformation. The angle between planes (Rh–Rh–O) and (O–P–O) is 32.7(1)°, and the distance of P from the Rh–Rh–O plane is 0.413(1) Å (Figure 4). Within each biaryl ligand, the average dihedral angle between the two naphthyl planes is 54.5(1)° (see Table S4).

Encumbrance around the hydrogen atoms at the 3- and 3′-positions was found to be moderate. The closest neighbors to these H atoms are the oxygen atoms connected to the binaphthyl moiety of adjacent BNP ligands (minimal distance H3···O 2.77(1) Å, Table S10, Supporting Information). Purely on the basis of sterics, a substitution of these hydrogens by atoms or groups with van der Waals radii smaller than 2.77 Å seemed therefore feasible, and fluorine, chlorine, and bromine atoms in particular.[32,33] The formation and the study of the stability of complexes **1c**, **1d**, and **1e** containing these electronegative atoms in proximity to the lone pairs of the adjacent oxygens was attempted.

Bromo-substituted binaphthyl phosphoric acid **3c** (R^1 = Br) was first prepared, according to the literature procedure.[34] The synthesis of the corresponding complex was attempted using the experimental conditions used for **1a** (chlorobenzene, 155 °C, 18 h). Differences were immediately noticed, as the exchange of the acetate ligands was incomplete after 18 h. The crude contained an inseparable mixture of heteroleptic and

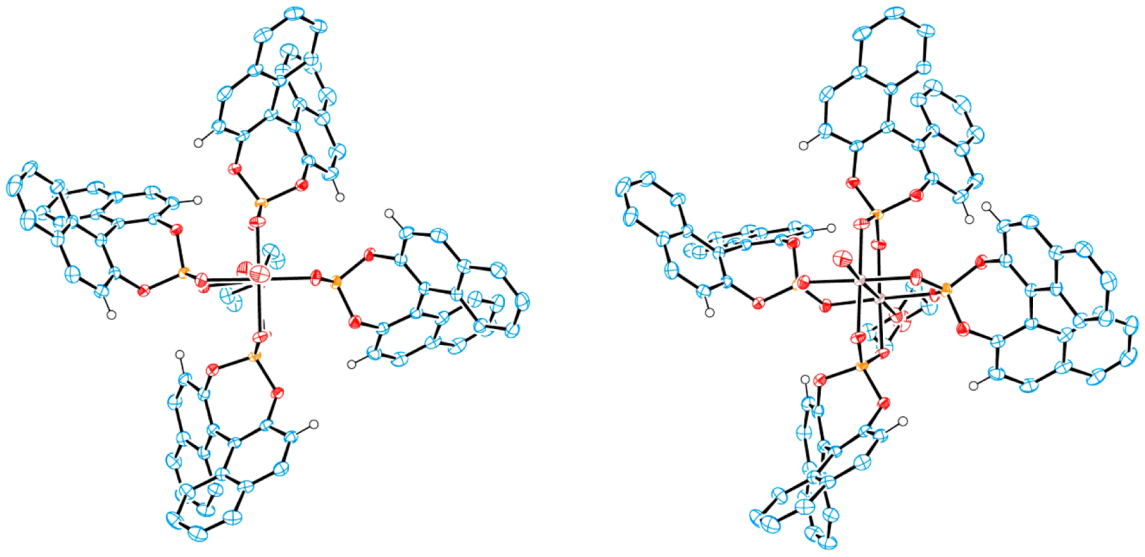


Figure 3. ORTEP views along the Rh–Rh axis (left) and on the side (right) of the crystal structure of (*R*)-**1a**. Thermal ellipsoids are drawn at 50% probability. All hydrogen atoms, except those at 3,3′-positions, and solvent molecules are omitted for clarity.

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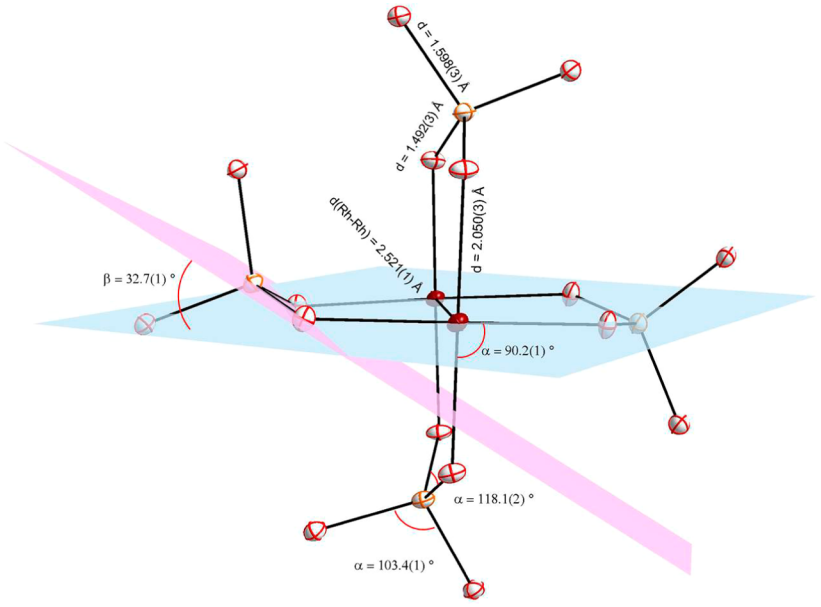
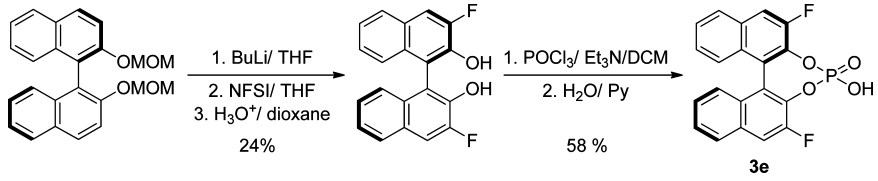


Figure 4. Rh−Rh core of **1a** with defined planes, selected distances, and angles (Table S2, Supporting Information).

Scheme 2. Synthesis of 3,3′-Difluoro 1,1′-Binapthyl Phosphoric Acid 3e

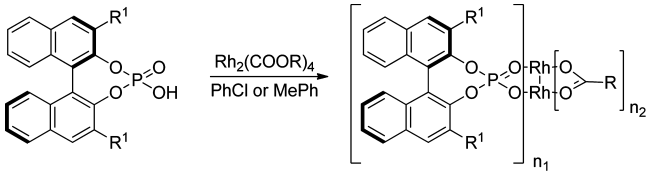


homoleptic dirhodium complexes with phosphate and acetate ligands around the metals. Prolongation of the reaction time to 24 h or the use of a 16-fold excess of acid **3c** did not lead to a complete exchange of the acetates.

3,3′-Dichloro and 3,3′-difluoro-1,1′-binaphthyl hydrogen phosphates, **3d** and **3e**, respectively, were then tested, hoping that the formally smaller chlorine and fluorine atoms would enable the exchange of the ligands. These binol-derived acids have, to our knowledge, never been reported in the literature. Their preparation was however straightforward starting from MOM-protected (*R*)-binol.[35] As described in Scheme 2 (fluoro series), a selective deprotonation with *n*-BuLi (3.5 equiv) at 0 °C (THF, 60 min) followed by treatment with an electrophilic source of chlorine (C_2Cl_6, 4 equiv)[36] or fluorine (NFSI, 6 equiv) and acidic hydrolysis in 1,4-dioxane afforded the 3,3′-dichloro and 3,3′-difluoro binaphthol in 34% and 24% combined yield (X-ray data in Table S11 for the fluoro binol, Supporting Information). Then, reaction with phosphorus oxychloride and hydrolysis in the presence of pyridine gave acids **3d** and **3e** in 50% and 58% yields, respectively.

Unfortunately, the exchange of acetate by hydrogen phosphate ligands **3d** and **3e** was also incomplete. In the case of dichloro **3d**, it was possible to isolate, in low 3% yield, homoleptic complex **1d**, made of four phosphates, while with difluoro **3e**, heteroleptic complex **6**, made of three phosphate and one acetate ligand, was characterized with a 5% yield. In view of these results, explained by the relatively poor leaving group ability of acetate ligands, dirhodium precursor $Rh_2(TFA)_4$ (TFA = trifluoroacetate) was used instead of $Rh_2(OAc)_4$. The exchange reaction was first tested with 3,3′-dibromo-1,1′-binaphthyl hydrogen phosphate **3c**. A less complicated crude mixture was obtained, and the major component **4** was isolated in 78% yield. This complex, made of two phosphate and two trifluoroacetate ligands around the Rh−Rh bond, was analyzed by NMR spectroscopy. The *cis*- or *trans*-disposition of the bridging ligands could not, however, be ascertained (Scheme 3).

Scheme 3. Ligand Exchange Reactions of 3c, 3d, and 3e with $Rh_2(OAc)_4$ and $Rh_2(TFA)_4$



3c: R^1 = Br
3d: R^1 = Cl
3e: R^1 = F

4: R^1 = Br, R = CF_3, $n_1 = n_2 = 2$ (78 %)
1d: R^1 = Cl, R = CH_3, $n_1 = 4$ (3 %)
6: R^1 = F, R = CH_3, $n_1 = 3$, $n_2 = 1$ (5 %)

Trying to find a solution for making the homoleptic derivatives, we reflected on the synthesis of complex **1b**, which is effective despite the presence of rather large R^1 methyl substituents.[26] We considered that its success is the result of the electron-rich nature of ligands of **1b**, this ligand being able to substitute the acetates of $Rh_2(OAc)_4$ more easily than ligands of **1c** or **1d**.[37] Then, modifications of the binaphthyl skeleton of these acids that would enable (i) a transformation into an electron-rich moiety and (ii) the possibility to still introduce halogen atoms at the desired 3,3′-positions would be favorable for complete substitution. With this guideline, a partial

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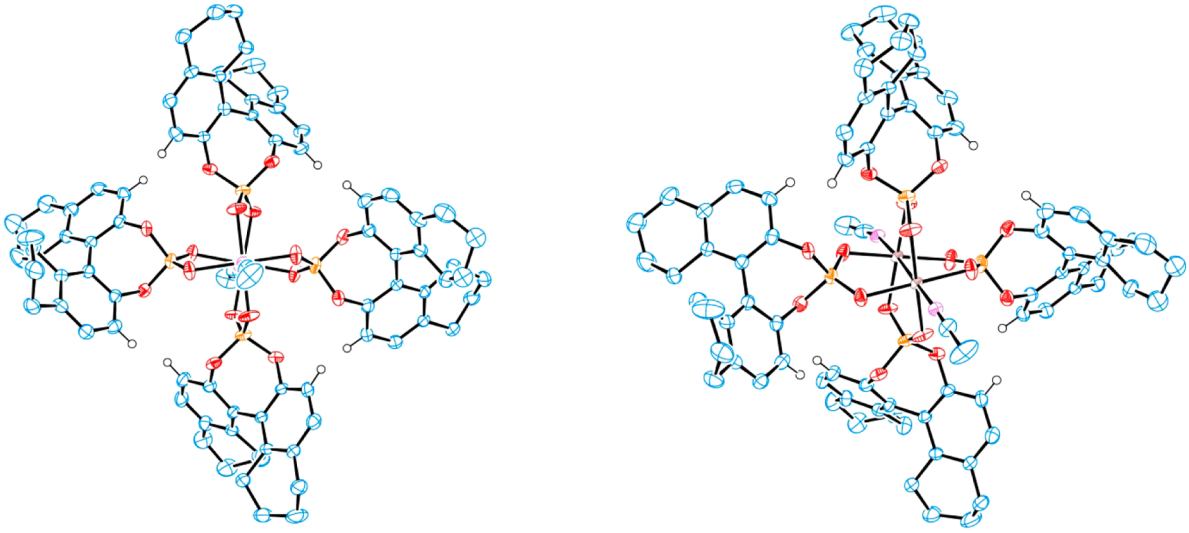

Figure 5. Crystal structure of pseudo-C_4-symmetrical tetrakis[(*R*)-1,1′-(5,5′,6,6′,7,7′,8,8′-octahydrobinaphthylphosphate]dirhodium, Rh_2[(*R*)-H_8-BNP]$_4$, **2a**.

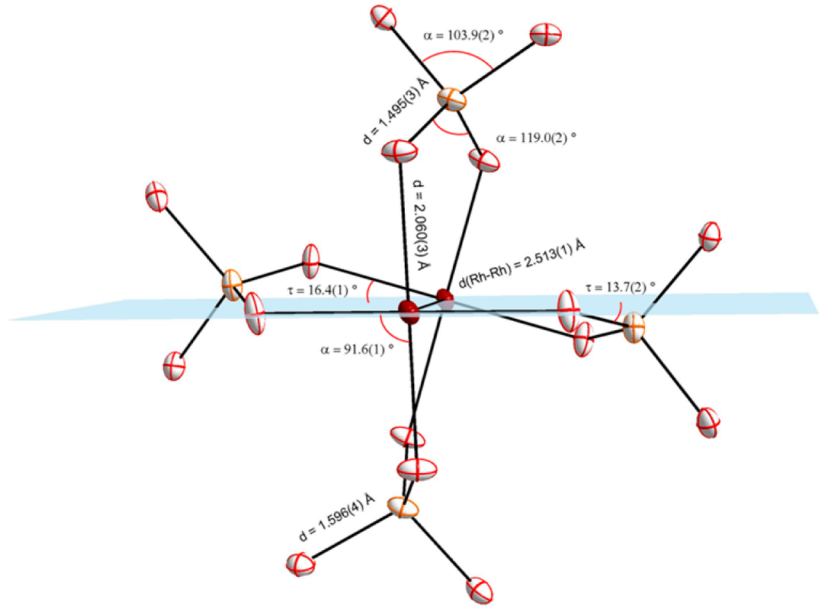

Figure 6. Rh−Rh core of **2a** with defined plane and selected distances and angles (Tables S7−S9).

saturation of the naphtho rings was considered as a possible solution.[38] (*R*)-(5,5′,6,6′,7,7′,8,8′-Octahydro)binaphthyl phosphoric acid **7a**[39] and its 3,3′-dibrominated analogue **7b** were prepared according to literature procedures.[40]

Refluxing eight equivalents of acid **7a** with $Rh_2(OAc)_4$ in chlorobenzene for 18 h resulted in the expected formation of the desired complex **2a** (82%).[41] Monocrystals were obtained from the mixture of acetonitrile and dichloromethane, and a structural X-ray analysis was performed (Figure 5, Table S6 in the Supporting Information). The resulting complex presented again a pseudo-C_4-symmetrical geometry and two molecules of acetonitrile as apical ligands on the rhodium atoms. The Rh−Rh bond distance is 2.513(1) Å, very close to that in complex **1a** (Table S7, Supporting Information).

For each ligand, a twist of the chelating ring can be noticed with a mean torsion angle O−Rh−Rh−O of 16.4(1)° (Figure 6, Table S9, Supporting Information). The average dihedral angle between the two phenyl planes is around 59.9(1)° (Table S8), 5° more than for compound **1a**. This larger value for the torsion angle was expected on the basis of previous observations.[42] It might be the reason for the slightly increased average O−P−O angle value observed within the chelating ring (118.9° and 118.2° for **2a** and **1a**, respectively), which in turn might be the reason for the twisted envelope-like (Rh−Rh−O−P−O) conformation (Figure 6, Table S7).

Measurement on each half of the complexes of the distances between the four H3 and H3′ atoms revealed an interesting aspect. For compound **2a**, these hydrogen atoms are distant on average by 7.12 and 7.20 Å on each half, forming comparable quadrilaterals of rather rectangular shape.

The chiral pockets created by the ligands around the rhodium atoms are thus virtually identical on each side for **2a**, and their size is intermediate to those measured for **1a**. In fact, the analogous analysis performed on **1a** revealed a contrasted situation. The average distances between H3 and H3′ atoms are 5.95 and 7.53 Å on each side respectively, indicating the

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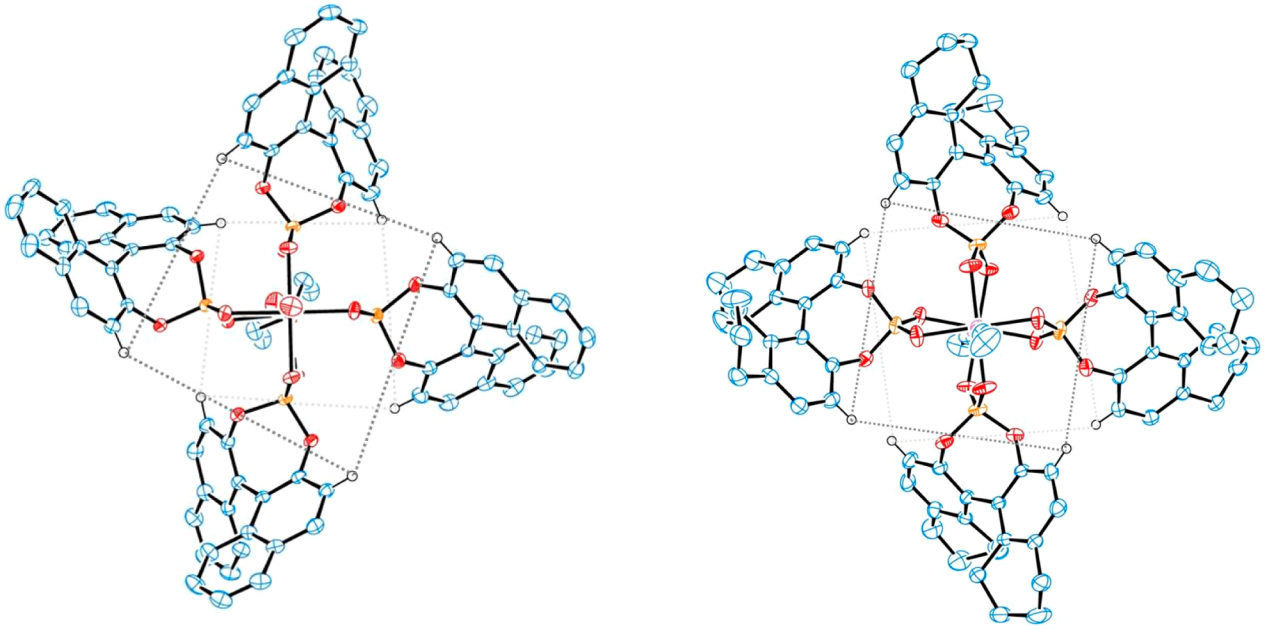
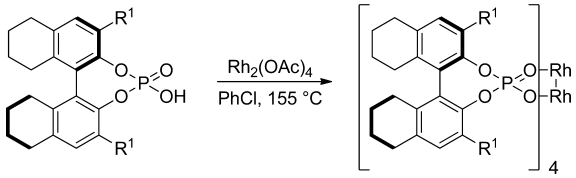


Figure 7. Comparison of complexes **1a** (left) and **2a** (right) considering the free volume of the apical electrophilic sides of rhodium atoms.

existence of a tight ligand pocket around one rhodium atom and a much larger one around the other (Table S10, Supporting Information). The quadrilaterals are drawn in Figure 7 (left) and compared to that of **2a** (right). Interestingly, the tight pocket surrounds the bound 1,4-dioxane molecule and not the small water ligand. The ligand exchange reaction was then performed with 3,3′-dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-binaphthyl hydrogen phosphate **7b**. In this case, in contrast to **3c**, the process went to completion and the homoleptic complex **2b** was isolated in 30% yield (Scheme 4). This positive result seems to validate the hypothesis of easier exchange reactions with partially saturated biaryl ligands. Crystals of **2b** were obtained from a 1,4-dioxane solution. The quality was sufficient to determine a C_4-symmetrical arrangement of the ligands, but insufficient for a more precise X-ray analysis. Introducing even larger substituents would formally be interesting, but X-ray structures of **2a** and **2b** indicate that formation of such complexes is highly unlikely for steric reasons.

Scheme 4. Synthesis of Complexes 2a and 2b



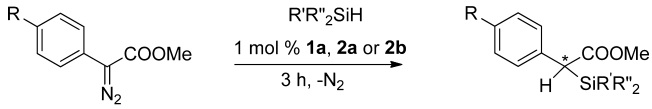
7a: R^1 = H
7b: R^1 = Br

2a: R^1 = H (82 %)
2b: R^1 = Br (30 %)

With complexes **2a** and **2b** in hand, their catalytic efficiency was evaluated using first the cyclopropanation of styrene with methyl phenyldiazoaceate **8a**, a reaction known to occur with the classic BNP catalyst **1a** (Scheme 5).[25] While both **2a** and **2b** performed well in terms of reactivity (80% and 74% yields), a lower selectivity was achieved. Cyclopropane **9** was obtained as a single diastereomer in 38% and 23% ee, respectively; all three catalysts afforded the product in the same predominant enantiomeric form.

In view of these rather negative results, another attempt was performed using the Si−H insertion reactions of methyl phenyldiazoacetates **8** (Scheme 5). Reactions of this type had been reported only in dirhodium catalysis with chiral carboxylate-derived complexes.[43−57] For instance, Moody and co-workers showed that $Rh_2(MEPY)_4$ affords the highest selectivity (55% ee) of a series of dirhodium carboxylates and carboxamidates.[51] Davies et al. reported the application of $Rh_2(DOSP)_4$ in this reaction to afford products of type **10** with 85% ee,[45] and the group of Hashimoto developed a $Rh_2(PTPA)_4$ complex that provided the insertion products with enantioselectivity values up to 72%.[49]

Scheme 6. Dirhodium-Catalyzed Si−H Insertions of Phenyldiazoacetates

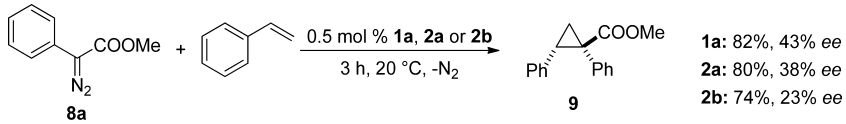


8
R = H, OMe, NO_2

R' = R" = Et
R' = R" = Ph
R' = Ph; R" = Me

10

Scheme 5. Dirhodium-Catalyzed Cyclopropanation of Styrene



8a

9

1a: 82%, 43% *ee*
2a: 80%, 38% *ee*
2b: 74%, 23% *ee*

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Table 1. Dirhodium-Catalyzed Si−H Insertions of Phenyldiazoacetates

entry	catalyst	diazo (R =)	silane	solvent	T [°C]	yield [%]	ee [%]
1	**1a**	H (**8a**)	Et_3SiH	CH_2Cl_2	25	83 (**10a**)	47; (−)-**10a**
2	**1a**	H (**8a**)	Me_2PhSiH	CH_2Cl_2	25	28 (**10b**)	43; **10b**
3	**1a**	H (**8a**)	Ph_3SiH	CH_2Cl_2	25	16 (**10c**)	44; **10c**
4	**1a**	H (**8a**)	Et_3SiH	$CHCl_3$	25	60 (**10a**)	49; (−)-**10a**
5	**1a**	H (**8a**)	Et_3SiH	toluene	25	90 (**10a**)	34; (−)-**10a**
6	**1a**	H (**8a**)	Et_3SiH	cyclohexane	25	42 (**10a**)	38; (−)-**10a**
7[a]	**1a**	H (**8a**)	Et_3SiH	CH_2Cl_2	−78	66 (**10a**)	63; (−)-**10a**
8	**1a**	OMe (**8d**)	Et_3SiH	CH_2Cl_2	25	81 (**10d**)	62; (−)-**10d**
9	**1a**	NO_2 (**8e**)	Et_3SiH	CH_2Cl_2	25	46 (**10e**)	44; (−)-**10e**
10	**2a**	H (**8a**)	Et_3SiH	CH_2Cl_2	25	72 (**10a**)	44 ; (−)-**10a**
11	**2b**	H (**8a**)	Et_3SiH	CH_2Cl_2	25	48 (**10a**)	20; (+)-**10a**

[a]12 h reaction time at −78 °C.

Methyl-2-diazophenylacetate **8a** (R = H) and $Rh_2(BNP)_4$ **1a** were first chosen as model reactant and catalyst (1 mol %), respectively. The silanes Et_3SiH, $PhMe_2SiH$, and Ph_3SiH were tested, and the results are reported in Table 1 (entries 1 to 3). Et_3SiH provided the corresponding product **10a** in good yield (83% yield) and with the best enantiomeric excess (47% ee) of the three silanes. Et_3SiH was thus used for further optimization. A rapid evaluation of common solvents (toluene, cyclohexane, $CHCl_3$, CH_2Cl_2) was performed, and it indicated that CH_2Cl_2 was better as far as yield and enantiomeric purity of **10a** are concerned. Low temperature (−78 °C) improved the selectivity of the reaction (63% ee) at the expense of the reactivity however (**10a**: 66% after 12 h). Selectivity could also be improved using more reactive diazo compound **8d** (R = *p*-MeO), as resulting product **10d** was obtained in 62% ee. Substitution of the diazo reactant with an electron-withdrawing group (**8e**: R = *p*-NO_2) had the reverse effect on yield and enantiomeric excess.

Partially saturated catalysts **2a** and **2b** were then tested. In the case of catalyst **2a** and substrate **8a**, a slight decrease of reactivity and selectivity was observed at room temperature (72% yield, 44% ee), the major enantiomer having the same absolute configuration as that obtained predominantly with **1a**. For the reaction with complex **2b**, adduct **10a** was afforded in only 48% yield and 20% enantiomeric excess, the product being of opposite (dextrorotatory) configuration of the previous examples. Obviously, unlike what had been desired initially, lower reactivity and enantioselectivity were obtained with 3,3′-disubstituted complex **2b**, an effect of the bromine atoms being clear from the reversal of the absolute sense of stereoinduction.

CONCLUSION

In summary, the synthesis and X-ray structural analyses of Pirrung's $Rh_2(BNP)_4$ and partially saturated complex **2a** were achieved. Only in the case of the ligand derived from octahydrobinol was it possible to form the homoleptic dirhodium complex with bromine atoms at the 3,3′-positions of the diols. Complexes **1a**, **2a**, and **2b** were briefly tested in the cyclopropanation of styrene and the Si−H insertion reactions of methyl phenyldiazoacetates. In both instances, substitution with bromine atoms was detrimental to reactivity and selectivity.

ASSOCIATED CONTENT

Supporting Information

Spectroscopic data for novel compounds and procedures describing the synthesis of stated compounds are available free of charge via the Internet at http://pubs.acs.org. CCDC-904048 to CCDC-904050 contain the supplementary crystallographic data for this paper (compounds **1a**, **2a**, and (*R*)-3,3′-difluoro-1,1′-bi-2-naphthol). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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