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Synthesis of novel planar chiral Ag and Rh N-heterocyclic carbene complexes derived from [2.2]paracyclophane and their application in ultrasound assisted asymmetric addition reactions of organoboronic acids to aldehydes

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ABSTRACT

Three novel planar chiral N-heterocyclic carbene silver and rhodium complexes based on [2.2]paracyclophane have been prepared. These could be used as catalysts/precatalysts for the asymmetric 1,2-addition of organoboronic acids to aldehydes. We optimized the reaction conditions and have applied ultrasonic irradiation in the asymmetric arylation for the first time. Under ultrasound irradiation, the combination of planar chiral NHC–Ag complex **5** and $RhCl_3$ can achieve higher catalytic activities in the asymmetric addition of organoboronic acids to aldehydes.

1. Introduction

Since N-heterocyclic carbenes (NHCs) are excellent σ-donors and form rather strong metal–carbon bonds, NHC–metal complexes exhibit higher air and thermal stability than those containing phosphines.[1] These factors have made NHC a promising alternative ligand to the currently used phosphines.[2] The successful applications of chiral phosphines in asymmetric catalysis are currently applicable to NHCs and their metal complexes.[3] Despite the considerable effort that has been devoted to this field, the design and synthesis of novel chiral NHCs to enhance their enantioselectivity is still a challenge.[4] Moreover, a better understanding of NHC design strategies and NHC applications in metal-based asymmetric catalysis would promote future development in this field.

Chiral diarylmethanols are important intermediates for the synthesis of biologically and pharmaceutically active compounds.[5] A general method for the synthesis of optically active diarylmethanols is the Rh-catalyzed asymmetric addition of organoboronic acids to aldehydes. Since Miyaura first reported the Rh-catalyzed asymmetric addition of organoboronic acids to aldehydes in 1998,[6] much attention has been shifted to a practical strategy: either to improve enantioselectivity or accelerate the reaction by using new catalyst systems.[7–9] Among these catalyst systems, Hayashi has developed several novel and effective chiral NHC–Cu complexes for the asymmetric addition of arylboronates to isatins in 2010.[8] Shi has recently reported other chiral NHC–Pd complexes and their successful application in the catalytic enantioselective arylation of aldehydes and ketones.[9] Shi has also shown that when the reactions were performed at a lower temperature, higher enantioselectivities were obtained.[9] Inspired by these results, we turned our attention to the preparation of planar chiral NHC–metal complexes and an investigation of new catalyst systems for the asymmetric addition reaction of organoboronic acids to aldehydes. Using chiral NHC–Rh complexes at lower reaction temperatures may be an efficient method to improve the enantioselectivity.[8,9] As a chiral source, planar chiral [2.2]paracyclophane derivatives have been successfully applied in asymmetric catalysis.[10] However, the application of structurally well-defined chiral [2.2]paracyclophane-based NHC–Rh complexes in catalytic asymmetric addition of organoboronic acids to aldehydes has not been explored to date.

Recently, our group has exploited the use of planar chiral [2.2]paracyclophane-based NHCs as ligands for the in situ Rh-catalyzed asymmetric arylation of aldehydes.[11] However, there are three drawbacks in our previous system:[11b] (1) the reaction temperature could not be lowered below 80 °C; (2) the scope of the aldehydes that were used in the catalysis reaction is somewhat limited; and (3) the structure of the NHC–Rh complex is not clear. The planar chiral [2.2]paracyclophane-based NHCs not only produced transition metal catalysts in situ, but also led to the isolation of metal complexes, which would allow further fine-tuning of catalyst properties. Few reports have considered the NHC–Rh complex catalyzed asymmetric addition of organoboronic acids to aldehydes. To the best of our knowledge, the reactions did not proceed well at room temperature even at elevated temperatures. It is worth noting that lowering the temperature may be a key strategy to achieve highly stereocontrolled reactions.[9]

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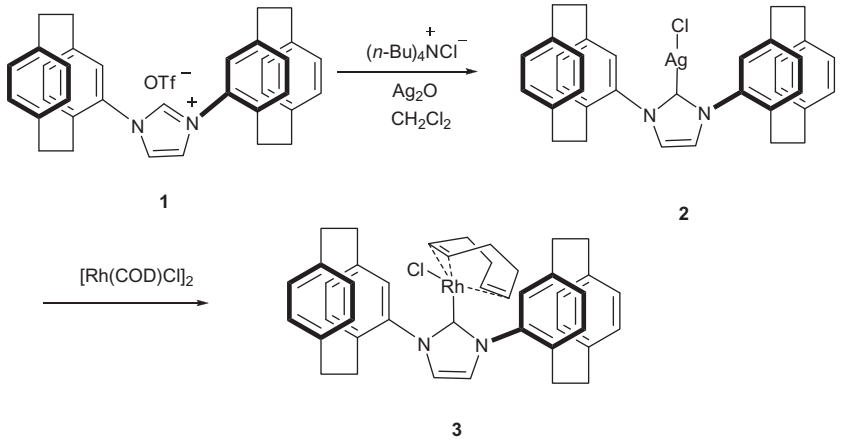
Recently, ultrasound has been used widely as a tool to enhance the yields and rates of many chemical reactions.[12] The use of ultrasound in chemical reactions provides specific activation based on a physical phenomenon, known as acoustic cavitation.[13] We wondered whether under sonication conditions the asymmetric addition reaction would provide higher yields and enantioselectivities. Herein, we report the synthesis of novel planar chiral imidazol-2-ylidene complexes of silver and rhodium and their application in the ultrasound-assisted rhodium-catalyzed asymmetric addition of organoboronic acids to aldehydes.

2. Results and discussion

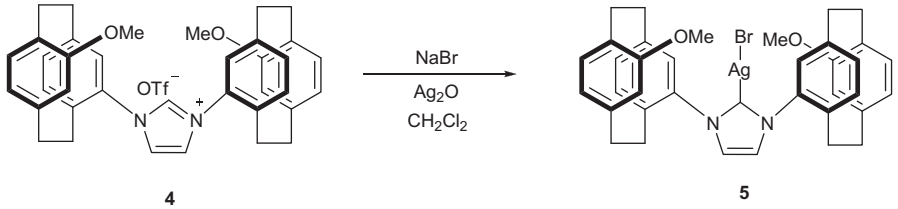
We designed and synthesized three new planar chiral NHC–Ag and NHC–Rh complexes based on the [2.2]paracyclophane skeleton. The synthetic route to the new NHC–metal complexes is shown in Schemes 1 and 2. The NHC complexes were synthesized from enantiomerically pure *N*,*N*′-bis[(R_p)-(−)-4-[2.2]paracyclophanyl]imidazolium triflate **1** and *N*,*N*′-bis[(R_p)-(−)-12-methoxy-4-[2.2]paracyclophanyl]imidazolium triflate **4**, which can be obtained by following the previous literature.[11] All of our attempts to prepare free carbene from the imidazolium salt using standard deprotonating agents such as *tert*-BuOK or NaH failed. Deprotonation using silver oxide as base has been widely used to synthesize NHC–Ag complexes which can transfer the carbene ligands to a variety of other metals.[2e,14] According to this strategy, the imidazolium triflate **1** was treated with an excess of Ag_2O in anhydrous CH_2Cl_2, but no reaction occurred. By anion exchange of the imidazolium triflate **1** with tetrabutylammonium chloride in the presence of Ag_2O in anhydrous CH_2Cl_2, the NHC–Ag complex **2** could be obtained in moderate yield.[15] However, the ion exchange product was contaminated by tetrabutylammonium chloride, although it could be purified by repeated recrystallization from dichloromethane and hexane. As an alternative procedure, NaBr was used instead of tetrabutylammonium chloride for the preparation of NHC–Ag **5**.[16] Accordingly, the bromo[*N*,*N*′-bis[(R_p)-(+)-12-methoxy-4-[2.2]paracyclophanyl]imidazol-2-ylidene]silver **5** was also synthesized by treating *N*,*N*-bis[(R_p)-(−)-12-methoxy-4-[2.2]paracyclophanyl]imidazolium triflate with NaBr and Ag_2O in CH_2Cl_2. NHC–Ag **2** underwent a facile reaction with $[Rh(COD)Cl]_2$ to form an NHC–Rh complex **3**. The complexes chloro[*N*,*N*′-bis[(R_p)-(+)-4-[2.2]paracyclophanyl]imidazol-2-ylidene]silver **2**, bromo(*N*,*N*′-bis[(R_p)-(+)-12-methoxy-4-[2.2]paracyclophanyl]imidazolium)silver **5**, and chloro(η^2,η^2-1,5-cyclooctadiene)[*N*,*N*′-bis[(R_p)-(+)-4-[2.2]paracyclophanyl]imidazole-2-ylidene]rhodium **3** were characterized by ^{1}H NMR, ^{13}C NMR, high-resolution mass spectrometry (HRMS), and elemental analysis. The absence of an N–CH–N resonance in the ^{1}H NMR spectra confirmed the formation of the carbene complexes. The ^{13}C NMR, high-resolution mass spectrometry, or elemental analysis further confirmed the molecular structures. The structure of the novel planar chiral NHC–Rh complex **3** was determined by X-ray diffraction (Fig. 1).

With the planar chiral NHC–metal complexes in hand, we examined their application in the asymmetric addition of organoboronic acids to aldehydes.

Our study began with structurally well-defined chloro(η^2,η^2-1,5-cyclooctadiene)[*N*,*N*′-bis[(R_p)-(+)-4-[2.2]paracyclophanyl]imidazole-2-ylidene]rhodium **3** under the analogous conditions as used in our previous studies of the rhodium-catalyzed asymmetric arylation of aldehydes[11] (Table 1). The reaction of phenylboronic acid and 1-naphthaldehyde was performed with 3.0 mol % of catalyst in MeOH/DME (5:1) or *t*-BuOH/MeOH (5:1) at 80 °C for 3 h. Compared to our previous work, the enantioselectivities of the reaction were lower (Table 1, entries 1, 2). By screening bases in MeOH/DME (5:1) or *t*-BuOH/MeOH (5:1), we found that the addition of an excess of KF (6.0 equiv) significantly improved the enantioselectivities (Table 1, entries 3, 4). We further optimized the reaction conditions by tuning the solvent effect. Variation of the solvent showed that the *t*-BuOH/MeOH (5:1) was the best choice of solvent (Table 1, entries 5–10). Upon lowering the reaction temperature to rt almost no reaction



Scheme 1. Synthesis of planar chiral NHC–Rh **3**.



Scheme 2. Synthesis of planar chiral NHC–Ag **5**.

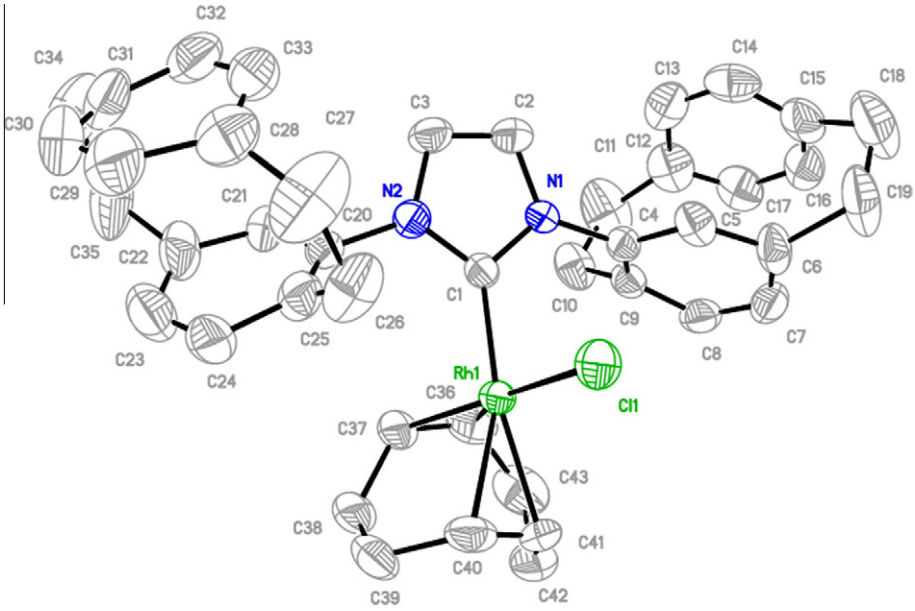


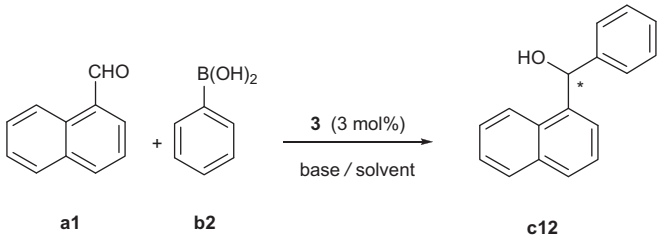
Figure 1. ORTEP drawing of NHC–Rh complex **3** showing atomic numbering scheme at 50% probability ellipsoids. Hydrogen atoms and H_2O molecules are omitted for clarity. Selected bond distance (Å) and angles (°): Rh(1)–C(1) = 2.019(5), Rh(1)–C(36) = 2.089(6), Rh(1)–C(37) = 2.119(5), Rh(1)–C(40) = 2.179(6), Rh(1)–C(41) = 2.206(5), Rh(1)–Cl(1) = 2.3862(14), C(1)–Rh(1)–C(36) = 93.5(2), C(1)–Rh(1)–C(37) = 94.4(2), C(36)–Rh(1)–C(37) = 39.2(3), C(1)–Rh(1)–C(40) = 158.0(2), C(36)–Rh(1)–C(40) = 96.5(3), C(37)–Rh(1)–C(40) = 81.3(2), C(1)–Rh(1)–C(41) = 166.2(2), C(36)–Rh(1)–C(41) = 80.5(3), C(37)–Rh(1)–C(41) = 88.8(2), C(40)–Rh(1)–C(41) = 35.8(3), C(1)–Rh(1)–Cl(1) = 89.04(14), C(36)–Rh(1)–Cl(1) = 155.9(2), C(37)–Rh(1)–Cl(1) = 164.26(18), C(40)–Rh(1)–Cl(1) = 89.82(17), C(41)–Rh(1)–Cl(1) = 91.53(18).

occurred, however, a 47% conversion and 36% ee were observed at 50 °C (Table 1, entries 11, 12). Significantly, lower temperature can afford the desired product with higher enantioselectivity.

Next, we screened different rhodium compounds as metal sources and NHC–Ag **2** as a precatalyst for the asymmetric addition reaction. $[Rh(COD)Cl]_2$ and $[Rh(COD)OH]_2$ were found to be less efficient in this reaction in terms of poor enantioselectivities (6–12% ee) (Table 2, entries 1, 2), and other rhodium compounds tested showed similar enantioselectivities (32–37% ee) (Table 2, entries 3–5), whereas $RhCl_3$ gave the highest enantioselectivity (Table 2, entry 6). It is known that the methoxy group on the [2.2]paracyclophanyl ligand backbone plays an important role in the catalytic process,[6,7a,b,11b] so the bromo[*N*,*N*′-bis[(R_p)-(+)-12-methoxy-4-[2.2]paracyclophanyl]imidazol-2-ylidene]silver **5** was then used as a precatalyst and $RhCl_3$ used as a rhodium source for this reaction. The reaction gave a moderate yield (51%) and enantioselectivity (52% ee). Reducing the reaction temperature to 40 °C, the combination of NHC–Ag **2** and $RhCl_3$ showed no catalytic activity (Table 2, entry 8), however, NHC–Ag **5** combined with $RhCl_3$ catalyzed this reaction to provide the desired product (33% yield, 58% ee) (Table 2, entry 9). In order to improve the yield, an ultrasonic oscillator was used as an alternative energy source to facilitate the chemical reactions. Under sonication (the reaction flask was clamped in an ultrasonic bath of 40 kHz frequency at 40 °C for the purpose of irradiation), using NHC–Ag **5** as precatalyst exhibited an astonishingly high catalytic activity (73% yield) (Table 2, entry 11), but the combination of NHC–Ag **2** and $RhCl_3$ showed a lower catalytic activity (14% yield; Table 2, entry 10). Encouraged by these results we embarked on the use of ultrasonic energy to assist the asymmetric addition of organoboronic acids to aldehydes.

Having optimized the reaction conditions, we finally evaluated the substrate scope with various aldehydes and organoboronic acids. As shown in Table 3, the optimized protocol was compatible with a wide variety of functional groups on both reaction partners, and in most cases, the reaction could proceed with notable efficiency (up to 94% yield) with 3 mol % catalyst loading. The electronic property of the arylaldehyde has an important effect on the enantioselectivity of the catalytic reaction. With electron-deficient arylaldehydes, the catalyst was more enantioselective (Table 3, entries 1–3, 5–10). However, the electron-rich aryladehydes **a5** and **a6** reacted with aromatic boronic acids **b2** and **b1** and afforded the corresponding adducts **c52** and **c61** in 41% and 39% ee, respectively (Table 3, entries 11, 12). Unfortunately, the reaction conditions above were not suitable for the heterocyclic substrates. The

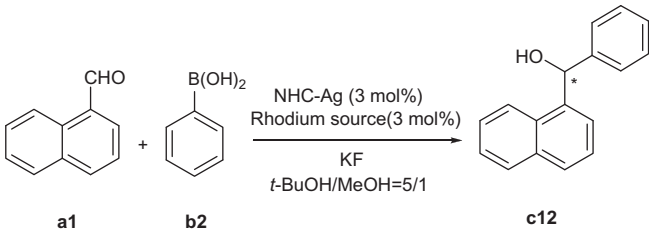
Table 1
Evaluation of solvent and base[a]



Entry	Solvent	Base	Yield[b] (%)	ee[c] (%)
1	MeOH/DME (5:1)	*t*-BuOK	85	8 (*R*)
2	*t*-BuOH/MeOH (5:1)	*t*-BuOK	84	12 (*R*)
3	MeOH/DME (5:1)	KF	86	26 (*R*)
4	*t*-BuOH/MeOH (5:1)	KF	88	28 (*R*)
5	MeOH	KF	64	21 (*R*)
6	*i*-PrOH	KF	57	21 (*R*)
7	DME/H_2O (10:1)	KF	67	4 (*R*)
8	Toluene/H_2O (5:1)	KF	51	2 (*R*)
9	$ClCH_2CH_2Cl/H_2O$ (1:1)	KF	84	6 (*R*)
10	*t*-BuOH/EtOH (5:1)	KF	72	10 (*R*)
11[d]	*t*-BuOH/MeOH (5:1)	KF	0	—
12[d]	MeOH/DME (5:1)	KF	47	36 (*R*)

[a] Reaction conditions: chloro(η^2,η^2-1,5-cyclo-octadiene)-[*N*,*N*′-bis[(R_p)-(+)-4-[2.2] paracyclophanyl]imidazole-2-ylidene]rhodium **3** (3 mol %), *t*-BuOK (1 equiv), or KF (6 equiv), phenylboronic acid (2 equiv), 1-naphthaldehyde (1 equiv), N_2, 80 °C, 3 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Column) analysis.
[d] Reaction temperature: 50 °C.

Table 2
Evaluation of the rhodium source and precatalyst[a]

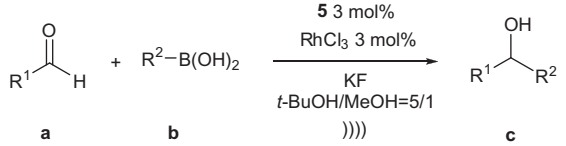


a1 b2 c12

Entry	Rhodium source	Ag-NHC	Yield[b] (%)	ee[c] (%)
1	$[Rh(COD)Cl]_2$	**2**	78	6 (*R*)
2	$[Rh(COD)OH]_2$	**2**	58	12 (*R*)
3	$[Rh(OAc)_2]_2$	**2**	83	37 (*R*)
4	$[Rh(NBD)Cl]_2$	**2**	81	36 (*R*)
5	$[Rh(C_2H_4)_2Cl]_2$	**2**	79	32 (*R*)
6	$RhCl_3$	**2**	87	48 (*S*)
7	$RhCl_3$	**5**	51	52 (*S*)
8[e]	$RhCl_3$	**2**	0	—
9[e]	$RhCl_3$	**5**	33	58 (*S*)
10[d,e]	$RhCl_3$	**2**	14	61 (*S*)
11[d,e]	$RhCl_3$	**5**	73	58 (*S*)

[a] Reaction conditions: Ag–NHC **2** or **5** (3 mol %), KF (6 equiv), phenylboronic acid (2 equiv), 1-naphthaldehyde (1 equiv), N_2, 80 °C, 3 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Column) analysis.
[d] Ultrasound irradiation.
[e] Reaction temperature: 40 °C.

Table 3
Scope of the methodology[a]



a b c

Entry	Ar^1	Ar^2	Yield[b] (%)	ee[c] (%)
1	1-Naphthyl **a1**	Phenyl **b2**	73 **c12**	58 (*S*)
2	1-Naphthyl **a1**	2-$MeOC_6H_4$ **b3**	72 **c13**	67 (+)
3	1-Naphthyl **a1**	3-$MeOC_6H_4$ **b4**	52 **c14**	52 (−)
4	Phenyl **a2**	1-Naphthyl **b1**	92 **c21**	44 (*R*)
5	4-ClC_6H_4 **a3**	Phenyl **b2**	57 **c32**	58 (*S*)
6	4-ClC_6H_4 **a3**	2-$MeOC_6H_4$ **b3**	87 **c33**	48 (+)
7	4-ClC_6H_4 **a3**	3-$MeOC_6H_4$ **b4**	67 **c34**	54 (*S*)
8	4-$MeOOCC_6H_4$ **a4**	Phenyl **b2**	94 **c42**	61 (*R*)
9	4-$MeOOCC_6H_4$ **a4**	2-$MeOC_6H_4$ **b3**	87 **c43**	58 (−)
10	4-$MeOOCC_6H_4$ **a4**	3-$MeOC_6H_4$ **b4**	76 **c44**	62 (+)
11	3-$MeOC_6H_4$ **a5**	Phenyl **b2**	72 **c52**	41 (−)
12	2,4,6-Trimethyl C_6H_2 **a6**	1-Naphthyl **b1**	58 **c61**	39 (+)
13	2-Furyl **a7**	1-Naphthyl **b1**	91 **c71**	24 (−)
14	2-Furyl **a7**	Phenyl **b2**	82 **c72**	20 (*S*)
15	2-Furyl **a7**	2-$MeOC_6H_4$ **b3**	74 **c73**	14 (+)
16	2-Furyl **a7**	3-$MeOC_6H_4$ **b4**	71 **c74**	24 (−)
17	2-Thienyl **a8**	1-Naphthyl **b1**	82 **c81**	20 (−)
18	2-Thienyl **a8**	Phenyl **b2**	59 **c82**	19 (*R*)
19	2-Thienyl **a8**	2-$MeOC_6H_4$ **b3**	81 **c83**	5 (−)
20	2-Thienyl **a8**	3-$MeOC_6H_4$ **b4**	71 **c84**	18 (−)
21	3-Pyridyl	Phenyl **b2**	0	—
22	Phenyl **a2**	2-Furyl **b5**	Trace	—
23	Phenyl **a2**	2-Thienyl **b6**	Trace	—
24	4-$MeOOCC_6H_4$ **a4**	2-Furyl **b5**	94 **c45**	27 (−)
25	4-$MeOOCC_6H_4$ **a4**	2-Thienyl **b6**	82 **c46**	10 (−)

[a] Reaction conditions: Ag–NHC **5** (3 mol %), $RhCl_3$ (3 mol %), KF (6 equiv), organoboronic acids (2 equiv), aldehydes (1 equiv), N_2, 40 °C, Ultrasound irradiation:)))) 3 h.
[b] Isolated yield.
[c] Determined by chiral HPLC (CHIRALPAK IA Column or Chiralcel OD-H column) analysis.

reactions of 2-furylaldehyde and 2-thienylaldehyde with various aromatic boronic acids **b1**, **b2**, **b3**, and **b4** afforded the corresponding products in moderate to high yields (59–91%) with low enantioselectivities (5–24% ee) (Table 3, entries 13–20). We also examined heteroaromatic boronic acids, very low activities were observed using phenylaldehyde as a substrate (Table 3, entries 22, 23). When an aromatic aldehyde with an electron-withdrawing group **a4** was employed, better activities were achieved (82% and 94% yield), but only low enantioselectivities were obtained (Table 3, entries 24, 25).

3. Conclusion

Three novel planar chiral N-heterocyclic carbene silver and rhodium complexes based on [2.2]paracyclophane have been synthesized and applied in the asymmetric addition of organoboronic acids to aldehydes. All of these complexes were fully characterized by ^1H and ^{13}C NMR, high-resolution mass spectrometry (HRMS), and elemental analysis. Single-crystal X-ray diffraction result further confirmed the molecular structure of NHC–Rh complex **3**. We optimized the reaction conditions and applied ultrasonic irradiation in the asymmetric arylation for the first time. Under ultrasound irradiation, the planar chiral NHC–Rh complexes can achieve higher catalytic activities in the asymmetric addition of aromatic boronic acids to arylaldehydes, and the best results are observed with a combination of NHC–Ag **5** and $RhCl_3$. However, the reaction conditions above were not suitable for the heterocyclic substrates, only low enantioselectivities could be obtained. Further modifications of [2.2]paracyclophane-based carbene–metal complexes as well as applications in asymmetric catalysis are currently underway in our group.

4. Experimental section

4.1. General

Commercially available reagents were used without further purification unless otherwise noted. Solvents were of reagent grade and purified by standard techniques. The planar chiral imidazolium salts **1** and **4** were obtained by following the previous literature.[11] Melting points were recorded on a melting point apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 at 298 K. HRMS spectra were recorded on an Agilent Technologies 6510 Q-Tof LC/MS. Enantiomeric excess was determined using HPLC on a Chiralpak IA chiral column. Optical rotations were taken on a polarimeter WZZ-2B equipped with a sodium lamp (λ = 589 nm). The concentration '*c*' has units of g/100 mL (or 10 mg/mL) unless otherwise noted.

4.2. Chloro[*N*,*N*′-bis[(R_p)-(+)-4-[2.2]paracyclophanyl]imidazol-2-ylidene]silver 2

A dry Schlenk tube flask was charged with *N*,*N*′-bis[(R_p)-(−)-4-[2.2]paracyclophanyl] imidazolium triflate **1** (63 mg, 0.1 mmol), tetrabutylammonium chloride (83 mg, 0.3 mmol), and Ag_2O (14 mg, 0.06 mmol). After backfilling with N_2 of the reaction tube, CH_2Cl_2 (2.0 mL) was added. The mixture was stirred in the absence of light for 24 h at room temperature. The resulting off-white precipitate was filtered and the solvent was reduced until the solution became cloudy. Subsequently hexane was added to precipitate the product. Pure product **2** was obtained as a white solid by repeated recrystallization from dichloromethane and hexane (29.4 mg, 47% yield). Mp >260 °C, R_f 0.2 (CH_2Cl_2/ethanol = 30:1); $[\alpha]_D^{20} = +73.3$ (*c* 0.21, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$, rt): δ 7.57 (d, *J* = 1.5 Hz, 2H), 6.80–6.62 (m, 14H), 3.25–2.84 (m, 16H); ^{13}C NMR

(75 MHz, $CDCl_3$, rt): δ 141.9, 139.6, 139.2, 138.5, 137.5, 134.6, 133.4, 133.3, 132.8, 129.4, 126.5, 122.5, 122.4, 35.3, 35.1, 34.9, 32.8. Anal. Calcd for $C_{35}H_{33}AgClN_2{\cdot}H_2O$: C, 65.38; H, 5.49; N, 4.36. Found: C, 65.34; H, 5.36; N, 4.74.

4.3. Chloro(η^2,η^2-1,5-cyclo-octadiene)-[*N*,*N*′-bis[(R_p)-(+)-4-[2.2]paracyclophanyl]imidazole-2-ylidene]rhodium 3

Under an atmosphere of nitrogen, a methanol (1 mL) solution of **2** (29.4 mg, 0.047 mmol) and $[Rh(COD)Cl]_2$ (13.0 mg, 0.024 mmol) was stirred at 60 °C for 12 h. The solvent was removed in vacuo, and the remaining yellow precipitate was then dissolved in dichloromethane (2.0 mL). The product was purified by column chromatography on silica gel (CH_2Cl_2/acetone = 20:1), the target compound **3** was obtained as a yellow solid (29.5 mg, 83% yield). The solid was recrystallized from hexane–CH_2Cl_2 to afford yellow crystals of the product for X-ray diffraction analysis. Mp: 186–188 °C, R_f 0.4 (CH_2Cl_2/ethyl acetate = 50:1); $[\alpha]_D^{20} = +47$ (*c* 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.77 (d, *J* = 1.9 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 6.91 (s, 1H), 6.79–6.62 (m, 10H), 6.56–6.49 (m, 2H), 6.41 (d, *J* = 1.7 Hz, 1H), 4.51–4.44 (m, 1H), 4.33 (s, 1H), 3.67–3.57 (m, 1H); 3.34–2.81 (m, 16H); 2.20 (s, 1H), 1.82–1.74 (m, 3H), 1.54–1.11 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 187.4, 186.8, 141.1, 140.4, 140.3, 140.1, 139.0, 138.5, 137.9, 137.6, 136.5, 135.1, 135.0, 134.4, 134.3, 133.8, 133.6, 132.8, 132.6, 132.4, 132.3, 132.0, 129.8, 129.6, 128.1, 121.8, 121.2, 96.6 (d, *J* = 7.3 Hz), 96.1 (d, *J* = 7.3 Hz), 68.8 (d, *J* = 14.7 Hz), 66.5 (d, *J* = 14.6 Hz), 35.8, 35.6, 35.5, 35.4, 35.0, 34.3, 32.6, 32.0, 29.7, 28.4, 27.9. Anal. Calcd for $C_{43}H_{44}ClN_2Rh{\cdot}0.5H_2O{\cdot}0.5CH_2Cl_2$: C, 67.10; H, 5.95; N, 3.60. Found: C, 67.06; H, 5.84; N, 3.22.

4.4. Bromo[*N*,*N*′-bis[(R_p)-(+)-12-methoxy-4-[2.2]paracyclophanyl]imidazol-2-ylidene]silver 5

Under an atmosphere of nitrogen, *N*,*N*′-bis[(R_p)-(−)-12-methoxy-4-[2.2]paracyclophanyl]imidazolium triflate (69 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (5.0 mL), Ag_2O (14 mg, 0.06 mmol) and NaBr (51 mg, 0.5 mmol) were added. The mixture was stirred in the absence of light for 3 days at room temperature. The resulting off-white precipitate was filtered and washed with three 25 mL portions of dichloromethane. The combined filtrates were collected, and the solvent was reduced until the solution became cloudy. Subsequently hexane was added to precipitate product **4** as a white solid (41.4 mg, 57% yield). Mp >186 °C (decomposition), R_f 0.2 (CH_2Cl_2/ethanol = 30:1); $[\alpha]_D^{20} = +125.2$ (*c* 0.27, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.90 (s, 2H), 6.91 (d, *J* = 1.7 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 2H), 6.53–6.45 (m, 4H), 6.00 (d, *J* = 1.6 Hz, 2H), 3.81 (s, 6H), 3.47–3.39 (m, 2H), 3.14–3.04 (m, 8H), 2.85–2.73 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 158.0, 141.8, 140.8, 138.3, 136.0, 134.8, 134.0, 132.6, 129.5, 127.6, 123.8, 121.6, 119.5, 59.3, 33.9, 33.1, 31.8, 30.1. HRMS (ESI): calcd for $C_{37}H_{36}Ag\,N_2O_2$ $(M-Br)^+$ 647.1828, found 647.1858.

4.5. General procedure for the optimization of the base and solvent for the arylation of aldehyde (Table 1)

First, chloro(η^2,η^2-1,5-cyclo-octadiene)[*N*,*N*′-bis[(R_p)-(+)-4-[2.2]paracyclophanyl] imidazole-2-ylidene]rhodium **3** (2.84 mg, 3.8×10^{-3} mmol, 3 mol %) was weighed into a dried tube equipped with a condenser under a nitrogen atmosphere. The solvent (1.0 mL) was added and the suspension was stirred at room temperature for 5 min. Then, *t*-BuOK (1 equiv) or KF (2–7 equiv), phenylboronic acid (30.5 mg, 0.25 mmol), and 1-naphthaldehyde (19.5 mg, 0.125 mmol) were added successively. The resulting mixture was stirred at 80 °C for 3 h. The reaction mixture was concentrated in vacuo and the residue was purified by chromatography (hexane/ethyl acetate = 15:1), to give the desired diarylmethanol as a slightly yellow oil at room temperature.

4.6. General procedure for the rhodium source evaluation (Table 2)

The NHC–Ag complex (3.8×10^{-3} mmol, 3 mol%) and rhodium source (3.8×10^{-3} mmol, 3 mol %) were added to 0.5 mL of anhydrous methanol in a dried tube equipped with a condenser under a nitrogen atmosphere. The mixture was stirred at room temperature overnight to give a yellow solution of the rhodium-complex. Then the solvent was removed in vacuum and *t*-BuOH/MeOH (5:1) (1.2 mL) was added and the suspension was stirred at room temperature for 5 min. Then, phenylboronic acid (30.5 mg, 0.25 mmol), KF (43.5 mg, 0.75 mmol), and 1-naphthaldehyde (19.5 mg, 0.125 mmol) were added successively. The resulting mixture was clamped in an ultrasonic bath of 40 kHz frequency at 40 °C for 3 h. The reaction mixture was concentrated in vacuo and the residue was purified by chromatography (hexane/ethyl acetate = 15:1), to give the desired diarylmethanol as a slightly yellow oil at room temperature.

4.7. General procedure for the scope of the methodology (Table 3)

The NHC–Ag complex **5** (2.73 mg, 3.8×10^{-3} mmol) and $RhCl_3$ (0.78 mg, 3.8×10^{-3} mmol) were added to 0.5 mL of anhydrous methanol in a dried tube equipped with a condenser under a nitrogen atmosphere. The mixture was stirred at room temperature overnight to give a yellow solution of the rhodium-complex. Then the solvent was removed in vacuum and *t*-BuOH/MeOH (5:1) (1.2 mL) was added and the suspension was stirred at room temperature for 5 min. Then, organoboronic acid (0.25 mmol), KF (43.5 mg, 0.75 mmol), and aldehyde (0.125 mmol) were added successively. The resulting mixture was clamped in an ultrasonic bath of 40 kHz frequency at 40 °C for 3 h. The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 15:1), giving the desired diarylmethanols. The following diarylmethanol products were identified by comparison to data reported in the literature.[11,17]

4.7.1. (1-Naphthyl) phenylmethanols c12 and c21

(*S*)-(−)-**c12**: 73% yield; $[\alpha]_D^{20} = -24.7$ (*c* 0.15, $CHCl_3$) with 58% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 50:1, flow 0.5 ml/min, detection at 254 nm), retention times 67.7 min (major) and 74.0 min (minor).

(*R*)-(+)-**c21**: 92% yield; $[\alpha]_D^{20} = +15.1$ (*c* 0.25, $CHCl_3$) with 44% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 100:1, flow 0.5 ml/min, detection at 254 nm), retention times 100.4 min (minor) and 108.3 min (major).

4.7.2. (1-Naphthyl) (2-methoxyphenyl) methanol c13

(+)-**c13**: 72% yield; $[\alpha]_D^{20} = +31.1$ (*c* 0.26, $CHCl_3$) with 67% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 50:1, flow 0.5 ml/min, detection at 254 nm), retention times 43.9 min (minor) and 52.3 min (major).

4.7.3. (1-Naphthyl) (3-methoxyphenyl) methanol c14

(−)-**c14**: 52% yield; $[\alpha]_D^{20} = -35.6$ (*c* 0.1, $CHCl_3$) with 52% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 50:1, flow 0.5 ml/min,

detection at 254 nm), retention times 74.1 min (major) and 100.8 min (minor).

4.7.4. (4-Chlorophenyl) phenylmethanol c32

(*S*)-(+)-**c32**: 57% yield; $[\alpha]_D^{20} = +25.6$ (*c* 0.13, $CHCl_3$) with 58% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 10:1, flow 0.5 ml/min, detection at 254 nm), retention times 14.9 min (minor) and 15.7 min (major).

4.7.5. (4-Chlorophenyl) (2-methoxyphenyl) methanol c33

(+)-**c33**: 87% yield; $[\alpha]_D^{20} = +15.9$ (*c* 0.25, $CHCl_3$) with 48% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 10:1, flow 0.5 ml/min, detection at 254 nm), retention times 15.7 min (minor) and 17.4 min (major).

4.7.6. (4-Chlorophenyl) (3-methoxyphenyl) methanol c34

(*S*)-(+)-**c34**: 67% yield; $[\alpha]_D^{20} = +3.3$ (*c* 0.37, $CHCl_3$) with 54% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 10:1, flow 0.5 ml/min, detection at 254 nm), retention times 32.4 min (minor) and 38.9 min (major).

4.7.7. [4-(Methoxycarbonyl)phenyl] phenylmethanol c42

(*R*)-(−)-**c42**: 94% yield; $[\alpha]_D^{20} = -20.0$ (*c* 0.35, $CHCl_3$) with 61% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 10:1, flow 1.0 ml/min, detection at 254 nm), retention times 13.9 min (minor) and 22.0 min (major).

4.7.8. [4-(Methoxycarbonyl)phenyl] (2-methoxyphenyl) methanol c43

(−)-**c43**: 87% yield; $[\alpha]_D^{20} = -17.6$ (*c* 0.31, $CHCl_3$) with 58% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 10:1, flow 1.0 ml/min, detection at 254 nm), retention times 12.5 min (minor) and 19.6 min (major).

4.7.9. [4-(Methoxycarbonyl)phenyl] (3-methoxyphenyl) methanol c44

(+)-**c44**: 76% yield; $[\alpha]_D^{20} = +27.9$ (*c* 0.40, $CHCl_3$) with 62% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 10:1, flow 1.0 ml/min, detection at 254 nm), retention times 17.0 min (minor) and 29.4 min (major).

4.7.10. (3-Methoxyphenyl) phenylmethanol c52

(*R*)-(−)-**c52**: 72% yield; $[\alpha]_D^{20} = -12.2$ (*c* 0.15, $CHCl_3$) with 41% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 50:1, flow 0.5 ml/min, detection at 254 nm), retention times 71.1 min (major) and 87.2 min (minor).

4.7.11. (2,4,6-Trimethylphenyl) (1-naphthyl) methanol c61

(+)-**c61**: 58% yield; $[\alpha]_D^{20} = +11.2$ (*c* 0.21, $CHCl_3$) with 39% ee; The ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 100:1, flow 0.5 mL/min, detection at 254 nm), retention times 64.8 min (major) and 73.5 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 8.22 (d, *J* = 3.3 Hz, 1H), 7.89 (d, *J* = 5.2 Hz, 1H), 7.80–7.86 (m, 7H), 6.53 (s, 1H), 2.30 (s, 9H), 2.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 137.2, 137.1, 137.1, 135.4, 134.1, 131.5, 130.4, 128.8, 128.5, 126.2, 125.6, 125.1, 125.0, 124.4, 70.9, 21.2, 20.9. HRMS (ESI): calcd for $C_{20}H_{19}$ $(M-OH)^+$ 259.1487, found 259.1493.

4.7.12. (2-Furyl) (1-naphthyl) methanol c71

(−)-**c71**: 91% yield; $[\alpha]_D^{20} = -4.0$ (*c* 0.18, CH_2Cl_2) with 24% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 20:1, flow 0.5 ml/min, detection at 254 nm), retention times 26.5 min (major) and 28.5 min (minor). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 7.97–8.00 (m, 1H), 7.81–7.88 (m, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.39–7.51 (m, 4H), 6.53 (s, 1H), 6.27–6.28 (m, 1H), 6.02 (d, *J* = 3.3 Hz, 1H), 2.59 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 155.2, 142.0, 135.8, 133.3, 130.1, 128.3, 125.7, 125.2, 124.9, 123.8, 123.1, 109.9, 107.5, 67.1. HRMS (ESI): calcd for $C_{15}H_{11}O$ $(M-OH)^+$ 207.0804, found 207.0814.

4.7.13. (2-Furyl) phenylmethanol c72

(*S*)-(−)-**c72**: 82% yield; $[\alpha]_D^{20} = -1.4$ (*c* 0.15, $CHCl_3$) with 20% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 100:1, flow 0.5 ml/min, detection at 254 nm), retention times 71.5 min (major) and 75.2 min (minor).

4.7.14. (2-Furyl) (2-methoxyphenyl) methanol c73

(+)-**c73**: 74% yield; $[\alpha]_D^{20} = +5.1$ (*c* 0.15, CH_2Cl_2) with 14% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 20:1, flow 0.5 ml/min, detection at 254 nm), retention times 35.5 min (major) and 39.2 min (minor).

4.7.15. (2-Furyl) (3-methoxyphenyl) methanol c74

(−)-**c74**: 71% yield; $[\alpha]_D^{20} = -7.8$ (*c* 0.14, CH_2Cl_2) with 24% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralcel OD-H column, *n*-hexane/*i*-propanol = 95:5, flow 0.5 ml/min, detection at 254 nm), retention times 49.4 min (major) and 54.8 min (minor).

4.7.16. (2-Thienyl) (1-naphthyl) methanol c81

(−)-**c81**: 82% yield; $[\alpha]_D^{20} = -8.2$ (*c* 0.15, CH_2Cl_2) with 20% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 20:1, flow 0.5 ml/min, detection at 254 nm), retention times 33.9 min (minor) and 36.8 min (major).

4.7.17. (2-Thienyl) phenylmethanol c82

(*R*)-(−)-**c82**: 59% yield; $[\alpha]_D^{20} = -1.7$ (*c* 0.3, $CHCl_3$) with 19% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 100:1, flow 0.5 ml/min, detection at 254 nm), retention times 96.3 min (major) and 99.4 min (minor).

4.7.18. (2-Thienyl) (2-methoxyphenyl) methanol c83

(−)-**c83**: 81% yield; $[\alpha]_D^{20} = -1.3$ (*c* 0.18, CH_2Cl_2) with 5% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 50:1, flow 0.5 ml/min, detection at 254 nm), retention times 70.5 min (minor) and 75.7 min (major).

4.7.19. (2-Thienyl) (3-methoxyphenyl) methanol c84

(−)-**c84**: 71% yield; $[\alpha]_D^{20} = -1.7$ (*c* 0.12, CH_2Cl_2) with 18% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 20:1, flow 0.5 ml/min, detection at 254 nm), retention times 41.0 min (minor) and 44.3 min (major).

4.7.20. [4-(Methoxycarbonyl)phenyl] (2-furyl) methanol c45

(−)-**c45**: 94% yield; $[\alpha]_D^{20} = -8.4$ (c 0.15, CH_2Cl_2) with 27% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/ethanol = 20:1, flow 0.5 ml/min, detection at 254 nm), retention times 67.9 min (minor) and 75.5 min (major).

4.7.21. [4-(Methoxycarbonyl)phenyl] (2-thienyl) methanol c46

(−)-**c46**: 82% yield; $[\alpha]_D^{20} = -10.4$ (c 0.21, CH_2Cl_2) with 10% ee; the ee value was determined by HPLC analysis using a chiral column (Chiralpak IA column, *n*-hexane/*i*-propanol = 10:1, flow 0.5 ml/min, detection at 254 nm), retention times 26.5 min (minor) and 29.4 min (major). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 8.03 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.26–7.29 (m, 1H), 6.93–6.96 (m, 1H), 6.90–6.91 (m, 1H), 6.11 (s, 1H), 3.91 (s, 3H), 2.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ 166.4, 147.4, 146.8, 129.4, 129.2, 126.3, 125.7, 125.4, 124.8, 71.4, 51.7. HRMS (ESI): calcd for $C_{13}H_{11}SO_2$ $(M-OH)^+$ 231.0474, found 231.0485.

4.8. Crystallographic analysis of NHC-Rh 3

Single crystals of complex **3** could be obtained from hexane–CH_2Cl_2 by slow evaporation of CH_2Cl_2. X-ray diffraction data were collected on a Bruker Smart APEXIICCD area-detector diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 273(2) K. The structure was solved by direct methods, and refined by full-matrix least-squares techniques using the SHELXTL-97[18] program. All of the non-hydrogen positions were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model.

The molecular structure of complex **3** in the solid state is shown in Figure 1. In the structure of **3**, the Rh–C(1) bond length of 2.019(5) Å compares well with those reported for other Rh–NHC complexes.[19] Due to the influences of the NHC and the chloro-ligand, a significantly longer bond (0.09 Å) in the rhodium to carbon distances of the cyclooctadiene (COD) is observed. While the Rh–C bond lengths for carbons C(36) and C(37) are located at 2.089(6) and 2.119(5) Å, respectively the Rh–C for carbons C(40) and C(41) are 2.179(6) and 2.206(5) Å, respectively. The Rh–Cl bond length (2.3862(14) Å) in **3** is only slightly longer than other carbene complexes with less steric hindrance.

Crystallographic data (excluding structure factors) for **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC **903887**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

Crystal data for **3.** $C_{43}H_{52}ClN_2O_4Rh$, M = 799.23, yellow, crystal dimension: 0.15 × 0.12 × 0.10 mm^3, orthorhombic, space group: $P2(1)2(1)2(1)$, a = 10.9922(9) Å, b = 12.3838(10) Å, c = 30.784(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 4190.5(6) Å^3, Z = 4, D_{calcd} = 1.267 g/cm^3, $F(000)$ = 1672, T = 273(2) K, μ = 0.512 mm^{-1}, θ Range: 2.11–25.05°, 21,808 measured reflections, 7368 unique reflections (R_{int} = 0.1045), min/max transmission factors 0.9271/0.9506, final agreement factors R_1 = 0.0531 and wR_2 = 0.1500, 7368/27/460 data/restraints/parameters, GOOF = S = 1.079, largest peak and hole 1.660 and −0.447 e/Å^3.

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