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Design and Synthesis of Chiral Heteroleptic Rhodium(II) Carboxylate Catalysts: Experimental Investigation of Halogen Bond Rigidification Effects in Asymmetric Cyclopropanation

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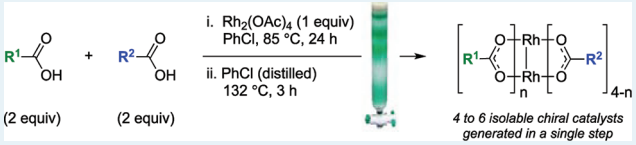
Supporting Information

ABSTRACT: A general method for the synthesis of chiral heteroleptic rhodium(II) tetracarboxylate catalysts is reported. The chlorinated TCPT unit was found to be an efficient polarity-control group, allowing the isolation of each complex from a mixture of six possible products. This approach contributes to enlarging the scope of accessible chiral Rh(II) catalysts and allowed further study of the halogen bond rigidification effect observed in chlorinated complexes.



KEYWORDS: *dirhodium, asymmetric catalysis, cyclopropanation, halogen bond, mixed ligand, heteroleptic catalyst*

Rhodium(II) tetracarboxylate complexes are among the most efficient and widely used catalysts for metal−carbene transformations.[1−4] Their use in C−H or X−H insertion chemistry,[5−14] dipolar cycloaddition,[15−17] cyclopropanation,[18−27] or aziridination[28−30] reactions has permitted the discovery of some of the most powerful C−C or C−X bond-forming processes in synthetic organic chemistry.[31−35] When chiral carboxylates are used as ligands, the transformations are rendered enantioselective through the enantiotopic control of the metal−carbene's environment. Although such a strategy has recently generated outgrowing interest, only a limited number of chiral templates have proven to induce high enantioselectivities (Figure 1).

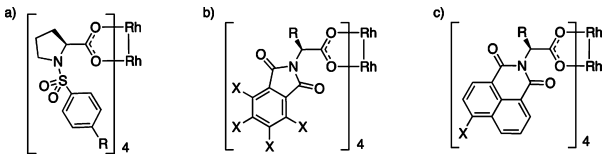


Figure 1. (a) Rhodium *N*-sulfonyl-(*S*)-prolinates. (b) Rhodium *N*-phthaloylaminocarboxylates. (c) Rhodium *N*-naphthaloylaminocarboxylates.

The three main types of complexes used are homoleptic (with four identical ligands, Figure 1), leaving only little flexibility for future catalyst design. Cotton[36−39] and Corey[40,41] independently reported the synthesis of chiral heteroleptic complexes of general structure $Rh_2(OAc)_n(L^*)_{4-n}$ from $Rh_2(OAc)_4$, although these methods do not permit the use of two different chiral carboxylates and are limited to carboxamidates and ortho-metalated arylphosphines as chiral ligands, L*.[42−47] Indeed, the synthetic methods available for the formation of Rh(II)-carboxylate dimers often preclude the isolation of the parent heteroleptic complexes if two different chiral ligands are simultaneously used. A statistical mixture of six complexes is thus obtained, for which only poor chromatographic separation is possible. To increase the possibilities of catalyst design and mechanistic studies in asymmetric metal−carbene processes, a comprehensive study leading to the isolation of such heteroleptic complexes is needed.

Recently, our group[21] and the group of Fox[26,48] have reported that the structure of the N-protective group in rhodium *N*-phthaloylaminocarboxylates (Figure 1b), along with the nature of the amino acid side-chain R, had a crucial impact on the active conformation and enantioinduction properties of the resulting catalyst.[49] More specifically, the presence of chlorine or bromine atoms on the phthaloyl ring (X = Cl or Br) significantly rigidifies its all-up conformation in solution through intramolecular halogen bonds between adjacent ligands (Figure 2).[50−56] The absence of such stabilizing

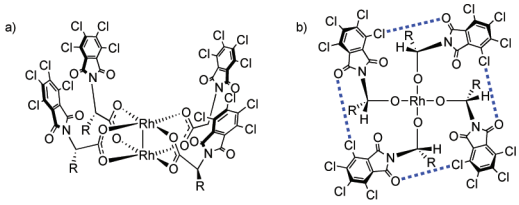


Figure 2. The all-up conformation of rhodium *N*-tetrachlorophthaloylaminocarboxylates (Figure 1b, X = Cl). (a) Side view. (b) Top view and the halogen bond rigidification effect.

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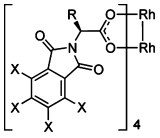
interactions enhances the conformational flexibility of the complex, leading to a drastic decrease in stereoselectivity for some methodologies.[20,21,49] To further study this halogen bond effect, we envisioned that independent modification of the ligands' structure using heteroleptic complexes would be necessary.

Herein, we report a general method for the synthesis of chiral heteroleptic rhodium(II) carboxylate catalysts through the use of the tetrachlorophthaloyl (TCPT) unit as a polarity-control group.[57] These studies permitted establishment of comprehensive rules for their chromatographic separation, allowing rapid access to a wide variety of new Rh(II) catalysts. The heteroleptic complexes synthesized were systematically evaluated in asymmetric cyclopropanation reactions, permitting further investigation of the halogen bond effect observed in our earlier work.[21] This method greatly expands the scope of available chiral rhodium(II) carboxylate catalysts and represents a valuable tool for the design of more efficient catalysts in asymmetric metal−carbene transformations.

Recently, we have been interested in the asymmetric synthesis of various diacceptor cyclopropanes via the Rh(II)-catalyzed cyclopropanation of alkenes with carbene precursors bearing geminal electron-withdrawing groups.[20−23] During the synthesis and purification of diverse Rh(II) complexes in view of their evaluation as catalysts, we rapidly noted a striking difference in the polarity of rhodium *N*-phthaloylaminocarboxylates, depending on the nature of X and R, with the chlorinated complexes bearing bulky R side chains being the least retained on SiO_2. The results depicted in Table 1 suggest that X is the dominant factor responsible for this difference in R_f, and the presence of small R groups generally provides a more polar complex.

Table 1. Influence of X and R on the Catalysts' Polarity



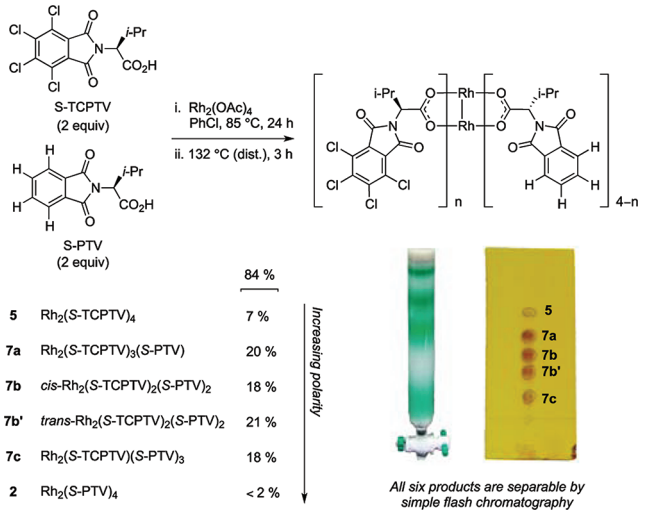
1	X = H, R = Me	Rh_2(*S*-PTA)$_4$
2	X = H, R = *i*-Pr	Rh_2(*S*-PTV)$_4$
3	X = H, R = *t*-Bu	Rh_2(*S*-PTTL)$_4$
4	X = Cl, R = Me	Rh_2(*S*-TCPTA)$_4$
5	X = Cl, R = *i*-Pr	Rh_2(*S*-TCPTV)$_4$
6	X = Cl, R = *t*-Bu	Rh_2(*S*-TCPTTL)$_4$

entry	catalyst	X	R	$R_{f\text{-}25}$[a]	$R_{f\text{-}50}$[b]
1	1	H	Me	0.00	0.15
2	2	H	*i*-Pr	0.02	0.35
3	3	H	*t*-Bu	0.05	0.46
4	4	Cl	Me	0.16	0.80
5	5	Cl	*i*-Pr	0.61	0.89
6	6	Cl	*t*-Bu	0.69	0.92

[a] R_f obtained at 25% EtOAc in hexane using SiO_2 TLC plates. [b] R_f obtained at 50% EtOAc in hexane using SiO_2 TLC plates.

We envisioned that such a difference in polarity could permit the isolation of the parent heteroleptic catalysts, as the number of chlorinated ligands present is different in each complex. To verify our hypothesis, we treated $Rh_2(OAc)_4$ with 2 equiv of chlorinated ligand (*S*)-TCPTV (X = Cl, R = *i*-Pr) and 2 equiv of nonchlorinated ligand (*S*)-PTV (X = H, R = *i*-Pr) under standard conditions for the formation of Rh(II)-carboxylate catalysts (Scheme 1). A mixture of five complexes separable by simple flash chromatography was obtained in a combined 84% yield, with an increasing number of nonchlorinated (*S*)-PTV ligands affording complexes with an increasing polarity. Interestingly, separation of the cis and trans isomers of Rh_2((*S*)-TCPTV)$_2$((*S*)-PTV)$_2$ was possible in this case, even

Scheme 1. Chromatographic Separation of the Chiral Heteroleptic Rhodium(II) Carboxylate Complexes



if both catalysts possess the same number of chlorinated/nonchlorinated ligands.

Using the TCPT unit as a polarity-control group, the same principle was applied to a variety of nonchlorinated carboxylic acids (Table 2). Both enantiomeric forms of ligand PTV could be used in the process, replaced with the more common ligand (*S*)-PTTL or the achiral version PTAiB (entries 1−5). Importantly, isolation of the different products was possible with two nonchlorinated acids, the difference in polarity being solely directed by the distinct amino acid side-chains of the ligands (entry 6). The phthalimide moiety could be replaced by a succinimide, a 1,8-naphthalimide, or by achiral nonimido ligand 2-naphthylacetate, in good yield and separation (entries 7−9). Interestingly, the tetrabromophthalimide (TBPT) unit, with a polarity similar to that of the TCPT group, also afforded a satisfying separation of the corresponding products in the reaction with (*S*)-PTV as the nonhalogenated partner (entry 10).

In analogy to the preparation of Rh(II)-phosphate catalysts,[58,59] the method is applicable to phosphoric acid (*R*)-BNP in combination with (*S*)-TCPTV, affording a separable mixture of rhodium(II) carboxylate phosphate complexes (Scheme 2). Such heteroleptic catalysts should display an intermediate reactivity between rhodium(II) carboxylate and rhodium(II) phosphate dimers. It is noteworthy that the separation of the 4−6 different catalysts formed in the reactions was generally also efficient using a simple automated combiflash apparatus. Moreover, the yield of formation of a chosen catalyst can be significantly increased with adjustment of the starting ligands' stoichiometry and iterative resubmission of the remaining undesired complexes to the reaction conditions (e.g., Rh_2((*S*)-TCPTTL)$_3$(PTAiB) **11a**, 19% yield, Table 2, entry 5 gives 61% isolated yield after 3 iterations).[60] This result highlights the thermodynamic equilibrium present between each heteroleptic complex at this temperature.

To evaluate the potential of these chiral heteroleptic rhodium(II) carboxylate dimers as catalysts,[47] we elected the cyclopropanation of alkenes with α-nitro diazoacetophenones as a model reaction[20,21] and rapidly identified the Rh_2(**A**)$_3$(**B**) complexes (with three chlorinated ligands) as an interesting

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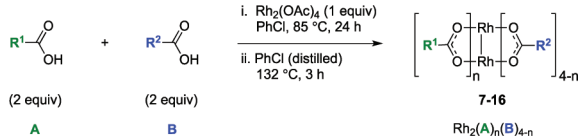
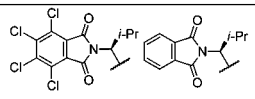
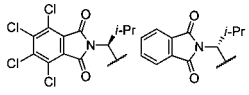
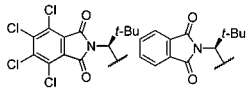
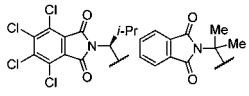
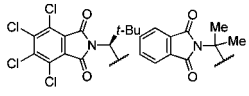
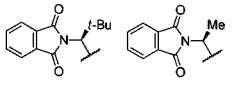
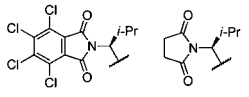
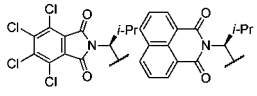
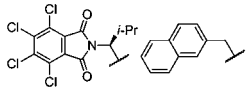
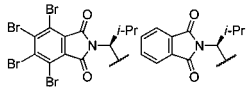
Table 2. Synthesis of Chiral Heteroleptic Rh(II) Catalysts



entry	R^1	R^2	products	product ratio[a]	total yield (%)[b]
1[c]			**7a-7c**	20:39:18 (7)	84 (85)
2			**8a-8c**	21:24:23 (21)	87 (92)
3[c]			**9a-9c**	19:24:19 (10)	72 (74)
4[c]			**10a-10c**	22:37:12 (5)	76 (79)
5[c]			**11a-11c**	19:40:23 (5)	85 (87)
6			**12a-12c**	18:29:23 (12)	82 (97)
7[c]			**13a-13c**	24:25:≤2 (9)	58 (65)
8[c]			**14a-14c**	19:29:22 (7)	77 (81)
9			**15a-15c**	15:26:18 (13)	72 (91)
10[c]			**16a-16c**	21:30:20 (9)	80 (89)

[a]Ratios of heteroleptic products are reported as follows: $Rh_2(A)_3(B)$/$Rh_2(A)_2(B)_2$/$Rh_2(A)(B)_3$ (yield of homoleptic products in parentheses). [b]Sum of isolated yields after one flash chromatography (total yield before chromatography in parentheses). [c]Cis and trans isomers of $Rh_2(A)_2(B)_2$ were separable.

class of catalysts to investigate the halogen bond rigidification effect mentioned earlier (Table 3).

Scheme 2. Synthesis of Heteroleptic Rhodium(II) Carboxylate Phosphate Complexes

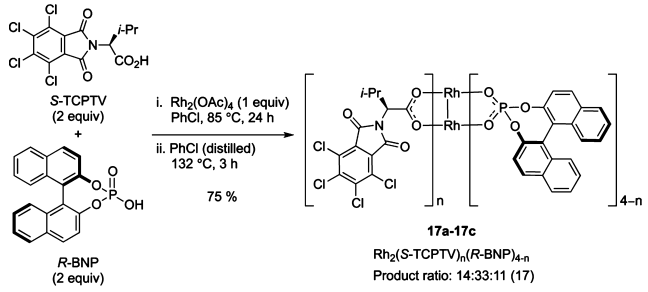
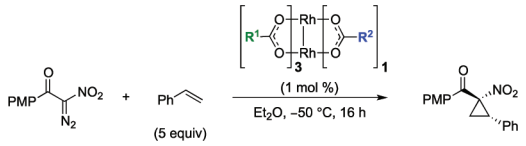


Table 3. Evaluation of the Chiral Heteroleptic $Rh_2(A)_3(B)$ Complexes As Catalysts in Asymmetric Cyclopropanation



entry	catalyst	yield (%)[a]	dr (*cis*/*trans*)[b]	ee (%)[c]
1	**5**	82	98:2	91.1
2	**6**	81	98:2	92.9
3	**7a**	71	94:6	91.2
4	**9a**	81	93:7	94.1
5	**10a**	76	93:7	95.0
6	**11a**	84	92:8	96.4
7	**13a**	85	93:7	89.5
8	**14a**	69	88:12	85.3
9	**15a**	72	88:12	<5

[a]Isolated yield of combined diastereomers. [b]Determined by ^{1}H NMR analysis of the crude mixture. [c]The ee of the cis isomer was determined by SFC analysis on chiral stationary phase.

The results displayed in Table 3 show that the tetrachlorophthalimide unit of the fourth ligand could be replaced with a phthalimide, a succinimide, or a 1,8-naphthalimide with similar levels of asymmetric induction compared with the corresponding optimal homoleptic catalysts **5** or **6** (entries 3−8). In sharp contrast, the use of 2-naphthylacetate as the fourth ligand (catalyst **15a**) furnished a racemic product in a diastereoselectivity similar to that obtained with $Rh_2(OAc)_4$ (88:12, entry 9).[20] Apparently, whether the fourth carboxylate is chiral or not, the *N*-imido moiety is necessary in all ligands to obtain a high asymmetric induction in this system. Cognizant of the sensitivity of the reaction toward the conformational rigidity of the catalyst used,[21] we hypothesized that such a difference in enantioinduction might in part be due to a lack of rigidifying halogen bonds in complex **15a**. Indeed, even if the heteroleptic complexes **7a**−**9a** and complex **15a** possess the same amount of chiral chlorinated ligands, only two halogen bonds are possible in catalyst **15a** (Figure 3). This feature, along with the absence of a bulky R side chain,[48] should lead to a less rigid complex and might be enough to produce conformational scrambling of the catalyst in our reaction conditions, leading to mediocre asymmetric induction.

Moreover, we noted that replacing one of the chlorinated ligands in $Rh_2((S)\text{-TCPTV})_4$ (**5**, entry 1) or $Rh_2((S)\text{-TCPTTL})_4$ (**6**, entry 2) with achiral nonchlorinated PTAiB had a beneficial impact on the asymmetric induction (catalysts **10a** and **11a**, entries 5−6). This effect might be the result of a

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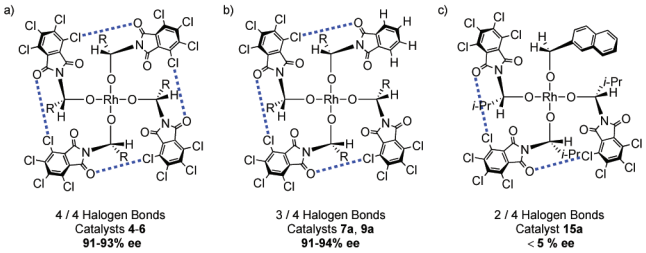

Figure 3. Representations of the expected intramolecular halogen bonds in (a) homoleptic *N*-tetrachlorophthaloylamino carboxylates (e.g., **4**–**6**), (b) heteroleptic complexes **7a** and **9a**, and (c) heteroleptic complex **15a**.

conformational change in the catalyst due to the presence of a *gem*-dimethyl group instead of the chiral center bearing the amino acid side-chain R in the fourth ligand. Indeed, although the presence of intramolecular halogen bonds significantly rigidifies the complex's conformation in solution,[21] it is known that the nature of the R side-chain can *also* importantly affect its three-dimensional structure.[48] To clarify the nature of this effect, we obtained an X-ray crystal structure of representative complex Rh_2((*S*)-TCPTTL)$_3$(PTAiB) (**11a**), revealing a conformation in which the achiral PTAiB points toward the opposite side of the complex, twisted by 60–75° from the all-up conformation of its homoleptic analog, Rh_2((*S*)-TCPTTL)$_4$ (**6**) (Figure 4).[21]

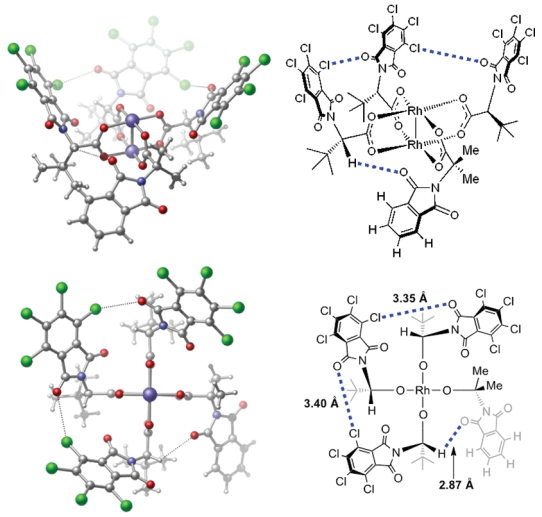

Figure 4. X-ray crystal structure of Rh_2((*S*)-TCPTTL)$_3$(PTAiB) (**11a**). Side view (top), top view (bottom), and distances of noncovalent interactions. Axial solvents (EtOH and H_2O) were omitted for clarity.

Although this structure permits only two intramolecular halogen bonds to exist (between the three chlorinated ligands), the presence of a third stabilizing interaction that could potentially reduce the flexibility of the complex, a CH–O hydrogen bond between the PTAiB fragment and the adjacent (*S*)-TCPTTL α-CH, was detected. This type of interaction is quite commonly found in peptides and proteins, affecting their secondary structure and playing an important role in their function and stabilization.[61,62] The C–H–O angle (120.9°) and the C–O distance (3.49 Å) observed in the crystal structure are in accordance with a CH–O hydrogen bond.[61] It is important to note that such a stabilizing contact would not be possible with complex **15a**, in which PTAiB is replaced by 2-naphthylacetate. From the X-ray structure, it is plausible that this type of interaction is also present between each TCPTTL unit, although with a weaker agreement with respect to the C–H–O angle observed. Although the reason why this α, α, α, β conformation provokes an increase in the enantioinduction of our system remains unclear, this constitutes the first report of a successful enantioselective transformation using such a catalyst, as this symmetry has long been overlooked as nonoperative for stereoinduction.[63,64]

In summary, we report the first comprehensive study for the efficient formation and isolation of chiral heteroleptic rhodium(II) carboxylate catalysts. This method features the use of the chlorinated TCPT unit as a polarity-control group, permitting isolation of each of the complexes formed. The heteroleptic catalysts obtained were evaluated in the asymmetric cyclopropanation of alkenes with α-nitro diazoacetophenones, permitting further investigation of the enantioinduction mechanism of the reaction, in which multiple noncovalent interactions were found to be mandatory for conformation rigidification of the catalysts in our system. This approach contributes to enlarge the scope of accessible chiral Rh(II)-carboxylate catalysts, allowing a more detailed and efficient catalyst design for future asymmetric metal–carbene transformations. Various mechanistic studies using heteroleptic rhodium(II) carboxylate catalysts are currently ongoing and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, compound characterization data, and NMR spectra for new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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