

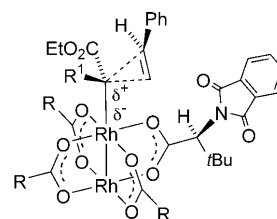
First X-ray Structure of a *N*-Naphthaloyl-Tethered Chiral Dirhodium(II) Complex: Structural Basis for Tether Substitution Improving Asymmetric Control in Olefin Cyclopropanation

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Dedicated to Professor Volker Schurig on the occasion of his 70th birthday

The transition-metal-catalyzed cyclopropanation of olefins with diazoesters occupies a prominent position in the field of asymmetric catalysis. This stems not only from being the reaction in which asymmetric catalysis by transition metals was first demonstrated, but also because of its prevalence in natural-product-based and synthetic drugs.^[1] Once this principle was demonstrated, highly selective catalysts were developed, mainly based on Cu^I and Rh^{II} associated with appropriate chiral nonracemic ligands.^[2] The intermediacy of metalcarbenes in transition-metal-catalyzed decomposition of diazo precursors is firmly established.^[1,2] In the case of the paddle-wheel dirhodium(II) catalysts based on amino acid derived ligands, enantioselectivity arises from the concerted control of the carbene-transfer step (metal to olefin) offered by the chiral ligand set flanking an axial coordination site of the dirhodium complex. A recent report discussed the role of the chiral crown cavity of the well-known Hashimoto catalyst [Rh₂{(*S*)-pttl}₄] (pttl = *N*-phthaloyl-(*S*)-

tert-leucinate) formed by the four *N*-phthaloyl units in this regard, Scheme 1.^[3a]



Scheme 1. Carbene-transfer step during styrene cyclopropanation with a carbene generated from a diazoester mediated by [Rh₂{(*S*)-pttl}₄].

Initially, diazoacetate esters were the preferred reagents although phenyl- and vinyl-substituted diazoacetates were found to be equally suitable carbene precursors when appropriately modified catalysts were used.^[4] Even though diazoacetates are not explosive, the same cannot be said for all diazo compounds and, in addition to their toxic and carcinogenic properties,^[5] alternative carbene precursors have an advantage when striving for very general routes to a broad range of cyclopropane syntheses such that industrial utilization is not problematic owing to serious safety risks.^[6] We have, therefore, investigated the possibility of in situ generation of such intermediates. Herein we report the synthesis of a set of dirhodium(II) carboxylate catalysts containing naphthoyl skeletons that contain the protected amino acids (*S*)-*N*-naphthoyl-*tert*-leucine, (*S*)-*N*-naphthoyl-phenyl alanine and their 3- or 4-substituted naphthoyl derivatives. These catalysts were used for the one-pot cyclopropanation of olefins with CH acidic reagents through intermediate phenyliodonium ylides to afford cyclopropane derivatives in up to 98% *ee*. We also report the first X-ray structure of a *N*-naphthaloyl-based catalyst, [Rh₂{(*S*)-nttl}₄] (nttl = *N*-naphthoyl-*tert*-leucine) as a di(ethyl acetate) adduct, which has

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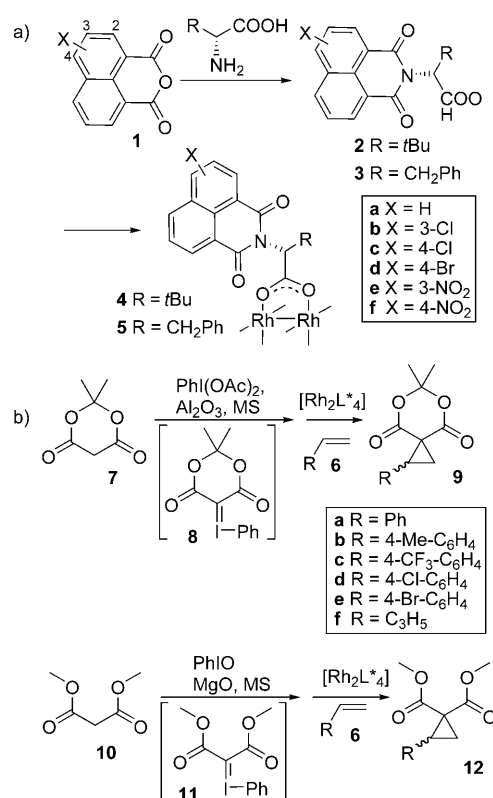
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provided a structural explanation for its exceptional capabilities in asymmetric cyclopropanations^[7] and provides evidence for the enhanced performance of analogues in this study that are substituted in the 3- and 4- positions.

An attempt to avoid the isolation of the diazo precursors for carbene transfer has been described by Aggarwal, who used thermal decomposition of sodium salts of tosylhydrazones in the presence of catalytic amounts of $\text{Rh}_2(\text{OAc})_4$ and sulfide for the in situ generation and decomposition of diazo compounds.^[6] Among the various approaches tried by us, carbene generation through α elimination in the presence of appropriate catalysts was not successful.^[8] Although the decomposition of diphenylsulfonium ylides in the presence of Cu and Rh catalysts afforded products resulting from enantioselective carbene transfer, the yields of the reaction were disappointing and the approach was abandoned.^[9] The decomposition of phenyliodonium ylides was more promising and we could show, by conducting selectivity studies, that the decomposition of preformed ylides with Rh^{II}^[10] or Cu catalysts^[11] proceeds through the same reactive intermediate as that of the corresponding diazo precursor, although secondary reactions that probably bypass metal-carbene intermediates may occur, in particular in intramolecular cyclopropanation reactions.^[12]

The main advantage in using phenyliodonium ylides relates to the possibility of carrying out carbene transfer in a one-pot procedure, in which the phenyliodonium ylide is generated and decomposed in situ in the presence of a transition-metal catalyst. The first one-pot procedure for asymmetric carbene transfer with copper catalysts was described by Dauban and co-workers although their main interest centered on nitrene transfer.^[13] At the same time, Du Bois and co-workers developed a one-pot procedure for Rh^{II}-catalyzed nitrene transfer through in situ generated phenyliodonanes.^[14] A one-pot procedure for Rh^{II}-catalyzed carbene transfer was described by Charette and Wutz,^[15] and independently by us.^[16,17] For the one-pot asymmetric cyclopropanation of olefins with Meldrum's acid (**7**) or dimethyl malonate (**10**), our previously described $[\text{Rh}_2\{(\text{S})\text{-nttl}\}_4]$ catalyst **4a** proved to be particularly suitable, Scheme 2.^[18] This catalyst uses *tert*-leucinate, which is derived from 1,8-naphthalene anhydride as the ligand. We were surprised to find that the introduction of substituents into the 4-position of the naphthalene ring (catalyst **4d**) produced a significant enantioselectivity enhancement that reached 98 and 82 % *ee* for pentene and styrene, respectively, when using dimethyl malonate as the carbene precursor.^[17] This encouraged us to examine the effect of 3-substituents and further ligand variations, such as the use of phenylalaninate, to replace *tert*-leucinate (Scheme 2a, catalysts **4a–f** and **5a–f**), and the effect of such variation on the enantioselectivity of the cyclopropanation reactions by using either **7** or **10** as the carbene precursors (Scheme 2b).

The optimization of the in situ generation and decomposition of phenyliodonium ylides has been previously reported.^[16,17] Reactions were carried out in CH_2Cl_2 with a tenfold excess of olefin in the presence of 5 mol % of the catalyst.



Scheme 2. a) Synthesis of the chiral ligands and catalysts. b) Asymmetric cyclopropanation of olefins by using in situ generated ylides (MS = molecular sieves).

The intermediate phenyliodonium ylide **8** was generated with $\text{PhI}(\text{OAc})_2$ for the reactions with **7**, whereas $\text{PhI}=\text{O}$ was used in the reactions with **10**. The efficiency of the catalysts was examined in the cyclopropanation of styrene **6a**, Table 1.

Table 1. Asymmetric cyclopropanation of styrene **6a** with **7** or **10** by using substituted $[\text{Rh}_2\{(\text{S})\text{-nttl}\}_4]$ catalysts **4a–f**.^[a]

Catalyst (X)	9a Yield [%]	9a <i>ee</i> [%] ^[b]	12a Yield [%]	12a <i>ee</i> [%] ^[c]
4a (H)	87	45	72	37
4b (3-Cl)	60	56	59	46
4c (4-Cl)	66	59	77	66
4d (4-Br)	73	92	75	82
4e (3-NO ₂)	45	54	43	37
4f (4-NO ₂)	62	69	60	66

[a] In CH_2Cl_2 , at 30 °C, tenfold excess of styrene. [b] and [c] Absolute configuration *R*.

In all cases that were investigated with the derivatized *tert*-leucinate ligand, and for both **7** and **10** as reagents, the introduction of substituents lead to an enantioselectivity enhancement. Substitution in position 4 produced a more selective catalyst than in position 3. The 4-Br substituent lead to the most selective catalyst with 92 % *ee* for the cyclopropanation of styrene **6a** with **7** and 82 % *ee* with **10**. The absolute configuration of the cyclopropanes **9a** and **12a** was *R* with all catalysts, as previously determined.^[16,17]

Still higher enantioselectivities were achieved for catalyst $[\text{Rh}_2\{(S)\text{-4-Br-nttl}\}_4]$ **4d** with other olefins, Table 2. With **7**, the highest *ee* value of 92% was observed with styrene **6a**,

Table 2. Asymmetric cyclopropanation of olefins **6a–f** with **7** or **10** by using $[\text{Rh}_2\{(S)\text{-4-Br-nttl}\}_4]$ **4d**.^[a]

Olefin (R)	9x Yield [%]	9x <i>ee</i> [%]	12x Yield [%]	12x <i>ee</i> [%]
6a (Ph)	73	92 (R)	75	82 (R)
6b (4-Me-C ₆ H ₄)	67	72 (R)	71	65 (R)
6c (4-CF ₃ -C ₆ H ₄)	62	55 (R)	62	87 (R)
6d (4-Cl-C ₆ H ₄)	45	43 (R)	65	90 (R)
6e (4-Br-C ₆ H ₄)	54	52 (R)	63	87 (R)
6f (C ₃ H ₅)	56	53 (R)	56	98 (S)

[a] In CH₂Cl₂, at 30 °C, tenfold excess of olefin.

but substituted styrenes reacted with lower *ee*. With **10**, 4-chlorostyrene **6d** produced a higher *ee* (90%) than the parent styrene **6a** with 82% *ee*, but the highest *ee* was recorded for 1-pentene **6f** (98%). For comparison, styrene and substituted-styrene cyclopropanation enantioselectivities with dimethyl diazomalonate reported in the literature were 50% *ee* at the most,^[19] until recently when Charette et al. reported an excess up to 96% *ee* for cyclopropanes containing geminal dicarboxy groups prepared by using diazo reagents and utilizing the trans-directing ability of an amide.^[7] However, the use of diazo reagents in such a reaction was unavoidable.

The substituent effects noted here on catalyst enantioselectivity performance is intriguing. The substituents are situated far away from the reactive center, so that a polar substituent effect appears unlikely. The data presently available do not allow a convincing explanation of the phenomenon. Similar spectacular effects on enantioselectivity have previously been reported by Hashimoto et al. for the *N*-phthaloyl-(*S*)-*tert*-leucinate-based catalyst $[\text{Rh}_2\{(S)\text{-pttl}\}_4]$ and ring substituted analogues, in which enantioselectivity for nitrene insertion increased from 27% for the parent to 70% for the tetrachloro-substituted *N*-phthaloyl system.^[20] However, in this latter case four Cl substituents per ligand were introduced, whereas in the case of the *N*-naphthaloyl ligand in this study, only one substituent is present.

Unfortunately we have been unable to grow crystals of **4b–f** that are suitable for X-ray crystallographic studies, which might have provided a structural basis for these variations in selectivity. However, we have succeeded with the structure determination of the unsubstituted catalyst **4a** as a di(ethyl acetate) adduct, Figure 1 a.^[21] The complex exhibits the so-called $\alpha,\alpha,\alpha,\alpha$ conformation^[22] in the solid state with all *N*-naphthaloyl units arranged to form a nearly square-shaped cavity (14.9 × 16.5 Å wide). The *N*-phthaloyl analogue (as a mono ethyl acetate adduct) was recently shown to adopt a similar chiral crown structural motif, though in that case a substantially narrower cavity dimension (11 × 15 Å) was discussed as being influential in the selective catalytic performance.^[3a]

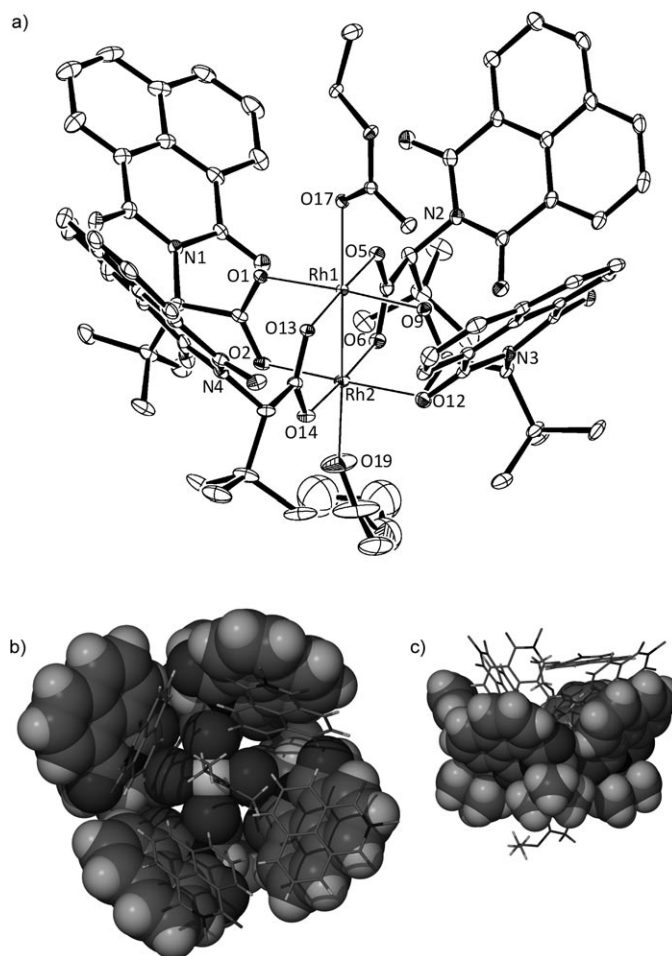


Figure 1. Molecular structure of $[\mathbf{4a}(\text{EtOAc})_2]$. Thermal ellipsoid diagram (a) and space-filling representations viewed into the square chiral crown cavity down the Rh–Rh bond (b, onto Rh1), and a side view (c). EtOAc and π -stacked *endo*-cavity-residing *N*-phthaloyl units of adjacent molecules are shown in stick form in (b and c). Selected bond lengths [Å] and angles [°]: Rh1–Rh2 = 2.3816(5), Rh–O_{eq} = 1.999(3)–2.059(3), Rh1–O17 = 2.360(3), Rh2–O19 = 2.280(4). *N*-Naphthaloyl plane (N1,N2,N3,N4)/Rh1 equatorial plane = 39.69(5), 57.94(6), 47.25(7), 52.32(6).

The wider *N*-naphthaloyl units of **4a** relative to $[\text{Rh}_2\{(S)\text{-pttl}\}_4]$ (namely, edge-fused aryl rings) may be responsible for this relatively subtle cavity shape change, as indeed could the four *N*-naphthaloyl units of adjacent molecules that are π -stacked within the cavity as a solid-state feature (two are present in the *N*-phthaloyl case, one each associated with the wider cavity sides).^[3a] *N*-Naphthaloyl incorporation maintains the chiral nature of the crown cavity surrounding the axial Rh coordination site through the clockwise twist of these groups, Figure 1 b. If **4d** is structurally similar to **4a**, the 4-Br substituents would lie at the cavity rim and are thus likely to exert a strong influence on enantiofacial discrimination of the incoming alkene during carbene transfer. In this regard, we note the improved performance of the 4-Br substituted catalyst **4d** over the 4-Cl analogue **4c**, in which the larger halide would clearly be expected to exert more influence at the cavity rim in the case of **4d**. Interest-

ingly, desymmetrization of the *N*-naphthaloyl units through 3- and 4-substitution could give rise to diastereomeric rotamers, some of which may be preferred for the chiral cavity, others may be ruled out on steric grounds, or others may even be responsible for drastic conformational changes in the complex such as $\alpha,\alpha,\alpha,\alpha$ to $\alpha,\alpha,\beta,\beta$ flipping (the latter is known for a related phenylalaninate complex).^[23] Such issues may underlie the selectivities observed here with a range of ligand substitution patterns.

On the other hand, the enantioselectivity of the Rh^{II} catalysts that contain a 1,8-naphthoyl-protected (*S*)-phenylalaninate ligand (**5a–f**) were very disappointing, Table 3. With **7**,

Table 3. Asymmetric cyclopropanation of styrene **6a** with **7** or **10** by using substituted [Rh₂[(*S*)-ntpa]₄] catalysts **5a–5f**.^[a]

Catalyst (X)	9a Yield [%]	9a ee [%] ^[b]	12a Yield [%]	12a ee [%] ^[c]
5a (H)	75	30	45	15
5b (3-Cl)	59	25	29	16
5c (4-Cl)	40	19	47	26
5d (4-Br)	70	43	45	31
5e (3-NO ₂)	40	15	43	12
5f (4-NO ₂)	45	35	40	18

[a] In CH₂Cl₂, at 30°C, tenfold excess of styrene. [b] and [c] Absolute configuration *R*.

the highest ee was 43% for cyclopropanation of styrene **6a**, which was obtained with the 4-Br substituted catalyst **5d**. The same catalyst also afforded the highest enantioselectivity (31%) of styrene **6a** with **10**. Results with other olefins were equally disappointing. Thus, pentene was cyclopropanated in the presence of the 4-Br substituted catalyst **5d** with 22 and 28% ee with **7** and **10**, respectively (data not shown). At this stage we cannot be certain of the grounds for the poor relative performance of the phenylalaninate-derived catalysts **5a–f** in comparison with the *tert*-leucinate series **4a–f**. We note, however, the contrasting solid-state structures of the well-known *N*-phthaloyl analogues based on these amino acids, with the (*S*)-phenylalaninate complex exhibiting an $\alpha,\alpha,\beta,\beta$ conformation lacking the crown cavity.^[23] If **5a–f** also adopt non-crown conformations, the positioning of the 4-Br substituents would still exert an influence on the trajectory of the olefin during carbene transfer (indeed **5d** performs best in this series), but the influence of all four 4-Br groups shrouding the rim of the chiral crown cavity would not be present in this case.

In summary, the one-pot procedure for carbene transfer by using CH acidic reagents such as **7** or **10** in the presence of an appropriate chiral Rh^{II} catalyst allows the generation and enantioselective transfer of metalcarbenes without the need to prepare the undesirable diazo precursors, or without the need to isolate the often unstable phenyliodonium ylide intermediates. The reactions afforded cyclopropanes in up to 92 and 98% ee. *tert*-Leucinate protected with 4-Br substituted 1,8-naphthalic anhydride was found to be an exceptionally selective ligand, whereas only unsatisfactory results were obtained with the 1,8-naphthoyl-protected phenylalaninate-based system. The X-ray structure of [Rh₂[(*S*)-nttl]₄] re-

vealed an $\alpha,\alpha,\alpha,\alpha$ conformation with a reasonably square chiral crown cavity formed by the *N*-naphthoyl units, which serves as a model that accounts for the 4-Br substituted analogue having greatly improved enantioselectivity through the cavity rim steric impedance. This structural study will, in the wider field of chiral dirhodium(II) catalyst usage,^[25] help in understanding the mechanistic insights of the asymmetric cyclopropanations of olefins through carbene-transfer reactions.

Experimental Section

Cyclopropanation with Meldrum's acid: Dichloromethane (10 mL) was added through a syringe into a round bottom flask (50 mL) containing a mixture of **7** (10 mmol, 1 equiv), PhI(OAc)₂ (1.4 equiv), [Rh₂(OAc)₄] or chiral rhodium(II) catalyst, (5 mol %), Al₂O₃ (2.3 equiv) and molecular sieves 4 Å (250 mg), followed by the addition of the olefin **6** (10 equiv). The reaction mixture was heated in a thermostatted oil bath to 30°C and stirred under argon. Samples (100 µL) were taken after several time intervals. The samples were filtered by using a syringe filter holder (0.2 µm pore size) and the organic layer was diluted with dichloromethane or ethyl acetate (100 µL) before being analysed by GC. The reaction progress was monitored qualitatively and quantitatively by GC–MS by using dodecane as an internal standard. When maximum conversion was reached (2–4 h), the reaction was terminated by filtration through celite. The residue on the celite was washed twice with dichloromethane. Evaporation of the combined filtrates under reduced pressure followed by chromatography on a silica-gel column with pentane/ethyl acetate (2:1 v/v) as the eluent afforded the desired cyclopropane derivatives **9a–f**. Cyclopropanation with dimethyl malonate was as previously described.^[16]

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Keywords: amino acids • crystal growth • cyclopropanes • homogeneous catalysis • rhodium

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