

A New Ligand Design Based on London Dispersion Empowers Chiral Bismuth–Rhodium Paddlewheel Catalysts

Santanu Singha,[§] Michael Buchsteiner,[§] Giovanni Bistoni, Richard Goddard, and Alois Fürstner*



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ABSTRACT: Heterobimetallic bismuth–rhodium paddlewheel complexes with phenylglycine ligands carrying TIPS-groups at the *meta*-positions of the aromatic ring exhibit outstanding levels of selectivity in reactions of donor/acceptor and donor/donor carbenes; at the same time, the reaction rates are much faster and the substrate scope is considerably wider than those of previous generations of chiral [BiRh] catalysts. As shown by a combined experimental, crystallographic, and computational study, the new catalysts draw their excellent application profile largely from the stabilization of the chiral ligand sphere by London dispersion (LD) interactions of the peripheral silyl substituents.

The first chiral dirhodium carbene characterized by X-ray crystallography was derived from diazoester **4a** and [Rh₂(PTTL)₄] (**1a**) (Figure 1).^{1–4} This particular paddlewheel complex had been chosen not only for its excellent pedigree in asymmetric catalysis^{5–26} but also because the reasons for its efficiency had been subject to debate.^{27–33} Interestingly, the four *N*-phthalimido substituents on the *tert*-leucine ligands were found to adopt an $\alpha,\alpha,\alpha,\alpha$ -conformation about the carbene ligand occupying an axial site on the

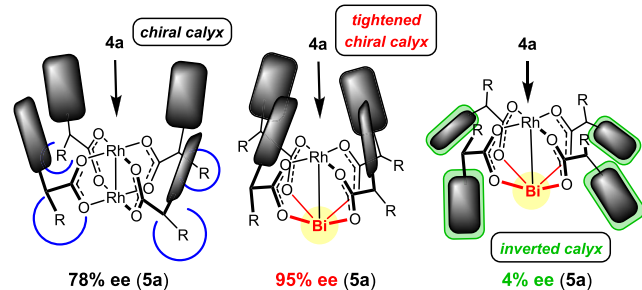
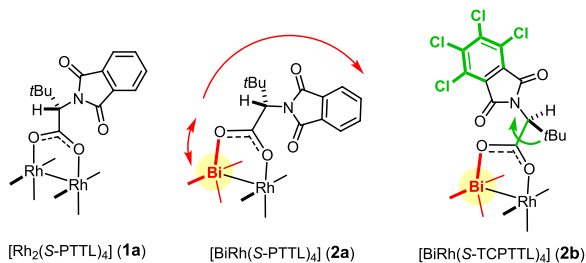
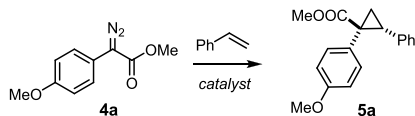


Figure 1. Prior art. The “paddles” in the schematic drawing represent the (substituted) phthalimido groups, R = *t*Bu.

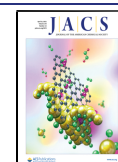
dirhodium core; this chiral calyx is maintained in solution.^{1,27,28} Under the premise that the enantiodetermining transition state features a similar overall structure, the data allowed the *sense* of induction in the cyclopropanation of styrene to be explained;¹ the moderate *level* of induction (78% ee) can also be rationalized by the fairly wide aperture of the chiral binding site, as observed in the solid state. Moreover, the two Rh atoms reside in notably different ligand environments: the *tert*-butyl groups form a narrow but essentially “achiral” pore about Rh₂; any competing background reaction at this site will reduce the optical purity of the product.¹

In a first foray to translate these insights into an improved catalyst design, the Rh₂ center of **1a** was formally replaced by Bi(+2).^{34–46} For its larger radius, this main group element imparts a conical shape onto the ligand sphere, which, in turn, tightens the chiral pocket at the Rh-site. Since Bi(+2) does not decompose the diazo ester, the racemic background reaction is essentially shut off. These effects are thought to synergize; they explain why the heterobimetallic complex [BiRh(PTTL)₄] (**2a**) led to much improved ee’s in many cases.³⁴ Limitations were encountered with less electron-rich donor/acceptor diazo derivatives, which gave rather poor results (see below).³⁴

Initial attempts to remedy this issue by tailoring the phthalimido groups largely met with failure. Although perhalogenated phthalimides have proven advantageous in many cases,^{47–50} the heterobimetallic complex **2b** gave almost racemic product. The X-ray structure revealed the likely cause: **2b** features an *inverted* calyx, in which the “chiral” environment envelopes the unreactive Bi(+2) site, whereas the Rh-atom sees the *tert*-butyl substituents.³⁴ The substituted phthalimido

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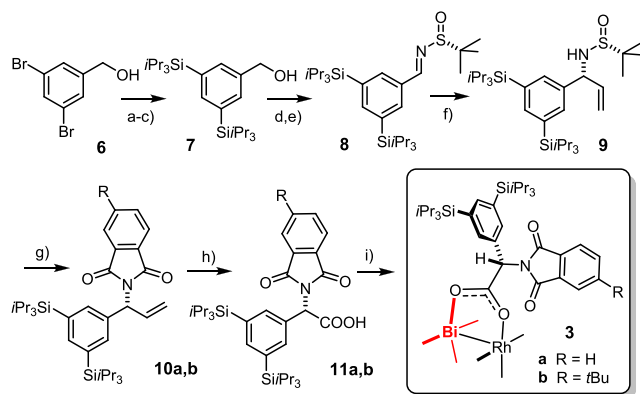
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groups are more encumbered and hence flank the Bi(+2) center, simply because the larger cation provides more space.³⁴

An improved design needs to provide rigorous control over the directionality of the chiral ligand sphere while allowing the substitution pattern to be fine-tuned. To this end, we planned to employ London dispersion as a noncovalent but attractive interaction to lock the desirable conformation in place. It is increasingly clear that multiple intramolecular contacts can outweigh steric repulsion and be structure-determining,^{51,52} although this effect might be more prevalent in (organo-metallic) catalysis than commonly appreciated,^{51,53–56} examples of deliberate use of London dispersion (LD) as a key design principle for the development of new catalysts with improved application profiles are exceedingly rare.^{57–59} Outlined below we present such a case.

To reach this goal, the *tert*-leucine-derived ligands of **2a,b**, which are too far apart for any LD among them,³⁴ were replaced by phenylglycine derivatives carrying TIPS-groups at the *meta*-positions of the aromatic ring; the latter were expected to mediate a sufficient number of intramolecular contacts to entail stabilization via dispersion interactions (Scheme 1).^{60–62} Commercial benzyl alcohol **6** was O-silylated

Scheme 1^a

^aReagents and conditions: (a) TIPSCl, DBU, CH₂Cl₂, 99%; (b) *t*BuLi, THF, –78 °C → rt, then TIPSCl, –20 °C → rt; (c) TBAF, THF, –20 °C → rt, 74% (over both steps); (d) PCC, CH₂Cl₂, 94%; (e) (*R*)-*t*BuS(=O)NH₂, Ti(OEt)₄, THF, 70 °C, 84%; (f) vinyl-magnesium bromide, Me₂Zn (50 mol %), THF, –78 °C, 87% (dr = 99:1); (g) (i) HCl/1,4-dioxane, MeOH; (ii) aq. NaOH, 90% (iii) (substituted) phthalic anhydride, Et₃N, toluene, reflux, 75% (**10a**), 73% (**10b**); (h) RuCl₃·H₂O (5 mol %), NaIO₄, CCl₄, MeCN, H₂O, 74% (**11a**, 96% ee), 69% (**11b**, 98% ee); (i) [BiRh(OCOCF₃)₄], toluene, reflux, 81% (**3a**), 94% (**3b**).

prior to metal/halogen exchange and quenching of the dilithio species with TIPSCl. Product **7** was elaborated into *tert*-butylsulfanyl imine **8**,⁶³ which reacted with vinylmagnesium bromide in the presence of ZnMe₂ to give **9** as a single isomer (dr ≈ 99:1). The auxiliary was removed and the phthalimide of choice⁶⁴ introduced before the double bond of **10** was cleaved with RuCl₃ cat./NaIO₄ to avoid racemization. The resulting acids **11**⁶⁵ were reacted with [BiRh(OCOCF₃)₄] in boiling toluene and the released trifluoroacetic acid trapped with K₂CO₃ in a Soxhlet apparatus to furnish complexes **3** in excellent yield.

Although **3a** crystallizes well, the many degrees of rotational freedom of the eight peripheral TIPS groups cause disorder. This complication notwithstanding, a data set meeting good

crystallographic standards was obtained (see the Supporting Information (SI)). As expected, complex **3a** adopts an $\alpha,\alpha,\alpha,\alpha$ -conformation, in which the silylated aryl rings envelope the Bi-center whereas the phthalimides form a narrow chiral pocket about Rh (Figure 2). The steric demand of the TIPS groups is

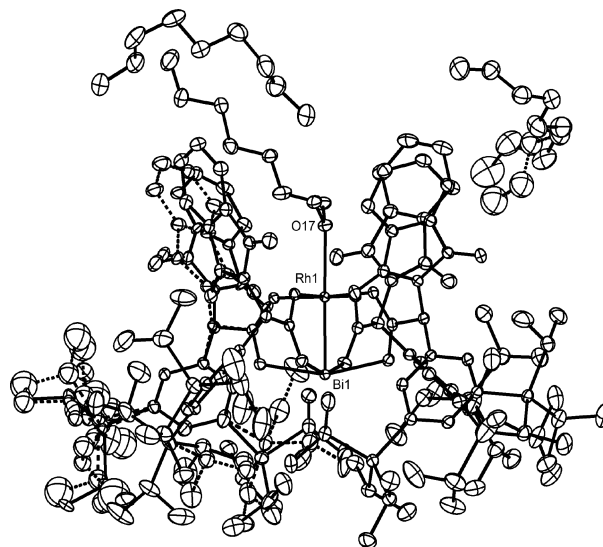


Figure 2. Structure of complex **3a** in the solid state; disordered parts are shown with dashed bonds, H atoms omitted for clarity; for further information, see the SI.

manifested in innumerable short H···H and H···C contacts in the periphery. The crystallographic data, however, do not allow us to decide whether these contacts mediate LD and are hence stabilizing, or whether they are repulsive as a consequence of steric hindrance.

This aspect was addressed by DFT calculations.^{66,67} To this end, the structures of **3a,b** were computed with and without D3 (BJ) dispersion correction at the PBE level of theory (see the SI).^{68,69} Details apart, the computations are unambiguous in that dispersion renders the structures notably more compact. In energetic terms, it entails stabilization of **3a** and **3b** by no less than –9.9 and –11.6 kcal·mol^{–1}, respectively.^{70,71} LD is therefore clearly a major structure determinant.⁷² Deconvolution validates the original design concept:⁷³ the TIPS-groups account for ~32% of ΔE_{disp} , whereas the contribution of the *t*Bu groups in **3b** is smaller but still appreciable (~12%); in structural terms, however, this extra factor visibly tightens the chiral binding site on the Rh-face in **3b** (Figure 3).

To explore the catalytic performance of the new heterobimetallic complexes, the cyclopropanation of styrene with the fluorinated diazo derivative **4b** was chosen as a test reaction (Table 1). Neither [Rh₂(PTTL)₄] (**1a**) nor [BiRh(PTTL)₄] (**2a**) gave good results,³⁴ whereas the new complex **3b** furnished product **5b** (R = Me) with 90% ee. The corresponding trichloroethyl ester proved even more successful:^{74,75} once again, replacement of **2a** by either of the new complexes led to massive improvements. The fact that **3a** and **3b** both perform very well but **3b** is the better of the two is in excellent accord with the conclusions drawn from the DFT calculations: the peripheral –TIPS groups make the larger contribution to the stabilization of the chiral ligand sphere, but the *t*Bu– substituents on the phthalimide residues pay an additional dividend. This notion is further supported by a

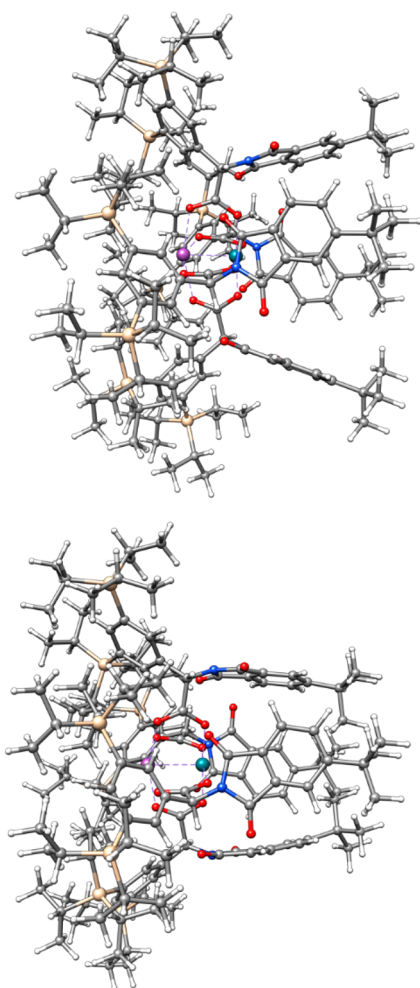
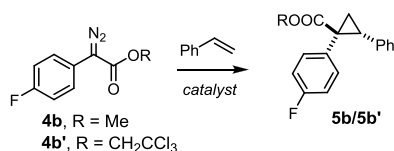


Figure 3. Side-view of the structure of **3b** as computed at the PBE/def2-SVP level of theory without (top) and with (bottom) D3 (BJ) dispersion correction

Table 1. Screening^a



Entry	R	Catalyst	Mol %	ee
1	Me	1a	1	32% ^b
2	Me	2a	1	35% ^b
3	Me	3b	1	90% ^b
4	CH ₂ CCl ₃	2a	1	58%
5	CH ₂ CCl ₃	3a	1	91%
6	CH ₂ CCl ₃	3b	1	95%
7	CH ₂ CCl ₃	3b	1	94% ^c
8	CH ₂ CCl ₃	3b	1	98% ^b
9	CH ₂ CCl ₃	3b	0.1	98% ^{b,e}
10	CH ₂ CCl ₃	3b	0.005	97% ^{b,e}
11	CH ₂ CCl ₃	3b	0.001	n.d. ^d

^aAll reactions were performed in pentane at RT; the yield of product (NMR) was $\geq 90\%$. ^bAt -10°C . ^cIn CH₂Cl₂. ^dIncomplete conversion after 24 h. ^e1 mmol scale

control experiment with a catalyst analogous to **3a** but lacking the peripheral TIPS-groups, which gave product **5b'** with only

24% ee (see the SI). The fact that the outcome is fairly independent of the medium (pentane versus CH₂Cl₂) can be taken as additional indirect evidence for LD being operative in solution.⁷⁶ Under the optimized conditions, product **5b'** was formed in essentially quantitative yield with 98% ee as a single diastereomer.

Formal replacement of a Rh(+2) center by Bi(+2) usually entails a loss in reactivity.^{34–38} When seen against this backdrop, the rate with which cyclopropane **5a** was formed by **3** even at -10°C is truly remarkable (Figure 4): conversion

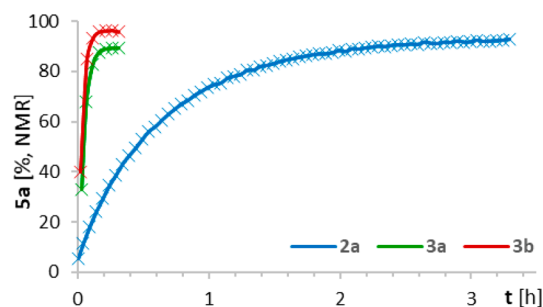


Figure 4. Kinetic profiling: Formation of **5a** using different BiRh-paddlewheel complexes (0.25 mol %, pentane, -10°C).

was complete within 10 min at 0.25 mol % catalyst loading, whereas it took >3 h with the parent complex **2a**.⁷⁷ The fact that the visibly more crowded catalysts lead to notably higher rates—in contrast to what one would expect from a confined space—indicates stabilizing LD interactions with the incoming substrate. The new design hence entails excellent selectivity and reactivity at the same time. The high solubility of **3a,b** in the common solvents even at low temperatures is an additional asset.

These rewarding results suggested that it should be possible to reduce the loading to partly compensate for the high molecular weights of **3a,b**. Indeed, no drop in productivity or optical purity was noticed—without any further optimization of the conditions—when the reaction was performed with only 0.005 mol % of **3b** on a mmol scale (Table 1, entry 10).⁷⁸ The robustness of these conditions was confirmed by the additional example shown in Table 2 (entry 6, 1.3 g scale).⁷⁹

The scope is broad, the level of induction is invariably excellent, and the reactions are typically very clean; therefore, basically quantitative yields were obtained in most cases (Table 2). α -Aryl- α -diazo esters comprising a strong donor substituent perform so well with the parent complex [BiRh(S-PTTL)₄] (**2a**) that there was no real need to resort to **3a,b** (entries 1–4).³⁴ However, diazoesters comprising less electron-rich aryl groups strongly benefitted from their use: in all cases investigated, **3b** led to significantly higher levels of induction, with ee's often approaching 99% (entries 5–21). This striking invariance of the results upon substantial modulation of the diazo compound is deemed another favorable distinguishing feature of the new catalyst.⁸⁰

Excellent results were also obtained with donor/acceptor α -diazo ketones (entries 24, 25), which previously required forcing conditions and recourse to special media.⁸¹ With catalyst **3b**, these challenging substrates react even at -10°C . Likewise, donor/donor carbenes are well behaved,^{2,82,83} again furnishing the corresponding cyclopropanes with outstanding levels of enantio- and diastereoselectivity (entries 26–28).

Table 2. Asymmetric [2 + 1] Cycloadditions^{a,b}

1		R = Ph	98% ee (90%)	>99% ee (99%)
2		R = CH ₂ SiMe ₃	99% ee (91%)	>99% ee (95%)
3		R = CH ₂ B(pin)	99% ee (73%)	98% ee (45%)
4		R = OBz	96% ee (57%)	99% ee (91%)
5		X = H	69% ee (84%)	96% ee (87%)
6		X = Br	91% ee (91%)	98% ee (97%)
7		X = COOMe	82% ee (89%)	99% ee (99%)
8		X = CN	68% ee (36%)	97% ee (99%)
9		X = B(pin)	99% ee (70%)	>99% ee (69%)
10		X = SO ₂ Me	97% ee (56%)	99% ee (85%) ^c
11		R = Ph	83% ee (99%)	98% ee (99%)
12		R = C ₄ H ₉	79% ee (72%)	96% ee (83%)
13		R = C=CSiMe ₃	77% ee (55%)	96% ee (65%)
14		R = CH ₂ Br	83% ee (52%)	99% ee (89%)
15		X = OMe	58% ee (92%)	87% ee (98%)
16		X = Br	74% ee (98%)	95% ee (99%)
17		X = F	80% ee (98%)	97% ee (97%)
18		X = COOMe	85% ee (99%)	98% ee (99%)
19		R =	91% ee (82%)	96% ee (87%) ^d
20		R =	73% ee (97%)	94% ee (99%)
21		R = 2-naphthyl	96% ee (85%)	99% ee (91%)
22			70% ee (85%)	96% ee (95%)
23			74% ee (80%)	98% ee (87%)
24		X = H	78% ee (25%)	91% ee (68%)
25		X = Br	89% ee (34%)	92% ee (75%)
26		X = H		99% ee (68%, dr > 50:1) ^d
27		X = OMe		97% ee (92%) ^{c,d}
28		X = NO ₂		95% ee (90%, dr > 50:1) ^{d,e}
29			96% ee (54%)	>99% ee (82%)
30		X = SiMe ₃	84% ee (98%)	97% ee (83%)
31		X = Cl	77% ee (81%)	98% ee (96%)
32				94% ee (72%)

^aColor code: black, **2a**; red, **3b**. ^bPentane, -10 °C, 1 mol % catalyst loading. ^cIn CH₂Cl₂/pentane. ^dAt rt. ^eIn CH₂Cl₂

In addition to (substituted) styrenes, many other terminal alkenes proved suitable, including vinyl benzoate, allyltrimethyl-

thylsilane, and allyl(pinacol)boronate, some of which have been rarely used before. Even allyl bromide reacts cleanly (entry 14): we are unaware of any prior use in asymmetric cyclopropanation. The same is true for *exo*-methylencyclobutane and -hexane, which furnish spirocyclic products (entries 22, 23); in these cases, the superiority of **3b** is particularly evident.

Although less comprehensive, the foray into the cyclopropanation of terminal alkynes was no less gratifying (entries 29–32). Most notable is the use of propargyl chloride, which leads to a multifunctional building block that promises rich downstream chemistry. Equally remarkable and largely unprecedented is the fact that cyclopropanation of a terminal alkyne is faster than insertion of the carbene intermediate into an unprotected alcohol (entry 32).^{84–87} To put these results into perspective, one has to note that [Rh₂(esp)₂]⁸⁸ or [Rh₂(OTpa)₄] (OTpa = triphenylacetate) as some of the most proficient achiral catalysts known to date furnished only complex mixtures on reaction with these functionalized alkynes.⁸⁹

Finally, the new catalysts were briefly examined in reactions other than [2 + 1] cycloadditions. Although a more systematic foray has to await further studies, the preliminary data obtained for prototype C–H and Si–H insertion reactions are promising (Table 3). When compared with the current state-

Table 3. C–H and Si–H Insertion Reactions^{a,c}

1		85% ee (49%) ^b	93% ee (73%) ^b
2			94% ee (93%) ^c
3		37% ee (25%)	94% ee (84%)
4		X = F	90% ee (62%)
5		X = OMe	95% ee (91%)

^aColor code as shown in Table 2; pentane, -10 °C, 1 mol % catalyst loading. ^bIn cyclohexane. ^cWith [Rh₂(R-PTAD)₄]: 56% ee (49%).⁹⁰

of-the-art,⁹⁰ the formation of a benzodihydrofuran by intramolecular insertion of a donor/donor carbene into a methyl ether makes a particularly compelling case (entry 2). Whereas **2a** performed poorly in the particularly taxing reaction of **4a** with Et₃SiH, **3b** resulted in clean conversion and an excellent overall result.^{11,91–98}

In summary, a new class of heterobimetallic paddlewheel complexes is presented, which take advantage of LD to stabilize the shape and directionality of the calyx that forms the chiral binding pocket. **3a,b** as the parent complexes of this series excel in cyclopropanation, cyclopropanation, and certain insertion reactions; as many variations of the conceptually new design can be envisaged, one may have high expectations for future generations of catalysts of this type. Opportunities along these and related lines^{99,100} are actively pursued in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c01972>.

Experimental Section containing supporting crystallographic data, computational data, characterization data, and NMR spectra of new compounds (PDF)

Accession Codes

CCDC 2063745–2063748 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Alois Fürstner – Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany; orcid.org/0000-0003-0098-3417; Email: fuerstner@kofo.mpg.de

Authors

Santanu Singha – Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany; orcid.org/0000-0003-4236-4366

Michael Buchsteiner – Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany; orcid.org/0000-0001-5169-3458

Giovanni Bistoni – Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany; orcid.org/0000-0003-4849-1323

Richard Goddard – Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany; orcid.org/0000-0003-0357-3173

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.1c01972>

Author Contributions

§S.S. and M.B. contributed equally

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Werlé, C.; Goddard, R.; Philipps, P.; Farès, C.; Fürstner, A. Stabilization of a Chiral Dirhodium Carbene by Encapsulation and a Discussion of the Stereochemical Implications. *Angew. Chem., Int. Ed.* **2016**, *55*, 10760–10765.
- (2) Werlé, C.; Goddard, R.; Fürstner, A. The First Crystal Structure of a Reactive Dirhodium Carbene Complex and a Versatile New Method for the Preparation of Gold Carbenes by Rhodium-to-Gold Transmetalation. *Angew. Chem., Int. Ed.* **2015**, *54*, 15452–15456.
- (3) Werlé, C.; Goddard, R.; Philipps, P.; Farès, C.; Fürstner, A. Structures of Reactive Donor/Acceptor and Donor/Donor Rhodium Carbenes in the Solid State and Their Implication for Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 3797–3805.

- (4) Tindall, D. J.; Werlé, C.; Goddard, R.; Philipps, P.; Farès, C.; Fürstner, A. Structure and Reactivity of Half-Sandwich Rh(+3) and Ir(+3) Carbene Complexes. Catalytic Metathesis of Azobenzene Derivatives. *J. Am. Chem. Soc.* **2018**, *140*, 1884–1893.

- (5) Hashimoto, S.; Watanabe, N.; Ikegami, S. Enantioselective Intramolecular C–H Insertion of α -Diazo- β -keto Esters Catalyzed by Homochiral Rhodium(II) Carboxylates. *Tetrahedron Lett.* **1990**, *31*, 5173–5174.

- (6) Watanabe, N.; Ogawa, T.; Ohtake, Y.; Ikegami, S.; Hashimoto, S. Dirhodium(II) Tetrakis[N-phthaloyl-(S)-tert-leucinate]: A Notable Catalyst for Enantiotopically Selective Aromatic Substitution Reactions of α -Diazocarbonyl Compounds. *Synlett* **1996**, *1996*, 85–86.

- (7) Kitagaki, S.; Anada, M.; Kataoka, O.; Matsuno, K.; Umeda, C.; Watanabe, N.; Hashimoto, S. Enantiocontrol in Tandem Carbonyl Ylide Formation and Intermolecular 1,3-Dipolar Cycloaddition of α -Diazo Ketones Mediated by Chiral Dirhodium(II) Carboxylate Catalyst. *J. Am. Chem. Soc.* **1999**, *121*, 1417–1418.

- (8) Tsutsui, H.; Abe, T.; Nakamura, S.; Anada, M.; Hashimoto, S. Practical Synthesis of Dirhodium(II) Tetrakis[N-phthaloyl-(S)-tert-leucinate]. *Chem. Pharm. Bull.* **2005**, *53*, 1366–1368.

- (9) For reviews, see refs 10–26 and the following: Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley: New York, 1998.

- (10) Doyle, M. P. Catalytic Methods for Metal Carbene Transformations. *Chem. Rev.* **1986**, *86*, 919–939.

- (11) Ye, T.; McKervey, M. A. Organic Synthesis with α -Diazo Carbonyl Compounds. *Chem. Rev.* **1994**, *94*, 1091–1160.

- (12) Doyle, M. P.; Forbes, D. C. Recent Advances in Asymmetric Catalytic Metal Carbene Transformations. *Chem. Rev.* **1998**, *98*, 911–935.

- (13) Padwa, A.; Weingarten, M. D. Cascade Processes of Metallo Carbenoids. *Chem. Rev.* **1996**, *96*, 223–269.

- (14) Davies, H. M. L.; Antoulinakis, E. G. Intermolecular Metal-Catalyzed Carbene Cyclopropanations. *Org. React.* **2001**, *57*, 1–326.

- (15) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. Stereoselective Cyclopropanation Reactions. *Chem. Rev.* **2003**, *103*, 977–1050.

- (16) Zhang, Z.; Wang, J. Recent Studies on the Reactions of α -Diazocarbonyl Compounds. *Tetrahedron* **2008**, *64*, 6577–6605.

- (17) Zhang, Y.; Wang, J. Catalytic [2,3]-Sigmatropic Rearrangement of Sulfur Ylide Derived from Metal Carbene. *Coord. Chem. Rev.* **2010**, *254*, 941–953.

- (18) Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. Modern Organic Synthesis with α -Diazocarbonyl Compounds. *Chem. Rev.* **2015**, *115*, 9981–10080.

- (19) DeAngelis, A.; Panish, R.; Fox, J. M. Rh-Catalyzed Intermolecular Reactions of α -Alkyl- α -Diazo Carbonyl Compounds with Selectivity over β -Hydride Migration. *Acc. Chem. Res.* **2016**, *49*, 115–127.

- (20) Gois, P. M. P.; Afonso, C. A. M. Stereo- and Regiocontrol in the Formation of Lactams by Rhodium-Carbene C–H Insertion of α -Diaoacetamides. *Eur. J. Org. Chem.* **2004**, *2004*, 3773–3788.

- (21) Davies, H. M. L.; Manning, J. R. Catalytic C–H Functionalization by Metal Carbenoid and Nitrenoid Insertion. *Nature* **2008**, *451*, 417–424.

- (22) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. Catalytic Carbene Insertion into C–H Bonds. *Chem. Rev.* **2010**, *110*, 704–724.

- (23) Zhu, S.-F.; Zhou, Q.-L. Transition-Metal-Catalyzed Enantioselective Heteroatom-Hydrogen Bond Insertion Reactions. *Acc. Chem. Res.* **2012**, *45*, 1365–1377.

- (24) Davies, H. M. L.; Lian, Y. The Combined C–H Functionalization/Cope Rearrangement: Discovery and Applications in Organic Synthesis. *Acc. Chem. Res.* **2012**, *45*, 923–935.

- (25) Gillingham, D.; Fei, N. Catalytic X–H Insertion Reactions Based on Carbenoids. *Chem. Soc. Rev.* **2013**, *42*, 4918–4931.

(26) Caballero, A.; Díaz-Requejo, M. M.; Fructos, M. R.; Olmos, A.; Urbano, J.; Pérez, P. J. Catalytic Functionalization of Low Reactive C(sp³)-H and C(sp²)-H Bonds of Alkanes and Arenes by Carbene Transfer from Diazo Compounds. *Dalton Trans.* **2015**, *44*, 20295–20307.

(27) Fox and coworkers were the first to propose that an “all up” conformation governs asymmetric cyclopropanations using **1a** and related catalysts; see ref **28** and the following: DeAngelis, A.; Dmitrenko, O.; Yap, G. P. A.; Fox, J. M. Chiral Crown Conformation of Rh₂(S-PTTL)₄: Enantioselective Cyclopropanation with α -Alkyl- α -diazoesters. *J. Am. Chem. Soc.* **2009**, *131*, 7230–7231.

(28) DeAngelis, A.; Boruta, D. T.; Lubin, J.-B.; Plampin, J. N.; Yap, G. P. A.; Fox, J. M. The Chiral Crown Conformation in Paddlewheel Complexes. *Chem. Commun.* **2010**, *46*, 4541–4543.

(29) See also: Lindsay, V. N. G.; Lin, W.; Charette, A. B. Experimental Evidence for the All-Up Reactive Conformation of Chiral Rhodium(II) Carboxylate Catalysts: Enantioselective Synthesis of *cis*-Cyclopropane α -Amino Acids. *J. Am. Chem. Soc.* **2009**, *131*, 16383–16385.

(30) Ghanem, A.; Gardiner, M. G.; Williamson, R. M.; Müller, P. First X-ray Structure of a *N*-Naphthaloyl-Tethered Chiral Dirhodium(II) Complex: Structural Basis for Tether Substitution Improving Asymmetric Control in Olefin Cyclopropanation. *Chem. - Eur. J.* **2010**, *16*, 3291–3295.

(31) Goto, T.; Takeda, K.; Shimada, N.; Nambu, H.; Anada, M.; Shiro, M.; Ando, K.; Hashimoto, S. Highly Enantioselective Cyclopropanation Reaction of 1-Alkynes with α -Alkyl- α -diazoesters Catalyzed by Dirhodium(II) Carboxylates. *Angew. Chem., Int. Ed.* **2011**, *50*, 6803–6808.

(32) Xue, Y.-S.; Cai, Y.-P.; Chen, Z.-X. Mechanism and Stereoselectivity of the Rh(II)-Catalyzed Cyclopropanation of Diazoindole: A Density Functional Theory Study. *RSC Adv.* **2015**, *5*, 57781–57791.

(33) Adly, F. G. On the Structure of Chiral Dirhodium(II) Carboxylate Catalysts: Stereoselectivity Relevance and Insights. *Catalysts* **2017**, *7*, 347.

(34) Collins, L. R.; Auris, S.; Goddard, R.; Fürstner, A. Chiral Heterobimetallic Bismuth-Rhodium Paddlewheel Catalysts: A Conceptually New Approach to Asymmetric Cyclopropanation. *Angew. Chem., Int. Ed.* **2019**, *58*, 3557–3561.

(35) For an alternative chiral [BiRh] complex, see: Ren, Z.; Sunderland, T. L.; Tortoreto, C.; Yang, T.; Berry, J. F.; Musaev, D. G.; Davies, H. M. L. Comparison of Reactivity and Enantioselectivity between Chiral Bimetallic Catalysts: Bismuth-Rhodium- and Dirhodium-Catalyzed Carbene Chemistry. *ACS Catal.* **2018**, *8*, 10676–10682.

(36) For achiral [BiRh] complexes, see refs **37–42** and the following: Dikarev, E. V.; Gray, T. G.; Li, B. Heterobimetallic Main-Group-Transition-Metal Paddle-Wheel Carboxylates. *Angew. Chem., Int. Ed.* **2005**, *44*, 1721–1724.

(37) Dikarev, E. V.; Li, B.; Zhang, H. Tuning the Properties at Heterobimetallic Core: Mixed-Ligand Bismuth-Rhodium Paddlewheel Carboxylates. *J. Am. Chem. Soc.* **2006**, *128*, 2814–2815.

(38) Hansen, J.; Li, B.; Dikarev, E.; Autschbach, J.; Davies, H. M. L. Combined Experimental and Computational Studies of Heterobimetallic Bi-Rh Paddlewheel Carboxylates as Catalysts for Metal Carbenoid Transformations. *J. Org. Chem.* **2009**, *74*, 6564–6571.

(39) Filatov, A. S.; Napier, M.; Vreshch, V. D.; Sumner, N. J.; Dikarev, E. V.; Petrukina, M. A. From Solid State to Solution: Advancing Chemistry of Bi-Bi and Bi-Rh Paddlewheel Carboxylates. *Inorg. Chem.* **2012**, *51*, 566–571.

(40) Sunderland, T. L.; Berry, J. F. Metal-Metal Single Bonds with the Magnetic Anisotropy of Quadruple Bonds: A Systematic Series of Heterobimetallic Bismuth(II)-Rhodium(II) Formamidinate Complexes. *Chem. - Eur. J.* **2016**, *22*, 18564–18571.

(41) Sunderland, T. L.; Berry, J. F. Expanding the Family of Heterobimetallic Bi-Rh Paddlewheel Carboxylate Complexes via Equatorial Carboxylate Exchange. *Dalton Trans.* **2016**, *45*, 50–55.

(42) Sunderland, T. L.; Berry, J. F. The First Bismuth(II)-Rhodium(II) Oxopyridinate Paddlewheel Complexes: Synthesis and Structural Characterization. *J. Coord. Chem.* **2016**, *69*, 1949–1956.

(43) Collins, L. R.; van Gastel, M.; Neese, F.; Fürstner, A. Enhanced Electrophilicity of Heterobimetallic Bi-Rh Paddlewheel Carbene Complexes: A Combined Experimental, Spectroscopic and Computational Study. *J. Am. Chem. Soc.* **2018**, *140*, 13042–13055.

(44) For general treatises of metal-metal bonded catalysts, see refs **45, 46**, and the following: Powers, I. G.; Uyeda, C. Metal-Metal Bonds in Catalysis. *ACS Catal.* **2017**, *7*, 936–958.

(45) Berry, J. F.; Lu, C. C. Metal-Metal Bonds: From Fundamentals to Applications. *Inorg. Chem.* **2017**, *56*, 7577–7581.

(46) Takaya, J. Catalysis Using Transition Metal Complexes Featuring Main Group Metal and Metalloid Compounds as Supporting Ligands. *Chem. Sci.* **2021**, *12*, 1964–1981.

(47) Yamawaki, M.; Tsutsui, H.; Kitagaki, S.; Anada, M.; Hashimoto, S. Dirhodium(II) Tetrakis[N-tetrachlorophthaloyl-(S)-*tert*-leucinate]: A New Chiral Rh(II) Catalyst for Enantioselective Amidation of C-H Bonds. *Tetrahedron Lett.* **2002**, *43*, 9561–9564.

(48) Goto, T.; Takeda, K.; Anada, M.; Ando, K.; Hashimoto, S. Enantio- and Diastereoselective Cyclopropanation with *tert*-Butyl α -diazopropionate Catalyzed by Dirhodium(II) Tetrakis[N-tetrabromophthaloyl-(S)-*tert*-leucinate]. *Tetrahedron Lett.* **2011**, *52*, 4200–4203.

(49) Tsutsui, H.; Yamaguchi, Y.; Kitagaki, S.; Nakamura, S.; Anada, M.; Hashimoto, S. Dirhodium(II) Tetrakis[N-tetrafluorophthaloyl-(S)-*tert*-leucinate]: An Exceptionally Effective Rh(II) Catalyst for Enantiotopically Selective Aromatic C-H Insertions of Diazo Ketoesters. *Tetrahedron: Asymmetry* **2003**, *14*, 817–821.

(50) This is not only true for dirhodium but also for diruthenium paddlewheel complexes; see: Miyazawa, T.; Suzuki, T.; Kumagai, Y.; Takizawa, K.; Kikuchi, T.; Kato, S.; Onoda, A.; Hayashi, T.; Kamei, Y.; Kamiyama, F.; Anada, M.; Kojima, M.; Yoshino, T.; Matsunaga, S. Chiral Paddle-wheel Diruthenium Complexes for Asymmetric Catalysis. *Nature Catal.* **2020**, *3*, 851–858.

(51) Wagner, J. P.; Schreiner, P. R. London Dispersion in Molecular Chemistry – Reconsidering Steric Effects. *Angew. Chem., Int. Ed.* **2015**, *54*, 12274–12296.

(52) Liptrot, D. J.; Power, P. P. London Dispersion Forces in Sterically Crowded Inorganic and Organometallic Molecules. *Nat. Rev. Chem.* **2017**, *1*, 0004.

(53) For established catalysts, in which dispersion was recognized as being critically important, see refs **54–56** and the following: Lyngvi, E.; Sanhueza, I. A.; Schoenebeck, F. Dispersion Makes the Difference: Bisligated Transition States Found for the Oxidative Addition of Pd(PtBu₃)₂ to Ar-OSO₂R and Dispersion-Controlled Chemoselectivity in Reactions with Pd[P(*i*Pr)(*t*Bu)₂]₂. *Organometallics* **2015**, *34*, 805–812.

(54) Saper, N. I.; Ohgi, A.; Small, D. W.; Semba, K.; Nakao, Y.; Hartwig, J. F. Nickel-catalysed anti-Markovnikov Hydroarylation of Unactivated Alkenes with Unactivated Arenes Facilitated by Non-covalent Interactions. *Nat. Chem.* **2020**, *12*, 276–283.

(55) Yepes, D.; Neese, F.; List, B.; Bistoni, G. Unveiling the Delicate Balance of Steric and Dispersion Interactions in Organocatalysis Using High-Level Computational Methods. *J. Am. Chem. Soc.* **2020**, *142*, 3613–3625.

(56) Eschmann, C.; Song, L.; Schreiner, P. R. London Dispersion Interactions Rather than Steric Hindrance Determine the Enantioselectivity of the Corey-Bakshi-Shibata Reduction. *Angew. Chem., Int. Ed.* **2021**, *60*, 4823–4832.

(57) The closest examples are those in which *intermolecular* London dispersion interactions enhance the interaction of a catalyst with the substrate; see refs **58, 59**, and the following: Lu, G.; Liu, R. Y.; Yang, Y.; Fang, C.; Lambrecht, D. S.; Buchwald, S. L.; Liu, P. Ligand-Substrate Dispersion Facilitates the Copper-Catalyzed Hydroamination of Unactivated Olefins. *J. Am. Chem. Soc.* **2017**, *139*, 16548–16555.

(58) Thomas, A. A.; Speck, K.; Kevlishvili, I.; Lu, Z.; Liu, P.; Buchwald, S. L. Mechanistically Guided Design of Ligands that

Significantly Improve the Efficiency of CuH-Catalyzed Hydroamination Reactions. *J. Am. Chem. Soc.* **2018**, *140*, 13976–13984.

(59) Xi, Y.; Su, B.; Qi, X.; Pedram, S.; Liu, P.; Hartwig, J. F. Application of Trimethylgermyl-Substituted Bisphosphine Ligands with Enhanced Dispersion Interactions to Copper-Catalyzed Hydroboration of Disubstituted Alkenes. *J. Am. Chem. Soc.* **2020**, *142*, 18213–18222.

(60) Dirhodium complexes bearing ligands derived from parent phenylglycine gave poor results in the few documented applications; see refs 61, 62, and the following: Pierson, N.; Fernández-García, C.; McKervey, M. A. Catalytic Asymmetric Oxonium Ylide – [2,3] Sigmatropic Rearrangement with Diazocarbonyl Compounds: First Use of C₂-Symmetry in Rh(II) Carboxylates. *Tetrahedron Lett.* **1997**, *38*, 4705–4708.

(61) Mattiza, J. T.; Fohrer, J. G. G.; Duddeck, H.; Gardiner, M. G.; Ghanem, A. Optimizing Dirhodium(II) Tetrakis-carboxylates as Chiral NMR Auxiliaries. *Org. Biomol. Chem.* **2011**, *9*, 6542–6550.

(62) Buck, R. T.; Coe, D. M.; Drysdale, M. J.; Ferris, L.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Sanghera, J. B. Asymmetric Rhodium Carbene Insertion into the Si–H Bond: Identification of New Dirhodium(II) Carboxylate Catalysts Using Parallel Synthesis Techniques. *Tetrahedron: Asymmetry* **2003**, *14*, 791–816.

(63) Robak, M. T.; Herbage, M. A.; Ellman, J. A. Synthesis and Applications of *tert*-Butanesulfonamide. *Chem. Rev.* **2010**, *110*, 3600–3740.

(64) For the use of *tert*-butyl phthalimide substituents, see: Adly, F. G.; Gardiner, M. G.; Ghanem, A. Design and Synthesis of Novel Chiral Dirhodium(II) Carboxylate Complexes for Asymmetric Cyclopropanation Reactions. *Chem. - Eur. J.* **2016**, *22*, 3447–3461.

(65) Separation of the enantiomers by HPLC on a chiral stationary phase is an alternative entry into optically pure ligand.

(66) Neese, F. Software Update: The Orca Program System, Version 4.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, *8*, e1327.

(67) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(68) Grimme, S.; Hansen, A.; Brandenburg, J. G.; Bannwarth, C. Dispersion-Corrected Mean-Field Electronic Structure Methods. *Chem. Rev.* **2016**, *116*, 5105–5154.

(69) Becke, A. D.; Johnson, E. R. A Density-Functional Model of the Dispersion Interaction. *J. Chem. Phys.* **2005**, *123*, 154101.

(70) A large number of benchmark studies showed that the D3 dispersion typically provides a lower bound for the coupled cluster dispersion computed using accurate techniques, see refs 68, 71, and the following: Bistoni, G. Finding Chemical Concepts in the Hilbert Space: Coupled Cluster Analyses of Noncovalent Interactions. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2020**, *10*, e1442.

(71) Schneider, W. B.; Bistoni, G.; Sparta, M.; Saitow, M.; Riplinger, C.; Auer, A. A.; Neese, F. Decomposition of Intermolecular Interaction Energies within the Local Pair Natural Orbital Coupled Cluster Framework. *J. Chem. Theory Comput.* **2016**, *12*, 4778–4792.

(72) The computed and the experimental structure of 3a show good congruence; the comparison is slightly obscured by diglyme coordinated to the axial site at Rh in the X-ray structure and the presence of solute in the unit cell.

(73) $\Delta E_{\text{disp}} = \Delta E_{\text{disp}}(\text{TIPS}) + \Delta E_{\text{disp}}(\text{tBu}) + \Delta E_{\text{disp}}(\text{rest})$; for details, see the SI.

(74) Guptill, D. M.; Davies, H. M. L. 2,2,2-Trichloroethyl Aryldiazoacetates as Robust Reagents for the Enantioselective C–H Functionalization of Methyl Ethers. *J. Am. Chem. Soc.* **2014**, *136*, 17718–17721.

(75) Liao, K.; Negretti, S.; Musaev, D. G.; Bacsá, J.; Davies, H. M. L. Site-selective and Stereoselective Functionalization of Unactivated C–H Bonds. *Nature* **2016**, *533*, 230–234.

(76) Schümann, J. M.; Wagner, J. P.; Eckhardt, A. K.; Quanz, H.; Schreiner, P. R. Intramolecular London Dispersion Interactions Do Not Cancel in Solution. *J. Am. Chem. Soc.* **2021**, *143*, 41–45.

(77) The methyl and the trichloroethyl esters 4a and 4a' react with almost the same rates; as expected for a donor/acceptor carbene, however, change of the aryl substituents exerts a marked effect; for details, see the SI.

(78) For even lower loadings under optimized conditions, see: Wei, B.; Sharland, J. C.; Lin, P.; Wilkerson-Hill, S. M.; Fullilove, F. A.; McKinnon, S.; Blackmond, D. G.; Davies, H. M. L. In Situ Kinetic Studies of Rh(II)-Catalyzed Asymmetric Cyclopropanation with Low Catalyst Loadings. *ACS Catal.* **2020**, *10*, 1161–1170.

(79) The absolute configuration of this and two additional products was determined by X-ray diffraction (Flack absolute structure parameter); see the SI.

(80) In comparison, the ee's in cyclopropanations with a similar set of α -aryl- α -diazoesters catalyzed by [Rh₂(PTAD)₄] are much less uniform: Chepiga, K. M.; Qin, C.; Alford, J. S.; Chennamadhavuni, S.; Gregg, T. M.; Olson, J. P.; Davies, H. M. L. Guide to Enantioselective Dirhodium(II)-Catalyzed Cyclopropanation with Aryldiazoacetates. *Tetrahedron* **2013**, *69*, 5765–5771.

(81) Denton, J. R.; Davies, H. M. L. Enantioselective Reactions of Donor/Acceptor Carbenoids Derived from α -Aryl- α -Diazoketones. *Org. Lett.* **2009**, *11*, 787–790.

(82) Bergstrom, B. D.; Nickerson, L. A.; Shaw, J. T.; Souza, L. W. Transition Metal Catalyzed Insertion Reactions with Donor/Donor Carbenes. *Angew. Chem., Int. Ed.* **2021**, *60*, 6864–6878.

(83) Zhu, D.; Chen, L.; Fan, H.; Yao, Q.; Zhu, S. Recent Progress on Donor and Donor-Donor Carbenes. *Chem. Soc. Rev.* **2020**, *49*, 908–950.

(84) We are aware of a single example using a free carbene generated by light-induced diazo decomposition, which afforded racemic product; see: He, F.; Koenigs, R. M. Visible Light Mediated, Metal-free Carbene Transfer Reactions of Diazoalkanes with Propargylic Alcohols. *Chem. Commun.* **2019**, *55*, 4881–4884.

(85) It is well established that chiral dirhodium paddlewheel complexes are hardly adequate for enantioselective –OH or –NH insertion and Doyle–Kirmse reactions, except for special cases or if chiral cocatalysts are added that largely account for the induction; this inability is inherent and basically rooted in the dissociation of the chiral rhodium moiety from the ylide primarily formed before the enantiodetermining [1,2]-H shift occurs. In line with this notion, the few test reactions performed with complexes 3 also afforded no or only moderate enantioselectivity; cf. the SI. For pertinent literature, see refs 17, 86, 87, and the following: Liang, Y.; Zhou, H.; Yu, Z.-X. Why is Copper(I) Complex More Competent Than Dirhodium(II) Complex in Catalytic Asymmetric O–H Insertion Reactions? A Computational Study of the Metal Carbenoid O–H Insertion into Water. *J. Am. Chem. Soc.* **2009**, *131*, 17783–17785.

(86) Jana, S.; Guo, Y.; Koenigs, R. M. Recent Perspectives on Rearrangement Reactions of Ylides via Carbene Transfer Reactions. *Chem. - Eur. J.* **2021**, *27*, 1270–1281.

(87) Ren, Y.-Y.; Zhu, S.-F.; Zhou, Q.-L. Chiral Proton-Transfer Shuttle Catalysis for Carbene Insertion Reactions. *Org. Biomol. Chem.* **2018**, *16*, 3087–3094.

(88) Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J. Expanding the Scope of C–H Amination through Catalyst Design. *J. Am. Chem. Soc.* **2004**, *126*, 15378–15379.

(89) These reactions were undertaken in an attempt to form racemic product as needed for accurate ee-determination.

(90) Lamb, K. L.; Squitieri, R. A.; Chintala, S. R.; Kwong, A. J.; Balmont, E. I.; Soldi, C.; Dmitrenko, O.; Castineira Reis, M.; Chung, R.; Addison, J. B.; Fettinger, J. C.; Hein, J. E.; Tantillo, D. J.; Fox, J. M.; Shaw, J. T. Synthesis of Benzodihydrofurans by Asymmetric C–H Insertion Reactions of Donor/Donor Rhodium Carbenes. *Chem. - Eur. J.* **2017**, *23*, 11843–11855.

(91) For leading references, see refs 92–94 and the following: Buck, R. T.; Doyle, M. P.; Drysdale, M. J.; Ferris, L.; Forbes, D. C.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Zhou, Q.-L. Asymmetric Rhodium Carbenoid Insertion into the Si–H Bond. *Tetrahedron Lett.* **1996**, *37*, 7631–7634.

(92) Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. Rhodium(II) (S)-N-(Arylsulfonyl)Prolinate Catalyzed Asymmetric Insertions of Vinyl- and Phenylcarbenoids into the Si–H Bond. *Tetrahedron Lett.* **1997**, *38*, 1741–1744.

(93) Kitagaki, S.; Kinoshita, M.; Takeba, M.; Anada, M.; Hashimoto, S. Enantioselective Si–H Insertion of Methyl Phenyl diazoacetate Catalyzed by Dirhodium(II) Carboxylates Incorporating N-Phthaloyl-(S)-Amino Acids as Chiral Bridging Ligands. *Tetrahedron: Asymmetry* **2000**, *11*, 3855–3859.

(94) Sambasivan, R.; Ball, Z. T. Metallopeptides for Asymmetric Dirhodium Catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 9289–9291.

(95) Zhang, Y.-Z.; Zhu, S.-F.; Wang, L.-X.; Zhou, Q.-L. Copper-Catalyzed Highly Enantioselective Carbenoid Insertion into Si–H Bonds. *Angew. Chem., Int. Ed.* **2008**, *47*, 8496–8498.

(96) Yasutomi, Y.; Suematsu, H.; Katsuki, T. Iridium(III)-Catalyzed Enantioselective Si–H Bond Insertion and Formation of an Enantioenriched Silicon Center. *J. Am. Chem. Soc.* **2010**, *132*, 4510–4511.

(97) Wang, J.-C.; Xu, Z.-J.; Guo, Z.; Deng, Q.-H.; Zhou, C.-Y.; Wan, X.-L.; Che, C.-M. Highly Enantioselective Intermolecular Carbene Insertion to C–H and Si–H Bonds Catalyzed by a Chiral Iridium(III) Complex of a D_4 -Symmetric Halterman Porphyrin Ligand. *Chem. Commun.* **2012**, *48*, 4299–4301.

(98) Chen, D.; Zhu, D.-X.; Xu, M.-H. Rhodium(I)-Catalyzed Highly Enantioselective Insertion of Carbenoid into Si–H: Efficient Access to Functional Chiral Silanes. *J. Am. Chem. Soc.* **2016**, *138*, 1498–1501.

(99) Caló, F.; Fürstner, A. A Heteroleptic Dirhodium Catalyst for Asymmetric Cyclopropanation with α -Stannyl- α -Diazoacetate. 'Stereo-retentive' Stille Coupling with Formation of Chiral Quarternary Centers. *Angew. Chem., Int. Ed.* **2020**, *59*, 13900–13907.

(100) Buchsteiner, M.; Martínez-Rodríguez, L.; Jerabek, P.; Pozo, I.; Patzer, M.; Nöthling, N.; Lehmann, C.; Fürstner, A. Catalytic Asymmetric Fluorination of Copper Carbene Complexes: Preparative Advances and a Mechanistic Rationale. *Chem. - Eur. J.* **2020**, *26*, 2509–2515.