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Chiral Heterobimetallic Bismuth-Rhodium Paddlewheel Catalysts: A Conceptually New Approach to

Asymmetric Cyclopropanation

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Dedicated to Professor Walter Thiel on the occasion of his 70th birthday

Abstract: Cyclopropanation reactions of styrene derivatives with donor/acceptor carbenes formed in situ are significantly more enantioselective when catalyzed by the heterobimetallic bismuth–rhodium complex **5a** endowed with *N*-phthalimido *tert*-leucine paddlewheel ligands rather than by its homobimetallic dirhodium analogue **1a**. This virtue is likely the result of two synergizing factors: the conical shape of **5a** translates into a narrower calyx-like chiral binding site about the catalytically active Rh center; the Bi atom, although fully solvent exposed, does not decompose aryl diazoacetates and is hence incapable of promoting a racemic background reaction. Moreover, ligand variation proved that successful catalyst design mandates that the anisotropy of the conical heterobimetallic core be matched by proper directionality of the ligand sphere.

Our group has recently published the first structure of a chiral dirhodium carbene complex in the solid state.^{1,2} We had chosen [Rh₂(PTTL)₄] (**1a**) as precatalyst for its excellent pedigree in asymmetric catalysis (Scheme 1).^{3,4,5} The derived electrophilic donor-acceptor carbene complex **3** was found to adopt an α, α, α -conformation: all *N*-phthalimido substituents of the *tert*-leucine derived paddlewheel ligands are oriented toward the same side, thus crafting a chiral calyx about one of the two rhodium atoms; the immediate environment about the second rhodium center formed by the four *tert*-butyl groups is essentially "achiral".^{6,7} Detailed spectroscopic studies showed that this

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conformation is well retained in solution at low temperature, as is necessary to maintain the integrity of this highly reactive and sensitive complex.¹



Scheme 1. Top: Preparation and reactivity of the dirhodium donor/acceptor carbene 3, the structure of which was solved by crystallographic means and NMR spectroscopy; bottom/left: structure of 3 in the solid state (the carbene unit was removed to show the conformation of the paddlewheel ligands about the dirhodium core);¹ bottom right: schematic drawing of the possible basic conformers that a chiral dirhodium tetracarboxylate complex can adopt; complex 3 is essentially a manifestation of the C_d symmetric extreme¹⁰

Although these experimental data describe the ground state, it is tempting to assume that the overall shape of the complex is preserved in the stereodetermining transition state passed through in the reaction of **3** with styrene as a prototypical substrate; this would lead to the formation of cyclopropane **4a**, which is indeed the major product.¹ For the correct prediction of the relative and

absolute stereochemistry, it also seems legitimate to consider in more detail why the level of asymmetric induction is modest (78% ee).⁸ In contrast to other conceivable basic conformers that such paddlewheel complexes might adopt (Scheme 1), an essentially C_4 symmetric "all up" array exposes two notably different rhodium faces:^{9,10} Although our X-ray data showed that the achiral pore of **3** between the *tert*-butyl groups is narrower than the aperture of the chiral calyx, it remains large enough that CH_2CI_2 can enter and coordinate to Rh2 (see Scheme 1).¹ If a diazo derivative reaches Rh2 and gets decomposed to the corresponding metal carbene, a racemic background reaction will ensue and the ee of the resulting product **4a** drops. With this critical aspect in mind, it becomes clear why previous empirical catalyst optimization exercises had led to complexes such as $[Rh_2(PTAD)_4]$ (**1b**) bearing adamantyl residues in lieu of the *tert*-butyl groups (Scheme 2), which likely block the achiral face more efficiently and hence result in higher enantioselectivities in many applications.¹¹



Scheme 2. Top: Established design concept for chiral dirhodium paddlewheel complexes that tries to prevent racemic background reactions by steric means; bottom: alternative concept pursued herein capitalizing on the use of heterobimetallic precatalyts

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Outlined herein is a conceptually different approach to catalyst optimization which builds upon recent insights into structure and bonding in heterobimetallic paddlewheel carbene complexes (Scheme 2).^{12,13,14} Specifically, combined experimental, spectroscopic and computational studies showed that formal replacement of one Rh["] center in the bimetallic core for Bi["] enhances the electrophilic character of the resulting carbenes to a significant extent, although the rate of metalcarbene formation is manifestly slower.¹⁴ More important in the present context is the fact that the bismuth site seems to lack any notable Lewis acidity and proved incapable of decomposing ethyl diazoacetate.^{12-14,15} Even though the ionic radius of bismuth is larger than that of rhodium and the bismuth center hence certainly more exposed, any deleterious background reaction should cease. Furthermore, the different radii impart a conical shape on the heterobimetallic core, which likely translates into a narrower chiral pocket and hence potentially improves the level of asymmetric induction. As these factors might synergize, it seemed worthwhile to pursue this design concept in more detail. As shown below, heterobimetallic complexes can indeed outperform their homobimetallic cousins in catalytic cyclopropanation to a considerable extent, provided that the directionality of the bismuth-rhodium tetracarboxylate cage finds proper correspondence in the ligand sphere. This boundary condition, however, is not necessarily met by the design principles governing contemporary asymmetric dirhodium catalysis. This communication complements a recent literature report describing preparation and use of a BiRh precatalyst with a different set of chiral ligands ([BiRh(TBSP)₄] (TBSP = *tert*-butylsulfonylprolinate).¹⁶







Figure 1. Structure of complex **5a**·EtOAc in the solid state; top: side view of the $\alpha, \alpha, \alpha, \alpha$ -calyx; bottom: Newman-type projection along the Rh–Bi axis (bottom); hydrogen atoms are omitted for clarity and anisotropic displacement parameters are shown at the 30% probability level

The targeted heterobimetallic precatalyst **5a** and its close relatives **5b**,**c** were prepared in excellent yield by mixing **7** with the appropriately protected *tert*-leucine derivative (Scheme 3). Heating of the mixture in toluene resulted in ligand exchange; to shift the equilibrium, the volatile trifluoroacetic acid was azeotropically removed by passing the condensing solvent through a Soxhlet extractor filled with powdered K_2CO_3 as described in detail in the Supporting Information. The crude material was

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then purified by an extractive work up and recrystallization to remove any acidic residues. Whereas [BiRh(TFA)₄] (**7**), serving as the starting point, is air sensitive and needs to be handled with care, complexes **5a-c** are indefinitely air-stable and easy to work with. Because they are somewhat hydroscopic, however, it is recommended to keep them dry or dry them prior to use.¹⁷

The structure of **5a** EtOAc in the solid state (Figure 1) proves that the co-crystallized EtOAc is bound to rhodium, whereas the bismuth center is unligated. This finding concurs with literature data which suggest that the Bi^{II} atom exhibits hardly any Lewis acidity.^{12,14} The ligand sphere adopts the $\alpha, \alpha, \alpha, \alpha$. conformation, presumably because this arrangement places the *tert*-butyl groups as the most bulky substituents at maximum distance from one another; their orientation toward the Bi center follows from the larger radius of this ion, which provides more space (see below). Since the resulting structure of **5a**. EtOAc is similar to that of the actual dirhodium carbene complex $\mathbf{3}$, ^{1,18} a comparison seems meaningful as one can take the coordinated EtOAc ligand as a dummy for the reactive carbene moiety. The Bi–O bonds (average 2.41 Å) are significantly longer than the Rh2–O bonds in 3 (average 2.03 Å), as is the Bi–Rh distance (2.503(1) Å) compared with the Rh1–Rh2 distance of **3** (2.400(1) Å). In line with our expectations, these geometric changes translate into a chiral pocket about the rhodium center in **5a** which is more confined than that of **3**.¹ Specifically, the aperture measures \approx 8.9 Å and ≈10.0 Å for the two main axes at the height of the coordinated carbonyl O-atom (Rh1–O1 2.305(7) Å), whereas the analogous distances in **3** at the level of the coordinated carbene C-atom (which is actually somewhat closer to rhodium, cf: Rh1–C1 2.004(9) Å) are ≈11.6 Å and ≈11.8 Å. Figure 1 clearly shows that there is no steric impediment whatsoever about the Bi-center that would prevent carbene formation from occurring if this site were catalytically active (note that a typical metal carbene bond is \geq 2 Å for an element of the sixth row).¹⁹

Encouraged by these structural attributes, we tested the catalytic properties of **5a-c** in asymmetric cyclopropanation reactions of substituted styrenes with a prototypical donor/acceptor diazo derivative as carbene precursor. For the sake of consistency, the reactions were performed in parallel with the homobimetallic analogue **1a**. As expected, complex **5a** reacted more slowly than **1a** (14 h

versus < 4 h) but gave a substantially better ee (Table 1), whereas complex **5b** bearing the more bulky NTTL substituent proved less selective. In view of the often excellent results with [RhRh(TCPTTL)₄] documented in the literature,²⁰ it first came as a surprise that the performance of the heterobimetallic analogue **5c** endowed with the identical chlorinated ligand set was disappointing; this outcome, however, became obvious after an X-ray structure of this complex had been solved (see below).

| MeO 2 conditions MeO 4 R | | | | | |
|--------------------------|-----|----------|--------|---------|------------------------|
| entry | R | Catalyst | T (°C) | Product | ee (%) |
| 1 | OMe | 1a | 20 | 4b | 67 (68) ^[b] |
| 2 | OMe | 5a | 20 | 4b | 73 |
| 3 | OMe | 5b | 20 | 4b | 53 |
| 4 | OMe | 5c | 20 | 4b | 4 |
| 5 | Н | 1a | 20 | 4a | 75 |
| 6 | Н | 5a | 20 | 4a | 86 |
| 7 | Н | 1a | -25 | 4a | 77 |
| 8 | н | 5a | -25 | 4a | 90 ^[c] |
| 9 | н | 1a | -40 | 4a | 79 |
| 10 | н | 5a | -40 | 4a | 95 ^[d] |

MeOOC

Table 1. Optimization of the Asymmetric Cyclopropanation of Styrene Derivatives^[a]

[a] unless stated otherwise, the reactions were carried out in pentane using 1 mol% of the indicated catalyst; [b] literature data in brackets, see ref. 8; [c] in CH_2Cl_2 as the solvent, the ee was only 76%; [d] an ee of 93% was reached when the reaction was carried out in CH_2Cl_2 at $-78^{\circ}C$ (1 d) and $-45^{\circ}C$ (1 d), but the conversion remained incomplete ($\approx 80\%$)

Focusing on **5a** as the most promising candidate, we were able to significantly improve the enantioselectivity of product **4b** by lowering the temperature in pentane as the preferred solvent, whereas the homobimetallic complex **1a** responded much less to this change. Reactions with a set of representative substrates confirmed the trend (Chart 1) in that the use of **5a** as precatalyst invariably led to cyclopropanes with notably higher optical purity than its dirhodium congener **1a**, even though most reactions using **5a** had to be carried out at -10° C for solubility reasons, whereas **1a** worked at -40° C. It is of note, however, that the substituent on the phenyl ring of the transient push-pull

carbene complexes exerts a strong effect on the level of induction in either catalyst series (compare **4a**, **4i** and **4j**). The superiority of catalyst **5a** also extends to the asymmetric cyclopropenation of phenylacetylene with formation of compound **4k**. The absolute stereochemistry of products **4a** and **4k** was determined by comparison with literature data;²¹ all other compounds were assigned by analogy.



Chart 1. Comparison of heterobimetallic and homobimetallic paddlewheel complexes (**5a**) and (**1a**) in cyclopropanation/cyclopropenation reactions (1 mol% catalyst loading, pentane): ^[a] at -40° C; ^[b] -10° C

The strikingly different level of asymmetric induction reached with complexes **5a-c** as well as their very different solubility deserve further comment. While the best performing precatalyst **5a** slowly dissolves in common organic solvents such as CH_2Cl_2 or toluene, the solubility of **5b** and **5c** is poor. We had already noticed during their synthesis (Scheme 3) that **5b** and **5c** start to precipitate even

from boiling toluene. Crude **5b** could eventually be recrystallized from hot CH_2CI_2 , but **5c** required refluxing chlorobenzene for this purpose, indicating an exceptional thermal stability. X-ray diffraction data revealed the reasons for this surprisingly different behavior: the monomeric units of complex **5a** lack short intermolecular contacts, whereas complexes **5b,c** both self-assemble into supramolecular aggregates of considerable beauty. As shown in Figure 2 for **5c** (and Figure S-3b for **5b**), six such entities form a capsule via extensive π -stacking interactions between the extended *N*-substituents. In case of **5c**, peripheral halogen bonding interactions^{1,22,23} between the perchlorinated phthalimide groups seem to further stabilize the resulting supercluster, which is difficult to disassemble by solvation.



Figure 2. Structure of complex $5c \cdot Et_2O$ in the solid state. Top: monomeric [BiRh(TCPPTL]₄] unit adopting an "inverted" β , β , β , β -calyx; bottom: projection along the 3-fold axis in the crystal showing the assembly of six such units to form a supramolecular capsule; for more details, see the SI.

The arguably most striking structural feature of the structures of **5b**,**c** in the solid state, however, is the fact that the calyx is "inverted" relative to that of 5a: the six bismuth atoms of the hexamer are all directed inside the capsule, whereas the catalytically active rhodium atoms reside outwards within the essentially achiral microenvironment created by the *tert*-butyl substituents. This " $\beta_i \beta_j \beta_j \beta_j \beta_j$ conformer" is most likely enforced by the increased bulk of the extended phthalimide residues (NTTL, TCPTTL) in either complex, which are sterically more demanding than the tert-butyl groups and hence occupy the wider space about the larger Bi cation. The supramolecular assemblies in the solid state notwithstanding, ¹H NMR DOSY data showed that all three heterobimetallic complexes have basically the same hydrodynamic radius of \approx 7.4 Å in CD₂Cl₂ as the solvent (see the Supporting Information). The solubility of **5b,c** may be poor, but the small amount that eventually gets dissolved exists as a monomeric paddlewheel complex in solution. If the "inverted" calyx persists, the chiral induction is expected to be marginal: this is indeed the case for 5c (Table 1, entry 4), in which the differential between the size of the tetrachlorophthalimide (TCPTTL) and the tert-butyl substituents favor the poorly-inducing β , β , β , β -conformer; additional peripheral halogen bonding interactions further add to its stability. The situation is perhaps less clear-cut for 5b; it is tempting to speculate that the intermediate ee reached with this catalyst (Table 1, entry 3) reflects a "calyx flip-flop", in which the β , β , β , β -conformer observed in the solid state might equilibrate with the more enantioselective $\alpha, \alpha, \alpha, \alpha$ -conformer. Because of the very poor solubility at low temperature, however, this aspect could not yet be firmly established by spectroscopic means.

The exploratory study summarized above pursued an unorthodox approach to asymmetric rhodium carbene chemistry. The new concept capitalizes on the use of heterobimetallic precatalysts that allow a conceivable racemic background reaction to be avoided. An additional virtue is the conical shape of the BiRh core which renders the chiral binding site crafted by the chosen amino acid-derived

paddlewheel ligands narrower; these two factors are thought to synergize, as suggested by the much improved level of asymmetric induction reached with complex **5a** in a set of cyclopropanation reactions. In conceptual terms, however, it is important to recognize that any successful ligand design mandates that the anisotropy of the conical heterobimetallic core be matched by proper directionality of the ligand sphere; the comparison of the closely related complexes **5a-c** shows that linear extrapolations of successful concepts from the dirhodium tetracarboxylate estate do not necessarily meet this stringent condition but may actually be counterproductive. More systematic investigations are necessary to better understand how to conciliate the auspicious molecular shape with the necessary (physico)chemical qualities of chiral catalysts of this new type. Work along this and related lines of research²⁴ is currently in progress.

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Stretched and Bent: Formal replacement of one Rh atom in a classical dirhodium tetracarboxylate paddlewheel complex by Bi results in a concial shape of the precatalyst: while the wide-open Bi site does not cause a racemic background reaction, the calyx-like chiral binding pocket about Rh is

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narrower and hence more effective. These two virtues likely synergize in asymmetric cyclopropanation reactions.

Keywords: Bimetallic Catalysts · Bismuth · Carbene Complexes · Cyclopropanation · Rhodium

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