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To be cited as: *Helv. Chim. Acta* 10.1002/hlca.202100042

Link to VoR: https://doi.org/10.1002/hlca.202100042

Helvetica Chimica Acta
HELVETICA
10.1002/hlca.202100042

$[Rh_2(MEPY)_4]$ and $[BiRh(MEPY)_4]$: Convenient Syntheses and Computational Analysis of Strikingly Dissimilar Siblings

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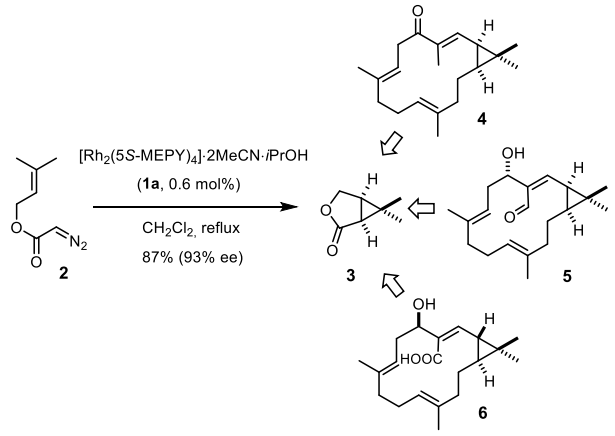
Dedicated to Prof. E. Peter Kündig on the occasion of his 75th birthday

$[Rh_2(MEPY)_4]$ is a versatile catalyst for asymmetric synthesis but its preparation requires purification by chromatography on surface-modified silica. A higher yielding procedure based on a more convenient work-up is presented herein. Likewise, a much improved method for the preparation of $[BiRh(OTfa)_4]$ is described, which makes this heterobimetallic complex readily available. Subsequent exchange of the trifluoroacetate ligands opens access to a so far underappreciated family of (chiral) paddlewheel complexes. While [BiRh] complexes comprising four carboxylate ligands are highly adequate for intermolecular asymmetric cyclopropanation reactions, $[BiRh(MEPY)_4]$ as the heterobimetallic cousin of $[Rh_2(MEPY)_4]$ was found to be surprisingly unreactive; DFT calculations uncover the reasons for this inertia.

Keywords: Bismuth • Carbenes • Cyclopropanation • Heterobimetallic Complexes • Rhodium

Introduction

A recent approach to an ensemble of different casbane diterpenes including compounds **4**-**6** capitalized on the use of the cyclopropyl lactone **3** as a key building block.[1] This compound is readily accessible by intramolecular cyclopropanation of diazoester **2** using $[Rh_2(5S\text{-}MEPY)_4]\cdot 2MeCN\cdot i PrOH$ (**1a**) as the catalyst[2-12] in our hands, **3** was obtained in 87% yield and 93% ee.[1]



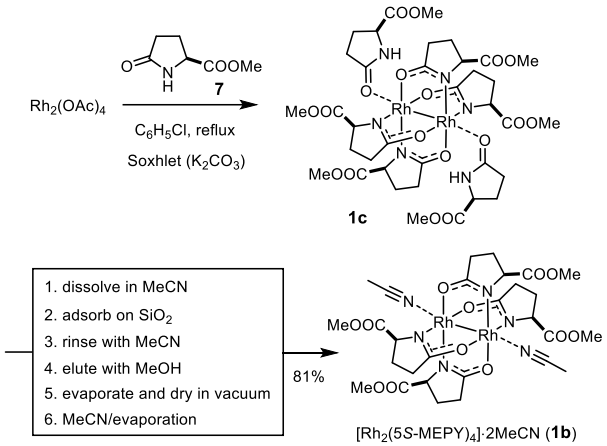
Scheme 1. Formation of a key building block for the total synthesis of casbane derivatives by intramolecular cyclopropanation; 5*S*-MEPY = methyl 2-pyrrolidinone-5(*S*)-carboxylate (methyl 5(*S*)-pyroglutamate)

Although the reaction worked well even when the catalyst loading was reduced to 0.6 mol%, a substantial amount of complex **1** was needed to ensure the material throughput necessary for this extensive total synthesis campaign. The preparation of **1a** is well described in the literature, but its isolation in analytically pure form hinges upon reversed phase chromatography using cyanopropyl-modified silica and the reported yield (58%) is not overly high;[2] therefore we were prompted to develop a more convenient and proficient method. Moreover, it was hoped that replacement of **1** by its heterobimetallic cousin $[BiRh(5S\text{-}MEPY)_4]$ (**13**) might lead to even better results: we have previously shown that certain bismuth-rhodium paddlewheel complexes outperform the parent dirhodium catalysts in terms of asymmetric induction in intermolecular cyclopropanation reactions.[13,14] Proof-of-concept notwithstanding, the preparation of such heterobimetallic complexes also needs to be improved; the quest for $[BiRh(5S\text{-}MEPY)_4]$ (**13**) hence provided an opportunity to develop a more convenient entry route and, at the same time, to investigate whether or not formal replacement of one of the rhodium atoms by the main-group element bismuth entails a better application profile in this particular case too.

Results and Discussion

An Improved Method for the Preparation of $[Rh_2(5S\text{-}MEPY)_4]\cdot 2MeCN$ (**1b**). Complex **1a** is made from commercial $[Rh_2(OAc)_4]$ on treatment with excess methyl 2-pyrrolidone-carboxylate (MEPY-H, **7**) in refluxing chlorobenzene overnight (13 h). Although the ligand exchange is a priori reversible, the reaction is driven to completion by passing the condensing solvent through a thimble filled with K_2CO_3 in a Soxhlet apparatus, which traps the released and co-evaporating HOAc.[2] To ensure reasonable rates, **7** has to be used in slight excess. The reaction is accompanied by a characteristic color change, in that the originally green solution turns dark red when heated overnight. For work up, all volatile materials were evaported in high vacuum, which causes another striking color change to give a deep blue/violet solid residue. It is this material that had to be purified by reversed phase chromatography in order to remove isomeric species[15] and afford bright-red (*cis*-2,2)-configured $[Rh_2(MEPY)_4]\cdot 2MeCN\cdot i PrOH$ (**1a**), carrying acetonitrile ligands at the axial

coordination sites and *i*PrOH as a co-crystallized solute in the unit cell as shown by X-ray crystallography.[2,3]



Scheme 2. Practical and high-yielding preparation of **1b** avoiding purification by reversed-phase chromatography

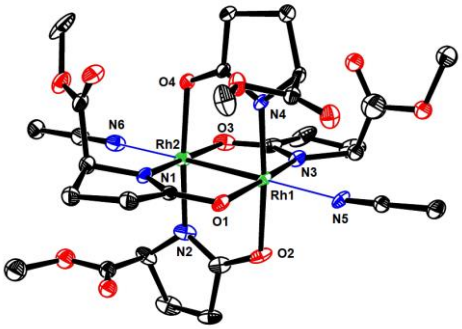
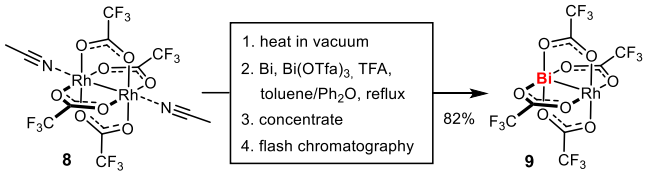


Figure 1. Structure of (*cis*-2,2)-configured [Rh$_2$(5*S*-MEPY)$_4$]·2MeCN (**1b**) in the solid state; H-atoms and disorder of two of the –COOMe groups not shown for clarity; for the full structure, see the Supporting Information.[1]

We chose to purify an aliquot of the crude blue material by subliming excess ligand (and possible impurities) off in high vacuum to give an analytically pure sample of what turned out to be [Rh$_2$(5*S*-MEPY)$_4$]·2(*S*-MEPY-H)$_2$ (**1c**) (Scheme 2). It is the additional ligand used to drive the reaction which occupies the axial sites; the interaction is obviously so strong that it persists even upon heating to 130-150°C at 10^{-3} mbar.[16] Gratifyingly though, MeCN as solvent is able to displace the axial MEPY-H ligands to give a red solution, which was adsorbed on ordinary silica. Rinsing of the resulting deep red solid material with MeCN allowed the excess **7** to be eluted and hence its re-coordination to be prevented. The product was then desorbed with MeOH, the filtrate evaporated, and the resulting solid material dried in vacuo at 100°C to give a turquoise powder, which was triturated with MeCN in order to provide a stabilizing yet defined axial ligand. This colorful and convenient procedure is described in detail in the Experimental Section and photographs are contained in the Supporting Information; it afforded [Rh$_2$(5*S*-MEPY)$_4$]·2MeCN (**1b**) in analytically pure form in 81% yield as a single isomer, within the limits of detection (600 MHz NMR). The identity of the complex follows from its spectroscopic and analytical data; in contrast to the original procedure,[2,4] the modified work up furnished **1b** free of any solute in the unit cell as confirmed by X-ray crystallography (Figure 1).

An Improved Procedure for the Preparation of Heterobimetallic [BiRh]-Paddlewheel Complexes. The chemistry of heterobimetallic [BiRh] paddlewheel complexes was pioneered by Dikarev and coworkers. The initial access routes had relied on solid phase syntheses;[17,18] later, these authors managed to prepare the prototype complex [BiRh(OTfa)$_4$] (**9**) by reaction of [Rh$_2$(OTfa)$_4$] (**8**) with Bi(OTfa)$_3$ and Bi metal in toluene/Ph$_2$O.[19] One of the recommended procedures for product isolation is sublimation at 125°C (10^{-3} mbar). Although **9**, once obtained in pure form, is stable in air for days, the sublimation proved not only rather low yielding (≈ 40%) but quite erratic in our hands: in one out of ca. four cases, the mixture spontaneously turned black, resulting in loss of material. Although the exact reasons could not be clarified, the decomposition is almost certainly not caused by inadvertent contact of the crude product with oxygen and/or moisture, as it occurred equally regularly under rigorously inert conditions; rather, we suppose that traces of remaining Bi metal, when superheated in the solid state, might entail deleterious over-reduction of the product complex which comprises a bismuth center in the unusual oxidation state +2.



Scheme 3. Practical and high-yielding preparation of the heterobimetallic complex **13** avoiding (erratic) purification by sublimation; TFA = trifluoroacetic acid

Gratifyingly, we found that sublimation is not needed altogether; rather, complex [BiRh(OTfa)$_4$] (**9**), free of any axial ligands, can be conveniently isolated by ordinary flash chromatography (Scheme 3). This simple procedure gave an improved yield of 82% and never met with failure, such that this precious complex is now deemed a well-accessible starting point for further investigations.

The trifluoroacetate groups of **9** can be readily displaced by other carboxylic acids (or other ligands);[20-22] for the low boiling point of the released TFA, which is again trapped by the Soxhlet method alluded to above,[2] the reaction proceeds well even in toluene rather than chlorobenzene. The examples shown in Scheme 4 using HOAc or the well-proven amino acid derivatives **14**[23,24] and **15**[25-27] illustrate this point. The resulting complexes **10** or **11** perform particularly well in intermolecular cyclopropanation reactions of donor-acceptor carbenes, for which [Rh$_2$(MEPY)$_4$] is not qualified. The level of asymmetric induction clearly surpasses that reached with the corresponding homobimetallic [Rh$_2$] complexes carrying the exact same paddlewheel ligands,[13] even though the rate of reaction is usually slower;[20,28] the comparison shown in Table 1

[1] CCDC 2068752 (**1b**), 2068750 (**10a**), 2068749 (**12**), and 2068751 (**13**) contain the supplementary crystallographic data for this work. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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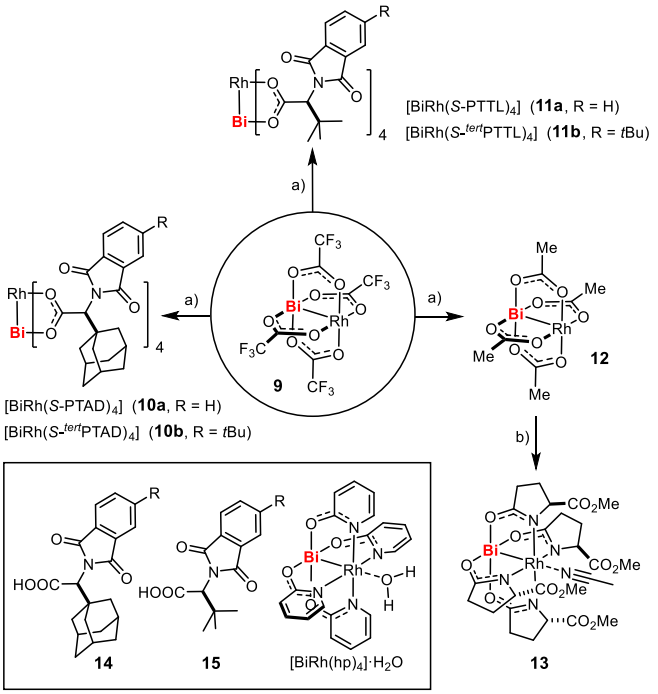
is representative. Catalysts of this type operate by adopting an α,α,α,α-conformation: the *N*-phthaloyl-protected amino acid residues point in one direction and craft a chiral binding site about the Rh-atom as proven by crystallographic data for an actual reactive carbene intermediate;[29-32] this conformation persists in solution and is likely selectivity-determining.[29,33-36] The larger ion radius of Bi(+2) imparts a conical shape onto the ligand sphere, which in turn makes the chiral binding site about Rh tighter and more effective.[13] Equally important is the fact that the Bi(+2) center, though solvent exposed and surrounded only by the "achiral" *t*Bu- or adamantyl parts of the ligands, does not decompose a diazo derivative and therefore does not lead to any racemic background reaction.[13] The structure of **10a** in the solid state illustrates these structural attributes (Figure 2).



Scheme 4. a) Acid, toluene, reflux/Soxhlet (K_2CO_3), 88% (**10a**, from **14a**); 92% (**10b**, from **14b**); 95% (**11a**, from **15a**); 99% (**11b**, from **15b**); 94% (**12**, from HOAc); b) **7**, chlorobenzene, reflux/Soxhlet (K_2CO_3), 81%

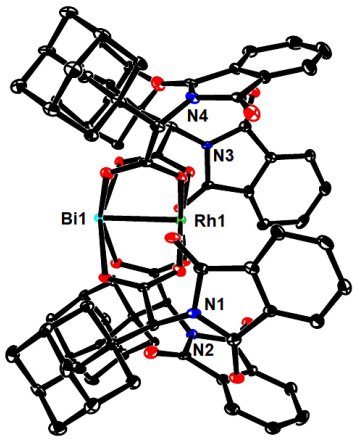


Figure 2. Structure of [BiRh(*S*-PTAD)$_4$] (**10a**) in the solid state; H-atoms and solute $CHCl_3$ in the unit cell not shown for clarity; for the full structure, see the Supporting Information.[1]

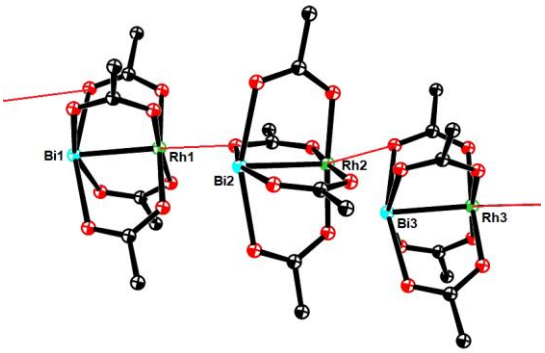
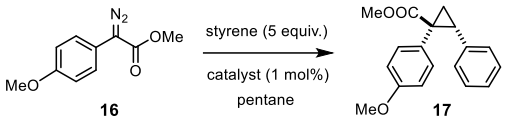


Figure 3. Structure of [BiRh(OAc)$_4$] (**12**) in the solid state; the Rh-atoms account for the formation of the coordination polymer, whereas the Bi-centers are unligated.[1]

Table 1. Preliminary Evaluation[a]



Nr	Substrate	Catalyst	T (°C)	Prod	Yield (%)	ee (%)
1	**2**	**1b**	40[b]	**3**	nd	93
2	**2**	**13**	40[b]	**n. r.**	---	---
3	**16**	**1b**	20[b]	**17**	37[c]	rac.
4	**16**	**13**	20[b]	**n. r.**	---	---
5	**16**	[BiRh(hp)$_4$]	20[b]	**n.r.**	---	---
6	**16**	[Rh$_2$(*S*-PTTL)$_4$]	20	**17**	90	75
7	**16**	[Rh$_2$(*S*-PTTL)$_4$]	−40	**17**	92	79
8	**16**	**11a**	20	**17**	87	86
9	**16**	**11a**	−10	**17**	88	97
10	**16**	**10a**	−10	**17**	52[c]	97
11	**16**	**10b**	−10	**17**	85[c]	88
12	**16**	**11b**	−10	**17**	87[c]	98

[a] all reactions were performed in pentane; yields of isolated pure compounds, unless stated otherwise; [b] in CH_2Cl_2; [c] NMR yield relative to mesitylene as internal standard; n. r. = no reaction; nd = not determined

The same ligand exchange process cannot be used to make [BiRh(5*S*-MEPY)$_4$], likely because the pK values of the trifluoroacetate ligands in **9** and the amide moiety of MEPY–H (**7**) are not well-matching.[2] This problem was solved by resorting to [BiRh(OAc)$_4$] (**12**)[21] as the starting material: even though this complex is a coordination polymer in the solid state (Figure 3), the more basic acetate ligands exchange with MEPY–H without incident to form [BiRh(5*S*-MEPY)$_4$]·MeCN (**13**) after recrystallization from MeCN/*i*PrOH.

[2] The exact mechanism of ligand exchange is unknown; it is reasonable to assume, however, that one of the initial steps consists in the reversible protonation of the carbonyl group of the leaving group by the protic incoming ligand. Since the amide group of MEPY is much less acidic that the carboxylic acids **14** or **15**, the use of complex **12** carrying more basic acetate ligands (rather than trifluoroacetates) was thought to be advantageous.

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The structure of **13** in the solid state (Figure 4) is very different from that of its [Rh_2]-congener **1b** (Figure 1). For the high oxophilicity of bismuth, all four O-atoms of the MEPY-ligands bind to this main group metal, thus forcing the four N-atoms of the amidates to ligate the catalytically active Rh-center where they form a very tight and arguably rigid C_4-symmetric chiral binding site ([4,0]$_O$-arrangement). Such self-sorting of the donor atoms is not observed in **1b**, which is C_2-symmetric; the two Rh centers are equivalent, featuring mixed coordination spheres comprised of two mutually *cis*-configured N- and two O-donor atoms each.

The change in the orientation of the chiral ligands enforced by incorporation of Bi(+2) has dramatic consequences: complex **13** was found incapable of decomposing diazoesters **2** or **16** to the corresponding metal carbenes; it hence proved inadequate for the formation of **3** by catalytic intramolecular cyclopropanation, as we had originally hoped. This failure came as a surprise in view of the good experiences with other chiral [BiRh] paddlewheel complexes such as **10** and **11** (Table 1).[13] We are aware of only one complex carrying oxypyridinate (hp) ligands which shows the same "[4,0]$_O$-pattern";[37] since no reactivity data had been reported for [BiRh(hp)$_4$]·H_2O, we re-prepared this sterically unencumbered complex and found it to be unreactive too vis-à-vis diazoester **16** (Scheme 4, Table 1). Therefore, electronic rather than geometric factors seem to be largely accountable for the missing performance, for which we tried to gain better understanding by computational means.

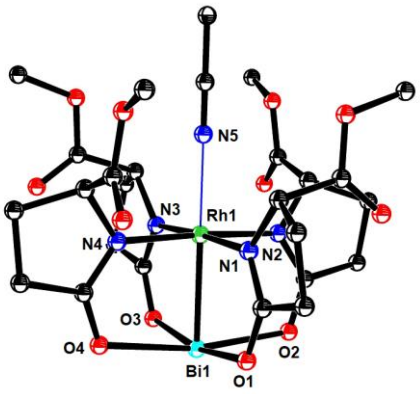

Figure 4. Structure of one of the two independent molecules of [$BiRh_2$(5*S*-MEPY)$_4$]·MeCN (**13**) in the unit cell, which differ from each other only in minor conformational detail; H-atoms not shown for clarity.[1]

Computational Study. A previous investigation from our laboratory into the electronic character of achiral homo- and heterobimetallic carbene complexes[28] had been based on all-electron calculations using the BP86 functional[38] and the valence triple-ζ basis set of the Karlsruhe group together with the scalar relativistic 0th-order regular approximation (ZORA Hamiltonian), as implemented in the ORCA program suite.[39] The computational results were carefully calibrated against advanced spectroscopic data (UV/Vis, resonance-Raman), which proved that the chosen level of theory was fully adequate;[28] it was therefore also used in the present context.

As expected, the computed and the experimental structures of **1b** and **13** in the solid state are in good agreement (for details, see the Supporting Information). The match pertains to the bond distances as well as to the conformational details, which were well reproduced in either case.

Removal of the axial MeCN ligands as a necessary prelude to any reaction with a diazo derivative is largely inconsequential in structural terms, as long as implicit solvent effects of CH_2Cl_2 were emulated by a conductor-like polarizable continuum model (CPCM).[3] The generated MO diagrams of "bare" [Rh_2(5*S*-MEPY)$_4$] and [BiRh(5*S*-MEPY)$_4$], however, reveal the markedly different electronic nature of these complexes (Figure 5). The LUMO is strongly metal-centered in either case but noticeably higher in energy in the heterobimetallic variant (−2.55 eV in **13** versus −3.71 eV in **1**): this situation is unfavorable as it renders attack of a diazo derivative onto the catalyst difficult. In addition to this electronic handicap, the very narrow pore formed by the C_4-symmetric arrangement of the esters about the axial binding site of **13** likely constitutes an additional steric impediment for substrate binding.

The HOMO of **13** features significant lobes on the Rh-atom as well as on the paddlewheel ligands, but not on Bi. Even though the Rh-atom is surrounded by all four N-atoms as the supposedly stronger donor sites of an amidate ligand, the HOMO of **13** (−4.65 eV) is lower-lying in energetic terms than that of **1** (−4.21 eV). Back-donation from the filled rhodium d-orbitals to a bound diazo derivative, however, is necessary for the extrusion of N_2 and the formation of the corresponding carbene complex to occur. The interactions between the 4d orbitals of [N_4]-ligated rhodium with the 6p orbitals of [O_4]-ligated bismuth are obviously weak and not outweighed by the particular positioning of the heteroatom donors.

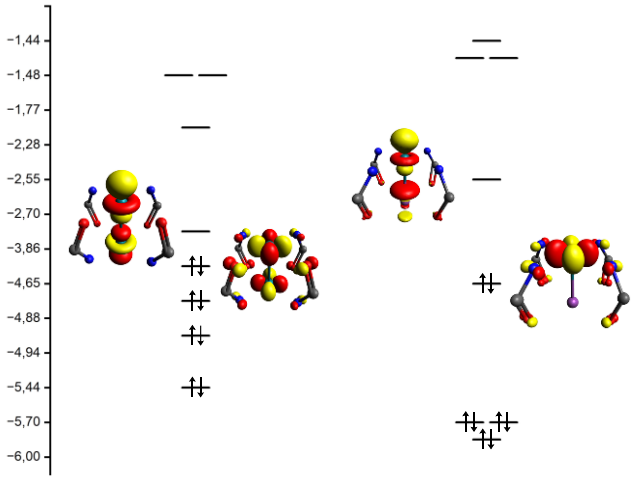

Figure 5. Molecular orbital scheme for bare [Rh_2(5*S*-MEPY))$_4$] (**1**, left) and [BiRh(5*S*-MEPY)$_4$] (**13**, right); the structures were truncated for sake of clarity; energy in eV (for further details, see the SI).

[3] When the calculations are carried out in the gas phase, a conformational change is observed for [Rh_2(MEPY)$_4$] in that one of the esters on each end of the dinuclear complex turns around to engage the –CO<u>O</u>Me atom with the Rh center; this interaction has a node that raises the energy of the LUMO. This interaction vanishes when the continuum solvent model for CH_2Cl_2 is applied.

The resulting large HOMO/LUMO gap in **13** (ΔE = 2.10 eV versus 0.50 eV in **1**) in combination with a narrow binding site likely accounts for the poor reactivity of [BiRh(5*S*-MEPY)$_4$]; this notion is in accord with previous conclusions that carbene formation is the rate-determining step in reactions catalyzed by achiral [BiRh] complexes.[20] From the conceptual viewpoint, this result implies that metal-metal bonding is a prime reactivity-determinant.[28,40] In order to harness the full potential of heterobimetallic cooperation in (chiral) carbene chemistry, future catalyst design must primarily aim at properly adjusting the net effect of the internal metallo-ligand as the arguably most critical parameter.

Conclusions

The literature route to [Rh$_2$(MEPY)$_4$] (**1**), a venerable catalyst in the area of rhodium carbene chemistry, has been improved in terms of practicality and yield. The same is true for the previously rather cumbersome approaches to heterobimetallic [BiRh] paddlewheel complexes, which are now readily available too. While chiral [BiRh] complexes comprising amino acid derived carboxylate ligands hold great promise for enantioselective catalysis,[13,14] the carboxamidate derivative [BiRh(MEPY)$_4$] (**13**) proved unreactive. This unexpected observation shows that it does not suffice to simply extrapolate successful concepts from dirhodium chemistry to the heterobimetallic estate; rather, the effect of the main-group metallo-ligand is the dominant reactivity-determining factor. Future work must hence try to gain deeper understanding for and better control over this particular parameter. For our long-standing interest in various aspects of metal carbene chemistry in general,[41-49] we are committed to doing so; encouraging lead findings along these lines have recently disclosed.[50]

Experimental Section

General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware using anhydrous solvents under argon. The solvents and reagents were purified by distillation over the indicated drying agents and were transferred under argon: chlorobenzene (CaH_2), toluene (Na/K alloy); pentane, MeCN, Et_3N (absorption solvent purification system based on molecular sieves). For the synthesis of **1b**, MeCN can be used as received. Flash chromatography: Merck silica gel 40-63 μm with predistilled or HPLC grade solvents. Preparative HPLC separations were carried out on an Agilent 1260 Infinity II Preparative LC System. GC analyses: Shimadzu GCMS-QP2010 Ultra instrument with a FID detector. IR: Alpha Platinum ATR instrument (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS: ESI-MS: ESQ 3000 (Bruker); EI: MAT 8200 (70 eV, Finnigan); accurate mass determinations: Bruker APEX III FT-MS (7 T magnet), Mat 95 (Finnigan), Thermo Scientific LTQ-FT, or Thermo Scientific Exactive. Optical rotations ([α]): A-Krüss Otronic Model P8000-t polarimeter, wavelength: 589 nm, concentration: (c/(10 mg/mL)). NMR: Bruker DPX 300, AVIII 400, AVIII 600 or AV600neo spectrometers (the latter two equipped with cryoprobes) in the solvents indicated at 25°C; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.2$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual $CDHCl_2$: $\delta_H \equiv 5.32$ ppm, [D$_6$]-DMSO: $\delta_C \equiv 39.5$ ppm, residual [D$_5$]-DMSO in [D$_6$]-DMSO: $\delta_H \equiv 2.50$ ppm). Signal assignments were established using HSQC, HMBC, COSY, NOESY and other 2D experiments. All commercially available compounds (abcr, Acros Organics, Alfa Aesar, FluoroChem, TCI Chemicals, Sigma-Aldrich, Strem Chemicals) were used as received, unless stated otherwise. For the preparation of previously unknown or not fully characterized chiral ligands, see the Supporting Information.

[Rh$_2$(5*S*-MEPY)$_4$]·2MeCN (**1b**). A two-necked 50 mL, round bottom flask equipped with a magnetic stir bar, an inert gas adapter on the side neck, and a Soxhlet apparatus topped by a reflux condenser, which also carries an inert gas adapter, was evacuated, flame-dried, and allowed to cool to ambient temperature before it was refilled with argon. A thimble containing a layer of dry sand and a layer of dry K_2CO_3 (4.4 g) was introduced into the Soxhlet apparatus under Ar before the gas adapter on the side neck was replaced by a glass stopper (instead of the Soxhlet extractor with the thimble, it is also possible to use a frit with a bridging side arm; a photograph of this set-up is contained in the Supporting Information).

The flask was charged with chlorobenzene (22.5 mL), which had been degassed prior to use by passing a stream of Ar through it for 20 min. Next, commercial [Rh$_2$(OAc)$_4$] (300.0 mg, 679 μmol) was added, followed by methyl 2-pyrrolidone-5*S*-carboxylate (**7**, 5*S*-MEPY–H, 651.0 mg, 4.7 mmol). The flask was immersed into a pre-heated oil bath (145°C) and the mixture stirred at this temperature for 13 h, causing a color change from green to dark red.[4] The mixture was allowed to reach ambient temperature and the solvent was evaporated in high vacuum (10^{-3} mbar) to give a deep blue/violet solid material. An aliquot of this compound was purified by subliming the excess ligand and any impurities off (130°C, 10^{-3} mbar), leaving a sample of analytically pure [Rh$_2$(5*S*-MEPY)$_4$]·2(*S*-MEPY–H)$_2$ (**1c**) behind; the spectral data are compiled below.

The crude blue compound was dissolved in MeCN (20 mL) under air to give a dark red solution. Silica gel (8 g) was added with stirring, resulting in decolorization of the solution. The now dark red solid material was filtered off and carefully rinsed with MeCN (3 x 50 mL); the combined MeCN filtrates were discarded. The still red silica was then washed with MeOH (3 x 50 mL) until it was colorless, and the combined blue MeOH filtrates were evaporated on a rotary evaporator to leave a violet solid material. This purification step was repeated three times.

A flame-dried Schlenk flask containing a magnetic stir bar was charged with this solid material. The compound was then heated in vacuum (10^{-3}

[4] Reaction time and temperature are important parameters to avoid accumulation of isomeric [Rh$_2$(5*S*-MEPY)$_4$] complexes and complexes resulting from incomplete substitution of the acetate ligands by MEPY, which result in lower yields of product and/or may compromise the performance of the catalyst, see ref. 15

mbar) for 14 h to 100°C with gentle stirring until the solid had taken a turquoise color. The flask was refilled with Ar and allowed to cool to ambient temperature before dry MeCN (1 mL) was introduced. After stirring for 5 min, the remaining solvent was evaporated and the product dried in vacuum to furnish the title complex as a red/violet solid material (473 mg, 81%). $[\alpha]_D^{20}$ = −335.7 (0.014 g/100 mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 4.32 – 4.27 (m, 2H), 3.95 (d, J = 8.7 Hz, 2H), 3.71 (s, 6H), 3.68 (s, 6H), 2.63 – 2.59 (m, 4H), 2.31 – 2.21 (m, 10H), 2.20 – 211 (m, 4H), 1.97 – 1.82 ppm (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 188.6, 188.3, 175.5, 175.2, 115.4, 66.8, 66.7, 52.1, 51.9, 31.8, 31.6, 26.1, 25.4, 3.07 ppm; IR (film) $\tilde{\nu}$ = 2950, 1729, 1608, 1428, 1279, 1193, 1168, 1117, 1043, 987, 686, 595 cm^{-1}; HRMS (ESI$^+$): *m/z* calcd. for $C_{28}H_{38}N_6O_{12}Rh_2$ [*M*+Na−(2×MeCN)]$^+$: 797.00190; found: 797.00231.

[[Rh$_2$(5*S*-MEPY)$_4$]·2(*S*-MEPY–H)$_2$ (1c). Prepared by sublimation as described above; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.62 (s, 2H), 4.34 (dd, J = 8.3, 6.7 Hz, 2H), 4.23 (dd, J = 8.8, 4.2 Hz, 2H), 3.97 (d, J = 7.0 Hz, 2H), 3.75 (s, 6H), 3.71 (s, 6H), 3.62 (s, 6H), 2.69 – 2.50 (m, 8H), 2.50 – 2.31 (m, 4H), 2.30 – 2.18 (m, 4H), 2.18 – 2.08 (m, 4H), 1.93 – 1.78 ppm (m, 4H): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.7, 187.5, 182.1, 175.7, 175.1, 171.6, 65.6, 65.1, 56.9, 52.4, 51.9, 51.8, 31.8, 31.5, 30.8, 25.9, 25.7, 24.2 ppm; IR (film) $\tilde{\nu}$ = 2950, 1734, 1666, 1606, 1426, 1356, 1277, 1236, 1193, 1168, 1116, 1042, 988, 926, 794, 685, 594, 509 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{36}H_{50}N_6O_{18}Rh_2$ [M^+]: 1060.12862; found: 1060.12861.

[BiRh(OTfa)$_4$] (9). [Rh$_2$(OTfa)$_4$]·2MeCN (**8**) (534 mg, 0.722 mmol) was heated to 80°C under high vacuum (10^{-3} mbar) for 1 h to remove the axially bound ligands; during this time, the color of the sample changed from purple to green. Next, Bi(OTfa)$_3$ (415 mg, 0.757 mmol),[51] freshly ground Bi metal (817 mg, 3.91 mmol), toluene (40 mL), Ph_2O (1.1 mL, 6.93 mmol) and trifluoroacetic acid (200 µL, 2.61 mmol) were added. The mixture was stirred at 115°C bath temperature for 16 h and the reaction progress was monitored by ^{19}F NMR analysis. The remaining Bi metal was allowed to settle and the supernatant was removed via cannula. The yellow filtrate was concentrated in vacuo. Most of the remaining Ph_2O was sublimed onto a cold (−30°C) sublimation finger at 50°C under high vacuum (10^{-3} mbar). The residue was purified by flash chromatography (toluene/MeCN, gradient 100:0 → 90:10); some black residue sticks on top of the column, whereas a broad yellow-brown band containing the product was collected (for photographs, see the Supporting Information). Evaporation of the product-containing fraction afforded the title complex as a yellow powder (855 mg, 82%). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): δ −74.2 ppm.

[BiRh(*S*-*tert*PTTL)$_4$]·EtOAc (11b). A mixture of complex **9** (51 mg, 0.067 mmol) and acid **15b** (106 mg, 0.335 mmol) in dry toluene (20 mL) was stirred at reflux temperature for 3 h, passing the condensing vapor through a Soxhlet apparatus containing a thimble filled with K_2CO_3; the reaction progress was monitored by ^{19}F NMR. Once full conversion was reached (ca. 3 h), the mixture was concentrated in vacuum and the residue was purified by flash chromatography (CH_2Cl_2/EtOAc, 99:1) to obtain the title complex as a yellow solid (110 mg, 99%). ^{1}H NMR analysis showed that one equivalent of EtOAc is bound to the complex. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 4.3 Hz, 4H), 7.76 – 7.62 (m, 8H), 4.89 (d, J = 3.9 Hz, 4H), 4.11 (q, J = 6.8 Hz, 2H), 2.04 (d, J = 4.2 Hz, 3H), 1.38 (d, J = 3.9 Hz, 36H), 1.25 (t, J = 5.6 Hz, 3H), 1.15 ppm (d, J = 4.2 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.9, 171.6, 168.3, 167.9, 158.3, 132.3, 130.8, 129.5, 123.3, 120.8, 61.4, 60.6, 35.9, 35.8, 31.3, 28.2, 21.2, 14.3 ppm; IR (ATR): $\tilde{\nu}$ = 1776, 1713, 1591, 1367, 1257, 1185, 1103, 840, 785, 753, 693, 565 cm^{-1}; HRMS (ESI$^+$) for $C_{72}H_{88}BiN_4O_{16}Rh$ [*M*+Na]$^+$: calcd: 1599.49464, found: 1599.49642.

[BiRh(*S*-*tert*PTAD)$_4$]·EtOAc (10b). Prepared analogously from **9** and acid **14b** as a yellow solid (205 mg, 92%). ^{1}H NMR analysis showed that one equivalent of EtOAc is bound to the complex. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 11.6 Hz, 4H), 7.74 – 7.65 (m, 8H), 4.70 (s, 4H), 4.11 (q, J = 7.1 Hz, 2H), 2.04 (s, 3H), 1.97 ppm (d, J = 12.9 Hz, 24H), 1.71 (dd, J = 17.2, 9.3 Hz, 36H), 1.38 (s, 36H), 1.25 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.6, 171.3, 168.5, 168.1, 158.3, 132.3, 130.8, 129.5, 123.3, 120.8, 62.1, 60.5, 39.5, 38.0, 37.1, 35.8, 31.3, 28.9, 21.2, 14.3 ppm; IR (ATR): $\tilde{\nu}$ = 2902, 1775, 1712, 1591, 1365, 1349, 1259, 1239, 1093, 1044, 841, 757, 693, 671, 564 cm^{-1}; HRMS (ESI$^+$) for $C_{96}H_{112}BiN_4O_{16}Rh$ [*M*+Na]$^+$: calcd: 1911.68244, found: 1911.68500.

[BiRh(OAc)$_4$] (12). Prepared analogously from **9** and HOAc (415 mg, 94%). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 1.88 ppm (s, 12H); ^{13}C NMR (101 MHz, [D$_6$]-DMSO): δ = 184.9, 22.2 ppm; IR (ATR): $\tilde{\nu}$ = 2939, 1530, 1484, 1378, 1345, 1261, 1042, 804, 688, 623, 545 cm^{-1}; HRMS (ESI$^+$) for $C_8H_{12}BiO_8Rh$ [*M*+Na]$^+$: calcd: 570.92833, found: 570.92784. The spectral data matched those reported in the literature.[21] Single crystals suitable for X-ray diffraction were grown by dissolving the sample in the minimum amount of hot MeOH, filtration of the turbid mixture, and slow cooling of the clear filtrate to ambient temperature.

[BiRh(5*S*-MEPY)$_4$] (13). A mixture of [BiRh(OAc)$_4$] (**12**, 101 mg, 0.184 mmol) and methyl 2-pyrrolidone-5*S*-carboxylate (**7**, 208 mg, 1.46 mmol) in dry chlorobenzene (15 mL) was stirred at reflux temperature for 12 h, passing the condensing vapor through a Soxhlet apparatus containing a thimble filled with K_2CO_3. The mixture was concentrated in vacuo and the residue was purified by preparative HPLC (150 mm Kromasil 5-C18, 5 µm, Ø 30 mm, MeCN/H_2O = 30/70, v = 35 mL/min, 308 K, t = 4.12 min) to obtain the title complex as a yellow solid (82 mg, 51%). Single crystals of the cetonitrile adduct suitable for X-ray diffraction were grown from a saturated MeCN/2-propanol solution. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.19 – 4.13 (m, 4H), 3.73 (s, 12H), 2.44 – 2.16 (m, 10H), 2.01 – 1.89 ppm (m, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 184.5, 176.6, 65.3, 52.6, 32.7, 28.5 ppm; IR (ATR): $\tilde{\nu}$ = 2926, 2854, 1735, 1667, 1583, 1535, 1454, 1412, 1357, 1299, 1232, 1195, 1172, 1109, 1023, 986, 922, 794, 769, 686, 538 cm^{-1}; HRMS (ESI$^+$) for $C_{24}H_{32}BiN_4O_{12}Rh$ [*M*+Na]$^+$: calcd: 903.07678, found: 903.07672.

Representative Procedure for Cyclopropanation Reactions. Methyl (1*S*,2*R*)-1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (17). A solution of the diazo ester **16** (20.6 mg, 0.1 mmol) in pentane (2 mL) was added to a solution of complex **11b**·EtOAc (1.7 mg, 0.001 mmol) and styrene (57 μL, 0.5 mmol) in pentane (3 mL) at −10°C. The resulting mixture was stirred for 24 h at −10°C before all volatile materials were evaporated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc, 20:1) to give the title compound as a colorless amorphous solid (24.5 mg, 87%, 98% *ee*). The optical purity was determined by HPLC (Chiralpak IB, ∅ 4.6 mm, 2% 2-propanol in *n*-heptane, 1 mL/min, 20 min, UV 225 nm): t_R 7.65 min (major) and t_R 8.48 min (minor); $[\alpha]_D^{20}$ = +4.6 (c = 1.6, $CHCl_3$) [ref.: $[\alpha]_D^{20}$ = +5.1 (c = 1, $CHCl_3$)];[52]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 – 7.04 (m, 3H), 6.96 – 6.91 (m, 2H), 6.80 – 6.74 (m, 2H), 6.69 – 6.63 (m, 2H), 3.72 (s, 3H), 3.66 (s, 3H), 3.07 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.12 (dd, *J* = 9.4, 4.8 Hz, 1H), 1.82 ppm (dd, *J* = 7.2, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 158.6, 136.6, 133.0, 128.2, 127.8, 126.9, 126.4, 113.3, 55.2, 52.8, 36.8, 33.3, 20.9 ppm. The recorded data are consistent with those reported in the literature.[52]

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

Acknowledgements

Generous financial support by the Fonds der Chemischen Industrie (Kekulé stipend to F. P. C.) and the Max-Planck-Gesellschaft is gratefully acknowledged. We thank Ms. V. A. Tran, Dr. C. Poidevin, Dr. D. Yepes and Dr. M. van Gastel for advice concerning the computational studies, Ms. C. Wirtz for NMR assistance, Mr. J. Rust. Dr. R. Goddard and Prof. C. W. Lehmann for solving the X-ray structures, and the analytical service groups of our Institute for excellent support.

Author Contribution Statement

[+] These authors contributed equally

M. B., L. R. C., F. P. C., S. S. performed the experiments, analyzed and compiled the data, *L. E. L.* optimized the conditions for the formation of **1** and performed the computational studies, *A. F.* conceived the project and wrote the manuscript.

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10.1002/hlca.202100042

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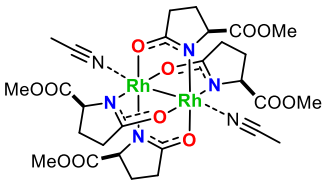
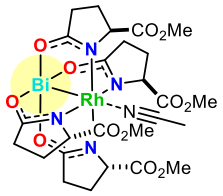
$[Rh_2(5S\text{-MEPY})_4]\cdot 2MeCN$



heteroleptic ligand sphere @ Rh

$[BiRh(5S\text{-MEPY})_4]\cdot MeCN$



"self-sorted" homoleptic ligand spheres @ Bi and Rh