

Combined Experimental and Computational Studies of Heterobimetallic Bi–Rh Paddlewheel Carboxylates as Catalysts for Metal Carbenoid Transformations

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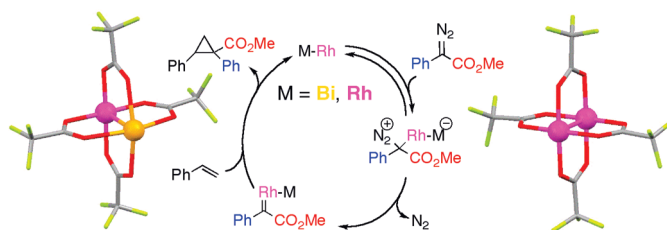
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The catalytic activity of heterobimetallic Bi–Rh paddlewheel carboxylate complexes has been evaluated for the first time in the context of metal carbenoid chemistry. The Bi–Rh carboxylate complexes were found to effectively catalyze both cyclopropanation reactions and C–H insertions as well as reactions involving ylide intermediates with similar selectivity profiles to analogous dirhodium complexes. The heterometallic complex $\text{BiRh}(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ was found to be approximately 1600 times less reactive than its homometallic analogue $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ toward the decomposition of methyl phenyldiazoacetate. The observed difference in reactivity is in good agreement with a computational model system where axial coordination to the second rhodium active site is considered for the dirhodium catalyst.

Introduction

Catalysis by dirhodium paddlewheel complexes has been an area of immense interest for the past three decades. These

entities are structurally characterized by a bimetallic core with a Rh–Rh single bond, bridged by four μ_2 -carboxylate, carboxamido, or phosphonate ligands. A large number of complexes have been synthesized in which the ligand structure has been diversified to a great extent. Many of these have been studied and used in catalysis.¹ The dirhodium catalysts have been remarkably successful in a range of transformations, particularly in metal nitrenoid and carbenoid chemistry^{1d} involving aziridinations, cyclopropanation/propene reactions,^{1h,o,2} C–H insertions,^{1d,3} and ylide transformations,^{1i,k,n,4} but also

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in Lewis acid-catalyzed processes.^{1i,5} The ability of such complexes to effectively catalyze a variety of reactions at low catalyst loadings has demonstrated their synthetic potential, particularly in the context of *chiral* catalysis where numerous examples of applications in syntheses of natural products and biologically relevant molecules have been reported.^{1d,3e,6} The ease at which simple modifications of the bridging groups on the catalyst brings about dramatic changes in reactivity makes these dirhodium complexes preferable to mononuclear copper or palladium counterparts.

The development of dirhodium paddlewheel catalysts has primarily focused on modifications of the electronic and/or steric properties of the ligands. Within chiral catalysis, the most successful classes are the *N*-arylsulfonylprolinates,^{1b,m,7} phthalimide protected amino acid derivatives,^{1m,8} carboxamides,^{1i,k,m,9} ortho-metalated arylphosphines,^{1m,10} and binaphthoyl phosphate complexes (Figure 1).^{1m,n,11} More recently, alternative modifications to the dirhodium scaffold have been explored in catalysis, such as mixed valence dirhodium(II,III) species,¹² complexes with axially coordinated N-heterocyclic carbenes (NHCs),¹³ and also mixed ligand (heteroleptic) systems.¹⁴ Computational and kinetic studies of dirhodium carboxylate-catalyzed carbenoid reactions have indicated that carbene binding occurs only at one of the two rhodium active sites at a time.¹⁵ This is supported by the observation that dirhodium complexes immobilized via coordination of

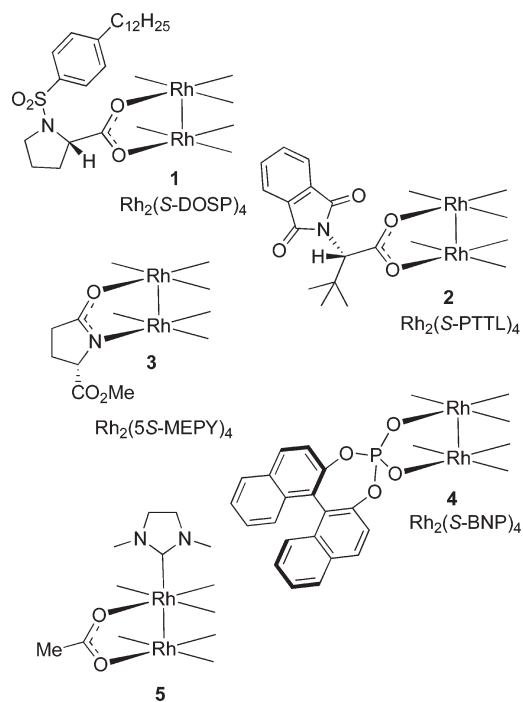


FIGURE 1. Various dirhodium catalysts.

polymer-bound pyridine to one active site still display selectivity and reactivity profiles comparable to those in homogeneous reactions.¹⁶ Dikarev and co-workers reported the syntheses and structural characterization of a new family of paddlewheel carboxylates in which one of the rhodium atoms has been replaced by bismuth—a significantly less expensive metal than rhodium.¹⁷ A preparative solid-state technique was developed, in which the ability of bismuth(II) trifluoroacetate to act as a metalloligand toward transition metal fragments was utilized to prepare $\text{BiRh}(\text{O}_2\text{CCF}_3)_4$ **II**, a heterobimetallic, homoleptic carboxylate complex.^{17b,c} Further developments of the technique were utilized in one-step syntheses of mixed-ligand carboxylates *cis*- $\text{BiRh}(\text{O}_2\text{CCF}_3)_2(\text{O}_2\text{C}^t\text{Bu})_2$ **I**, $\text{BiRh}(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ **III**, and the chiral complex $\text{BiRh}(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{C}(S-(+)-\text{Bu}))$ (Figure 2). The complexes have typical paddlewheel structural features, in which the bimetallic core has a bismuth–rhodium single bond and acts as an anchor for four μ_2 -ligands. The structures were shown to remain intact in solution and displayed Lewis acidity toward basic donors at the transition metal end only.^{17b,c}

The modification introduced in Bi–Rh systems offers the possibility of tuning the reactivity of the bimetallic core itself.^{17c} This is a novel approach to reactivity control in such systems. More importantly, the availability of the heterobimetallic carboxylates suggests a unique opportunity to probe the role of the effective dirhodium framework through comparative studies of the catalytic performance

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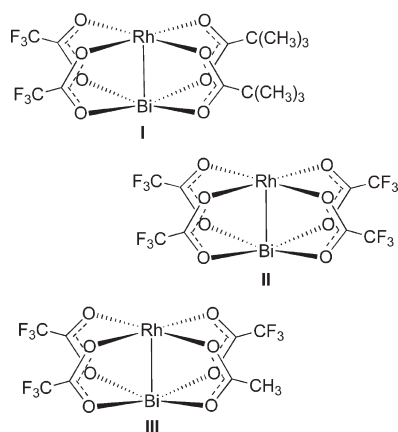


FIGURE 2. Bi–Rh carboxylate complexes.¹⁷

of the two systems. Such an investigation would reveal whether the dirhodium framework is a necessity to achieve efficient, catalytic reactions as well as the high levels of selectivity that are often observed. In this paper, we report a combined experimental and computational study to explore catalysis by heterobimetallic Bi–Rh carboxylates in the context of metal carbenoid chemistry. We will demonstrate that such species can act as catalysts for carbenoid-mediated transformations and, furthermore, show how they compare with analogous dirhodium catalysts in terms of reactivity and selectivity. The computational studies provide an evaluation of how the Bi–Rh core affects the mechanism in terms of catalytic activity and reactivity.

Results and Discussion

Catalytic Activity: Cyclopropanation Reactions. Catalytic activities of Bi–Rh complexes **I** and **II** were evaluated in the cyclopropanation reaction between styrene and methyl phenyldiazoacetate (**6a**, Table 1). The optimal conditions were determined to be 2 mol % catalyst under reflux when using dichloromethane as solvent. Full conversion was observed and the cyclopropane was formed in excellent yield (94%) and high diastereoselectivity (>95% de) with complex **II** as catalyst (Table 1, entry 2). $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ performed similarly in this reaction with 96% yield and >95% de (entry 3). Complex **I** gave somewhat lower yield (74%), but still very high diastereoselectivity (entry 1).

The effect of carbenoid structure was investigated with complex **I**. The acceptor carbenoid derived from ethyl diazoacetate (entry 4) produced the corresponding cyclopropane in 47% yield as a mixture of diastereomers (21% de). The diastereoselectivity is similar to previously reported values for this reaction when catalyzed by dirhodium catalysts.¹⁸ The acceptor–acceptor carbenoid derived from methyl diazomalonate was presumably not formed under the reaction conditions, since starting materials were recovered, even after 2 days at 40 °C (entry 5). Overall, the best result was obtained with methyl phenyldiazoacetate (**6a**) as carbenoid precursor and this diazo compound was therefore used for further studies. The success of the reactions shows that Bi–Rh complexes are capable of forming the carbenoid

TABLE 1. Scope of Carbenoid Structure in Cyclopropanation of Styrene

entry	compd	R =	R' =	catalyst	de (%) ^a	yield (%) ^b
1	a	Ph–	–CH ₃	I	94	74
2	a	Ph–	–CH ₃	II	> 95	94
3	a	Ph–	–CH ₃	$\text{Rh}_2(\text{TFA})_4$	> 95	96
4	b	H–	–CH ₂ –CH ₃	I	21	47
5	c	MeO ₂ C–	–CH ₃	I	N/A	N/R

^aMeasured by ¹H NMR of crude reaction mixture. ^bIsolated yields.

TABLE 2. Reaction between **6a** and Furan

entry	catalyst	product ratio (8:9) ^a	yield (%) ^b
1	I	70:30	80
2	II	47:53	96
3	$\text{Rh}_2(\text{TFA})_4$	44:56	95

^aMeasured by ¹H NMR of crude reaction mixture. ^bOverall isolated yields.

species; however, it was qualitatively observed that the Bi–Rh-catalyzed reactions appeared to proceed slower than those catalyzed by the dirhodium counterpart. The lack of other observable byproducts indicates that the intermediate displays similar selectivity to dirhodium carbenoids.

The decomposition of methyl phenyldiazoacetate (**6a**) in neat furan catalyzed by dirhodium catalysts affords products of monocyclopropanation (**8**) as well as an alkylation product (**9**) where the furan ring has been opened.¹⁹ The latter is believed to be formed via a mechanism in which the stabilization of charge build-up by the furan ring interrupts the cyclopropanation and forms a zwitterionic intermediate capable of undergoing the furan-unraveling reaction competitively.^{19b} By increasing the electrophilic character of the catalyst, more of the ring-opened product is normally observed.^{19a} When the reaction was catalyzed by the relatively electron-rich bismuth–rhodium complex **I**, the two products **8** and **9** were formed in a 70:30 ratio in 80% yield (Table 2, entry 1). The more electron-deficient complex **II** afforded an approximately 47:53 ratio of the two products in an excellent 96% overall yield (entry 2). $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ performed essentially identical with the latter (entry 3). For these reactions, bismuth–rhodium carbenoids again appear to display similar chemoselectivities to their dirhodium counterparts.

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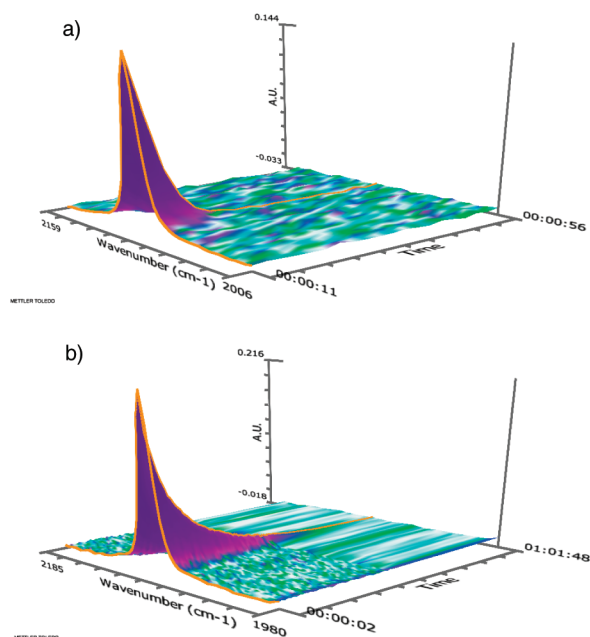


FIGURE 3. Disappearance of N=N stretch frequency of diazo compound as function of time for (a) $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ (0.2 mol %, over 45 s) and (b) complex **III** (2 mol %, over 62 min). The catalyst was injected at $t_0 = 10$ s.

Reactivity. To investigate the difference in reactivity between the two catalyst systems toward decomposition of phenyldiazoacetate, cyclopropanation reactions between methyl phenyldiazoacetate and styrene, catalyzed by complex **III** and $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$, respectively, were conducted with all the reagents present in the flask. After injection of the catalyst into a solution of the reagents in dichloromethane, the reaction progress was monitored by ReactIR, following the disappearance of the diazo N=N stretch frequency at $\sim 2100\text{ cm}^{-1}$. The reaction progress is shown in Figure 3a for $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ and in Figure 3b for **III**. The reaction catalyzed by $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ went to completion after ~ 16 s at 0.2 mol % catalyst loading (~ 500 turnovers). The reaction catalyzed by 2 mol % **III** went to completion after about 45 min (~ 50 turnovers). The average turnover frequencies for the two catalysts are $\text{TOF}_{\text{RhRh}} \approx 31\text{ s}^{-1}$ and $\text{TOF}_{\text{BiRh}} \approx 0.019\text{ s}^{-1}$, respectively. The dirhodium complex is therefore about ~ 1600 times more reactive than the Bi–Rh counterpart toward diazo decomposition. Even though the rate of the Bi–Rh-catalyzed reaction is significantly slower than that catalyzed by dirhodium, the former can still be a high-yielding process, because under standard reaction conditions the addition of the diazo compound is the rate-limiting process.

Electronic Effects. To probe the properties of dirhodium and bismuth–rhodium carbenoids, competition studies were carried out in order to quantify the chemoselectivity profiles. The cyclopropanation of styrene vs. para-substituted styrenes gives a measure of the level of benzylic charge build-up in the cyclopropanation transition state via the Hammett reaction constant (ρ) obtained for a series of para substituents (Scheme 1).²⁰ Good correlations were found when $\log(k_{\text{R}}/k_{\text{H}})$ was plotted against σ^+ substituent constants

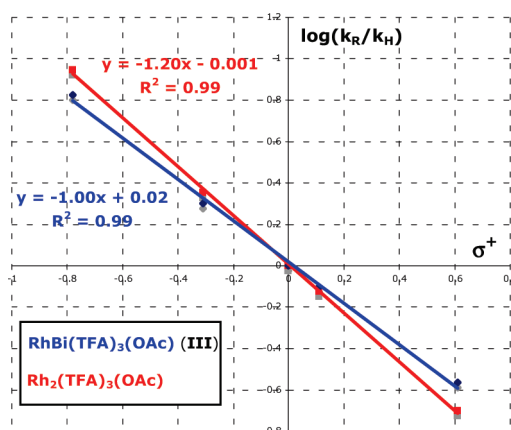
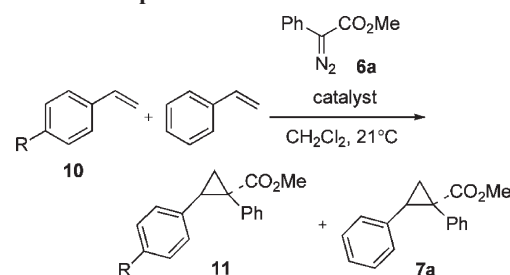
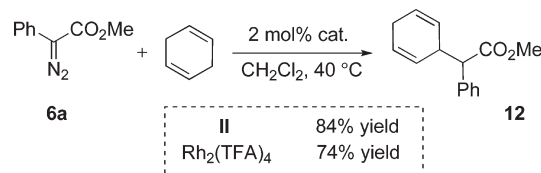


FIGURE 4. Hammett plot of cyclopropanation catalyzed by $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ and **III**.

SCHEME 1. Competition Studies



SCHEME 2. C–H Activation of 1,4-Cyclohexadiene



obtained from the literature²¹ for both catalyst systems (Figure 4). $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ appears to give a slightly more chemoselective carbenoid ($\rho = -1.20 \pm 0.02$) than **III** ($\rho = -1.00 \pm 0.03$).

C–H Insertion. 1,4-Cyclohexadiene is a highly activated system for C–H insertion due to hyperconjugative interactions between the methylene group and the two pendant double bonds.^{6d,22} The reaction proceeds cleanly with both $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and bismuth–rhodium complex **II** under the standard reaction conditions (Scheme 2). An 84% yield of **12** was isolated when the reaction was catalyzed by complex **II**, comparable to its dirhodium analogue (74% yield). This reaction demonstrates that the heterobimetallic complexes are capable of effectively catalyzing C–H insertion processes.

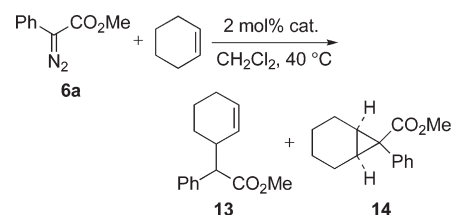
Due to the effectiveness of complex **II** in catalyzing C–H insertions, the catalyst was also tested with a substrate where C–H insertion occurs in competition with cyclopropanation chemistry. One such substrate is cyclohexene, where both reaction channels are important with most dirhodium

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TABLE 3. C–H Insertion vs. Cyclopropanation



entry	catalyst	product ratio (13:14) ^a	yield (%) ^b
1	II	79:21	52
2	Rh ₂ (TFA) ₄	84:16	57
3	Rh ₂ (OAc) ₄	75:25	50 ^c

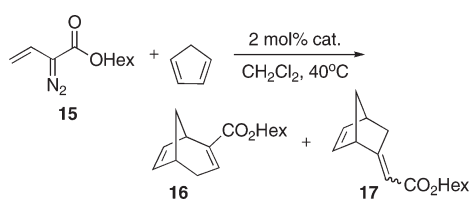
^aMeasured by ¹H NMR of crude reaction mixture. ^bOverall isolated yield. ^cFrom ref 22.

catalyst systems (Table 3).²² The decomposition of **6a** in the presence of cyclohexene and 2 mol % of complex **II** afforded a 79:21 mixture of C–H insertion product **13** versus cyclopropane **14** in an overall 52% yield. This is almost identical with the results obtained with Rh₂(O₂CCF₃)₄, which gave a 57% overall yield. For comparison, Rh₂(O₂CCH₃)₄ has been reported to give a 75:25 ratio of the two products in an overall 50% yield.²² These results further support that the selectivity of the Bi–Rh carbenoid is very similar to that of analogous dirhodium catalysts.

Vinylogous Reactivity. Transient metal vinylcarbenes can display electrophilic reactivity at the vinylogous position in addition to at the carbenoid carbon.²³ A test reaction for these competing pathways is the reaction between unsubstituted vinyl diazoacetate **15** and cyclopentadiene (Table 4) where product **16** is derived from a tandem cyclopropanation–Cope rearrangement (carbenoid reactivity) and **17** from vinylogous reactivity.^{23b,e} This mode of reactivity has been observed to increase with the electron-withdrawing capability of the catalyst, solvent polarity, and size of the ester group.^{23b} The reaction of **15** with cyclopentadiene catalyzed by rhodium–bismuth complex **III** gave a 50:50 ratio of the products in overall good yield (80%). The analogous reaction with Rh₂(O₂CCF₃)₃(O₂CCH₃) gave a 26:74 ratio of **16** to **17** in overall 82% yield. For comparison, Rh₂(O₂CCH₃)₄ gave a 63:37 ratio in 79% yield. These results indicate that the rhodium–bismuth carbenoid behaves as a slightly more electron-rich system since it displays less vinylogous reactivity. While the overall difference is not large, as evident from the aforementioned Hammet studies, the occurrence of vinylogous reactivity is particularly sensitive to the structure of the vinylcarbenoid complex.^{23b}

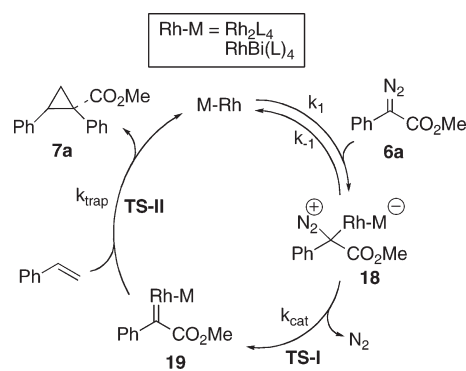
DFT Calculated Reaction Pathways. Reaction pathways for carbenoid formation and trapping were studied computationally for model systems. The cyclopropanation reaction of styrene with methyl phenyldiazoacetate (**6a**) with both dirhodium and Bi–Rh model catalysts was investigated in

TABLE 4. Vinylogous vs. Carbenoid Reactivity



entry	catalyst	product ratio (16:17) ^a	Z/E-ratio (17) ^a	yield (%) ^b
1	Rh ₂ (OAc) ₄	63:37	2.7:1	79
2	Rh ₂ (TFA) ₃ (OAc)	26:74	1.3:1	82
3	III	50:50	1.5:1	80

^aMeasured by ¹H NMR of crude reaction mixture. ^bOverall isolated yield.

SCHEME 3. Mechanism for Catalytic Cyclopropanation by Dirhodium Complexes^{1k,15,25}

density functional calculations. Computational details can be found in the Computational Methods section. The calculated reaction pathway involving phenyldiazoacetate and styrene catalyzed by Rh₂(O₂CH)₄ was recently reported.²⁴

The currently accepted mechanism for reactions of diazo compounds with dirhodium complexes was considered.^{1k,15,25} This involves complexation of the diazoacetate to the bimetallic catalyst, rate limiting nitrogen extrusion to form the intermediate metal carbenoid complex, and finally trapping by an alkene to form a cyclopropane product (Scheme 3).^{1k,15,25} Alternative mechanisms have been suggested in the literature, involving carboxylate ligand dissociation from the dirhodium core, but were not considered here since these are not yet widely accepted.^{14,26}

Figure 5 shows the reaction pathway calculated for the cyclopropanation reaction of methyl phenyldiazoacetate with styrene catalyzed by both dirhodium formate²⁴ (red pathway) and bismuth–rhodium formate (blue pathway). The former path was recently reported and is included here for comparison.²⁴ The calculated structures for the Bi–Rh pathway are indicated in the figure and are analogous to the dirhodium structures. Coordination of the diazo compound to the catalyst to form **18** is an exothermic process in both cases, but less so for the Bi–Rh system (–1.8 kcal/mol

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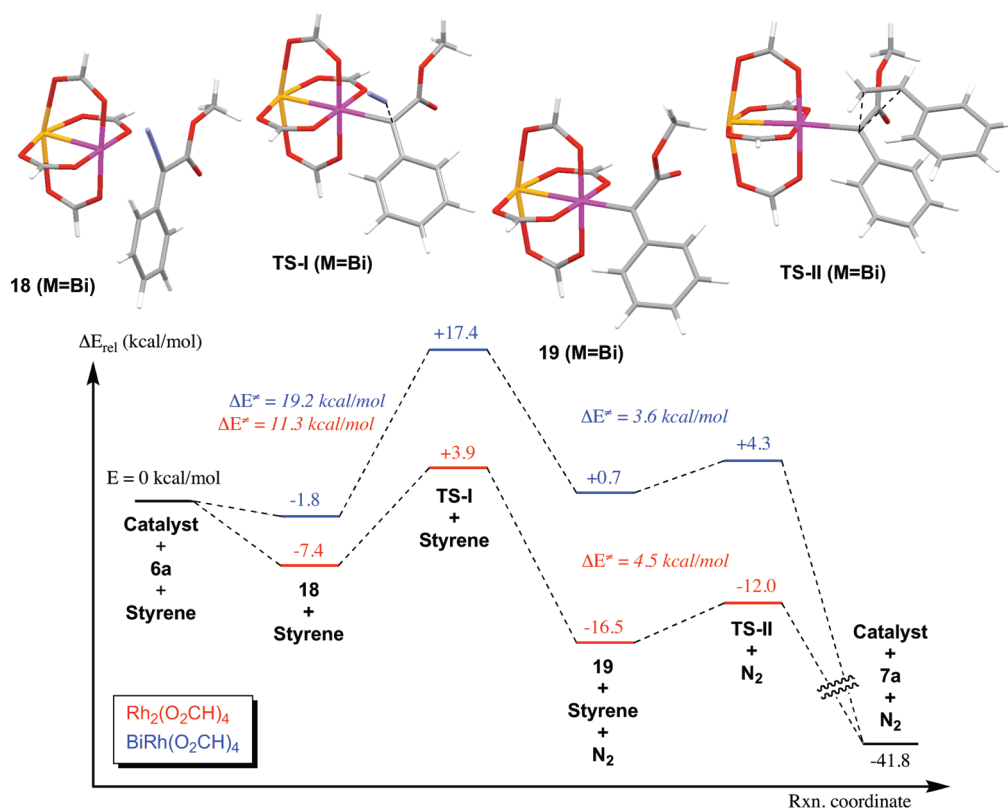


FIGURE 5. Potential energy surfaces (relative to free reactants) at the B3LYP/6-311G(2d,2p)[Rh-RSC + 4f][Bi-RLC]//B3LYP/6-31G*[Rh-RSC + 4f][Bi-RLC] level for dirhodium²⁴ and Bi–Rh models.

vs. -7.4 kcal/mol for dirhodium). The loss of nitrogen from the Bi–Rh complex via **TS-I** has a potential energy barrier of 19.2 kcal/mol, considerably higher than that for dirhodium (11.3 kcal/mol). As shown before, the Bi–Rh-catalyzed reactions were much slower (~ 1600 times) than the corresponding dirhodium catalyzed reactions. However, this difference in reaction rate would correspond to a smaller difference in barrier heights of the rate-limiting step than the computed 7.9 kcal/mol difference. One reason why the difference in the barriers is overestimated could be that the formate model may not be totally appropriate for the Bi–Rh system. Other factors discussed below may also change the difference in barrier heights. One striking difference between the two systems is that carbenoid formation is endothermic for Bi–Rh ($+2.5$ kcal/mol), but quite exothermic for dirhodium (-9.1 kcal/mol). Relative to the reactants, the Bi–Rh carbenoid complex **19** ($M = \text{Bi}$) is less stable by 0.7 kcal/mol, whereas the dirhodium carbenoid **19** ($M = \text{Rh}$) is stabilized by -16.5 kcal/mol. Despite this difference in thermodynamic stability, the kinetic stabilities of the two are not very different (3.6 kcal/mol barrier for cyclopropanation via **TS-II** for the Bi–Rh system vs. 4.5 kcal/mol for dirhodium). The difference in kinetic stabilities is presumably due to a reduced π -backbonding component in the Bi–Rh carbenoid system because of the relatively long Rh–C bond length (2.120 Å vs. 2.010 Å in dirhodium).²⁷ The presence of a significant carbenoid trapping barrier for the Bi–Rh carbenoid is a consequence of the donor group on the carbenoid

complex.²⁴ The calculations are consistent with the Hammett study, which showed only minor differences in selectivity between the two catalyst systems.

In light of the large calculated difference in potential energy barriers for the rate-determining steps of the two catalyst systems, which is in poor agreement with our experimental findings, it is likely that other effects may be involved that are not reflected in the described computational models. One such effect is the possibility that the dirhodium catalysts have an axially coordinated ligand on the second rhodium during the catalytic cycle.²⁸ No studies have been reported, to our knowledge, that explicitly describe the potential influence of such ligands on reactions at the other metal active site. Pirrung and co-workers could not demonstrate any evidence for this pathway from kinetic data, but only a few systems were investigated.^{15b} Since relatively electron-deficient catalysts were used in the present study, it is conceivable that the catalytic cycle may proceed with an axial ligand at the other rhodium center. This ligand may be solvent, adventitious water, or other coordinating groups in reactants or products (π -bonds, carbonyl groups).^{28d} For instance, carbonyl groups in the product, which is formed rapidly, could be a major contributor to this effect.²⁹ Bi–Rh complexes have been shown to exhibit Lewis acidity toward basic donor groups at the Rh end only,^{17c} hence, the

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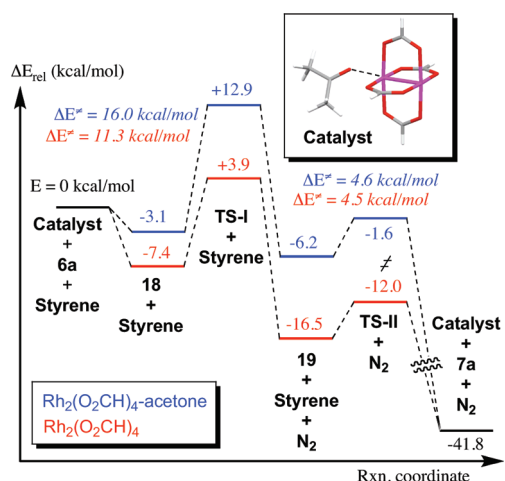


FIGURE 6. Influence of axial coordination on reaction pathway compared to the coordination-free system.²⁴ Potential energy surfaces (relative to free reactants) at the B3LYP/6-311G(2d,2p)-[Rh-RSC + 4f]/B3LYP/6-31G*[Rh-RSC + 4f] level.

effect is absent in this system. To study the effects of this phenomenon for dirhodium, the reaction pathway was recalculated for the dirhodium tetraformate system with an acetone molecule coordinated to the second rhodium as a model system. A comparison of the two pathways is given in Figure 6, with the catalyst structure indicated. For this catalyst system, the coordination of the diazo compound is less exothermic (−3.1 kcal/mol vs. −7.4 kcal/mol without axial ligand). A very large effect is seen in the nitrogen extrusion barrier (18 → TS-I), which is now increased to 16.0 kcal/mol, 4.7 kcal/mol higher than previously calculated. The now much smaller difference in this barrier between dirhodium and Bi-Rh systems (3.2 kcal/mol) is more consistent with the observed decomposition rate difference. An estimate of the difference in activation energies for the two catalysts can be made from the kinetic data reported above (for $\text{Rh}_2(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ and complex III) by applying the Arrhenius equation. A reactivity difference of ~1600 corresponds to roughly 4 kcal/mol difference in activation barriers—in good agreement with the calculations considering that the computational model affords a number of approximations, and considering the error bars of density functional calculations.

In the coordinated dirhodium system, the carbenoid complex formation is now less exothermic, only −3.1 kcal/mol. Another important observation is that the potential energy barrier for the product-determining step (19 → TS-II) is virtually unchanged by the presence of the coordinating ligand (4.6 kcal/mol vs. 4.5 kcal/mol). This suggests that the selectivity of such reactions is not much modified by the axial ligand, in agreement with previously reported studies with immobilized dirhodium complexes.¹⁶

The significance of the electron-withdrawing nature of the catalyst ligands was also investigated. Currently, only systems with strongly electron-withdrawing ligands are available for the Bi-Rh core (trifluoroacetate), and have therefore been used in the experimental part of this study.^{17b,c} The reaction pathway was calculated by using $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and $\text{BiRh}(\text{O}_2\text{CCF}_3)_4$ as catalysts (Figure 7). The calculations were conducted without reinvestigating the

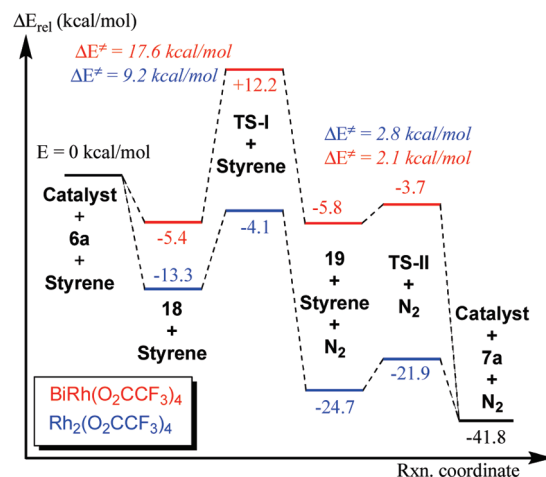


FIGURE 7. Potential energy surfaces (relative to free reactants) at the B3LYP/6-311G(2d,2p)[Rh-RSC + 4f][Bi-RhC]/B3LYP/6-31G*[Rh-RSC + 4f][Bi-RhC] level for trifluoroacetate bridged complexes.

role of a coordinating ligand on dirhodium for reasons of computational cost. The reaction pathways remain qualitatively the same as before, but significant potential energy differences can be observed. Coordination of the diazo compound to the catalyst complexes has become much more exothermic compared to the formate model systems (−5.4 kcal/mol for Bi-Rh and −13.3 kcal/mol for dirhodium). Since the introduction of the trifluoroacetate ligands rendered the diazo coordination process much more exothermic, it is likely that, at least very electron-deficient dirhodium complexes such as $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ undergo the catalytic cycle with axially coordinating groups at the second rhodium center, as discussed above. For $\text{BiRh}(\text{O}_2\text{CCF}_3)_4$, the nitrogen extrusion barrier is only 1.6 kcal/mol lower than that for the formate system (17.6 kcal/mol vs. the previously calculated 19.2 kcal/mol). This barrier decreased by 2.1 kcal/mol for the dirhodium system by introducing the trifluoroacetate ligands, a similar reduction to the former. The difference between rate-limiting barriers for the two systems remains about the same. The thermodynamic stabilities of the carbenoid complexes have changed significantly. For Bi-Rh, the carbenoid formation is now slightly exothermic (−0.4 kcal/mol), whereas it is much more exothermic for dirhodium (−11.4 kcal/mol). In accordance with more electrophilic systems, the cyclopropanation barriers are somewhat lower compared to those calculated in the former models, but the trend remains the same (Bi-Rh has a slightly lower barrier in the product-determining step).

Charge Distribution. Figure 8 shows the calculated charges on the two metal atoms in dirhodium formate (Rh^1 = blue, Rh^2 = red) and Bi-Rh formate (Rh^3 = violet, Bi = orange) along the reaction pathway for the cyclopropanation reaction. For the rhodium formate-catalyzed pathway, coordination of the diazoacetate leads to charge reduction for Rh^2 (red line) by about −0.2 units. This is in accordance with observations by Nakamura and co-workers in a computational study of diazomethane and methyl diazoacetate.^{15a} The drop in charge signifies reduction of Rh^2 and shows that it can act as an electron sink during the catalytic cycle.^{15a} For Bi-Rh formate, both Rh and Bi become only partially reduced during the coordination event. However,

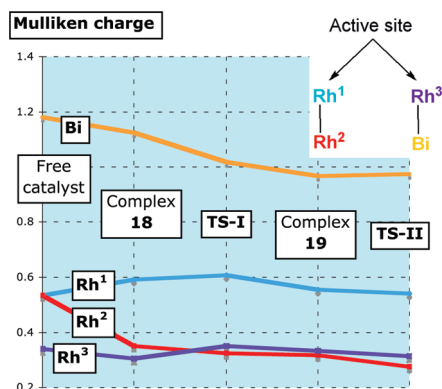


FIGURE 8. Charge distribution on heavy atoms as a function of reaction coordinate for dirhodium and Bi–Rh formate model systems.

upon formation of the carbenoid complex a reduction of about -0.2 charge units occurs for Bi, very similar to that of Rh^2 in the dirhodium system. This demonstrates that Bi can also act as a redox pool, facilitating the catalytic cycle. Further evidence for this comes from the elongation of the Rh –Bi bond during the reaction from 2.582 \AA to 2.649 \AA .

Conclusions

In this paper, we have demonstrated that heterobimetallic bismuth–rhodium paddlewheel carboxylate complexes can act as effective catalysts for metal carbenoid transformations at low catalyst loadings. The catalysts have been shown to effectively mediate cyclopropanation reactions and C–H insertion processes as well as reactions involving zwitterionic intermediates with donor/acceptor diazo compounds. The heterobimetallic complexes display similar chemo- and diastereoselectivities as their dirhodium analogues.

$\text{BiRh}(\text{O}_2\text{CCF}_3)_3(\text{O}_2\text{CCH}_3)$ decomposes methyl phenyldiazoacetate about ~ 1600 times slower than the corresponding dirhodium complex in the cyclopropanation reaction with styrene. DFT calculations of the reaction pathways with model systems are consistent with the observed reactivity difference only if axial coordination to the second rhodium atom in the dirhodium catalyst model is taken into account. Furthermore, the calculations support the observation that the selectivity profile of Bi–Rh donor/acceptor carbenoids is similar to that of analogous dirhodium carbenoids. A charge distribution analysis shows that the rhodium–bismuth core can act as a bifunctional electron pool, facilitating the

catalytic process similar to what has previously been described for dirhodium species.

Computational Methods

All calculations were performed with the Gaussian '03 software package,³⁰ using Density Functional Theory (the three-parameter hybrid functional B3LYP³¹) to locate stationary points on the potential energy surface. The structures were geometry optimized with a basis set consisting of the 1997 Stuttgart relativistic small-core ECP and corresponding basis set [Stuttgart RSC 1997 ECP]³² for Rh, augmented with a 4f-function ($\zeta_f(\text{Rh}) = 1.350$),²⁴ the 1997 Stuttgart relativistic large-core ECP and basis set [Stuttgart RLC 1997 ECP] for Bi,³³ and the split valence basis set 6-31G* for all other atoms (C, H, N, O, and F). This composite basis set is referred to as 6-31G*[Rh-RSC + 4f][Bi-RLC]. In this work, the discussion is based on single-point potential energies calculated at the B3LYP/6-311G(2d,2p)[Rh-RSC + 4f][Bi-RLC]/B3LYP/6-31G*[Rh-RSC + 4f][Bi-RLC] level. Stationary points were characterized by normal coordinate analysis at the 6-31G*[Rh-RSC + 4f][Bi-RLC] level of theory.³⁴ Transition states were confirmed to have a single imaginary vibrational mode whereas equilibrium structures were confirmed to have no imaginary vibrational modes. Transition states were further characterized by intrinsic reaction coordinate (IRC) analysis using default parameters with subsequent geometry optimization to confirm that the stationary points were smoothly connected to each other. Basis set definitions and pseudopotential parameters were obtained from the EMSL basis set exchange library.³⁵ Calculated structures have been visualized with use of Mercury.³⁶

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Supporting Information Available: Complete ref 30, experimental details and characterization data for all new compounds, and Cartesian coordinates, structures, and a summary of calculated parameters for all new structures reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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