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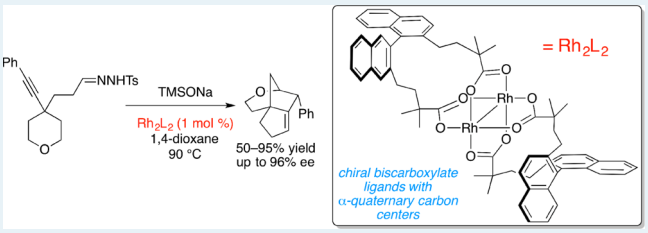
# A Binaphthyl-Based Scaffold for a Chiral Dirhodium(II) Biscarboxylate Ligand with α-Quaternary Carbon Centers

Po-An Chen,[‡] Krit Setthakarn,[‡] and Jeremy A. May*

Department of Chemistry, University of Houston, 3585 Cullen Blvd, Fleming Building Room 112, Houston, Texas 77204-5003, United States

Supporting Information

**ABSTRACT:** A chiral dirhodium(II) paddlewheel complex has been synthesized from biscarboxylate ligands derived from BINOL, and the resulting complex has been used in enantioselective carbene/alkyne cascade reactions. The ligand design was guided by requirements of α,α-dimethyl substituted carboxylates and bidentate ligands to ensure high levels of catalytic activity. Previously disclosed chiral complexes lack these features, resulting in low product yields. The design successfully replicated or exceeded the yields of the unusually effective achiral catalyst for the cascade reaction, $Rh_2(esp)_2$, which often shows unique reactivity. Promising enantioselectivity was observed for aldehyde-derived hydrazone substrates (29−96% ee), showing that the new scaffold has significant potential.




**KEYWORDS:** *enantioselective catalysis, rhodium(II) carboxylates, carbenes, cascade reaction, BINOL derivatives, chiral ligands*

Dirhodium(II) paddlewheel complexes[1] have proven to be highly effective at controlling carbene reactions, including cyclopropanations,[2] dipole formations,[3] X−H and C−H bond insertions,[4] and cascade reactions.[5] Motifs that include carboxylate,[6] amidate,[7] and phosphate-based[8] ligands have been synthesized and tested, but complexes with two bidentate ligands are still somewhat rare (see Figure 1).[9] This is largely due to the specific geometry required in the carboxylate binding, where precise right angles are needed.[9a] Chiral biscarboxylate ligands are even more rare and are often challenging to synthesize, with complexes **5**−**9**[10] comprising the examples of which we are aware.

Recently, we found that carbene/alkyne cascade reactions, which rapidly and efficiently construct intricate bridged polyclic molecules like **13** and **15**, are most effectively catalyzed by carboxylate ligands with α-quaternary centers, with the bidentate esp ligand usually performing the best (Figure 2A).[11] Two factors explain its ability to achieve reasonable turnover numbers (>150) for this reaction cascade: first, larger ligands protect the Rh-carbene intermediates (I or II) to suppress dimer formation and thus increase product yield. Second, the bidentate ligand is less prone to ligand exchange or loss, reducing open coordination sites on the metal.[9c] While $Rh_2(OPiv)_4$, which may be obtained at a lower cost, was comparable to $Rh_2(esp)_2$ (**2a**) for many transformations using hydrazones (see **14a**, Figure 2B), it was inconsistent, and $Rh_2(esp)_2$ was often better for difficult substrates like the ketone **14b**.

Previously described chiral Rh(II) catalysts bearing either monodentate or bidentate ligands did not provide suitable enantioselectivity in either the diazoester (≤20% ee for **13**, Figure 3A) or hydrazone reactions (<75% ee for **15a**, Figure 3B).[12] In the case of the diazoesters they also failed to effectively catalyze the formation of product (<40% yield **13**, <80 turnovers). For the hydrazone **14a**, a useful yield of bicyclic product **15a** was obtained at 90 °C if a high catalyst loading (5 mol %) was used, but lowering the reaction temperature to attempt to increase the enantioselectivity quickly eroded the product yield. The beneficial α-quaternary carbons of the carboxylates in $Rh_2(esp)_2$ and $Rh_2(OPiv)_4$ were not present in any of the chiral catalysts. The only readily available chiral catalyst with an α-tetrasubstituted carbon on the ligand, **7** (Figure 1), did not promote the reaction. Effective chiral versions of the esp ligand for enantioselective catalysis have not been identified, though Du Bois has reported interesting variants (see **5** and **6**).[13]

Unfortunately, converting the α-quaternary carbon center of the pivaloate or esp ligand to a differentially substituted chiral center capable of catalytic stereocontrol presents a significant synthetic problem,[13] especially when a desirable strategy would allow for the rapid synthesis of many ligand variants to explore stereoelectronic and steric factors that control reactivity and selectivity. Consequently, a new type of dirhodium complex incorporating axially chiral bisnaphthyl dicarboxylate ligands with α-quaternary centers (**16** and **17**, Figure 4) was designed and targeted for synthesis.[14] Modeling[15] suggested that either **16** (three carbons in the carboxylate chain) or **17** (four carbons in the carboxylate chain) would fit a dirhodium core and would bind in such a way that the naphthyl rings would project over the open coordination sites on the Rh to create a chiral pocket.

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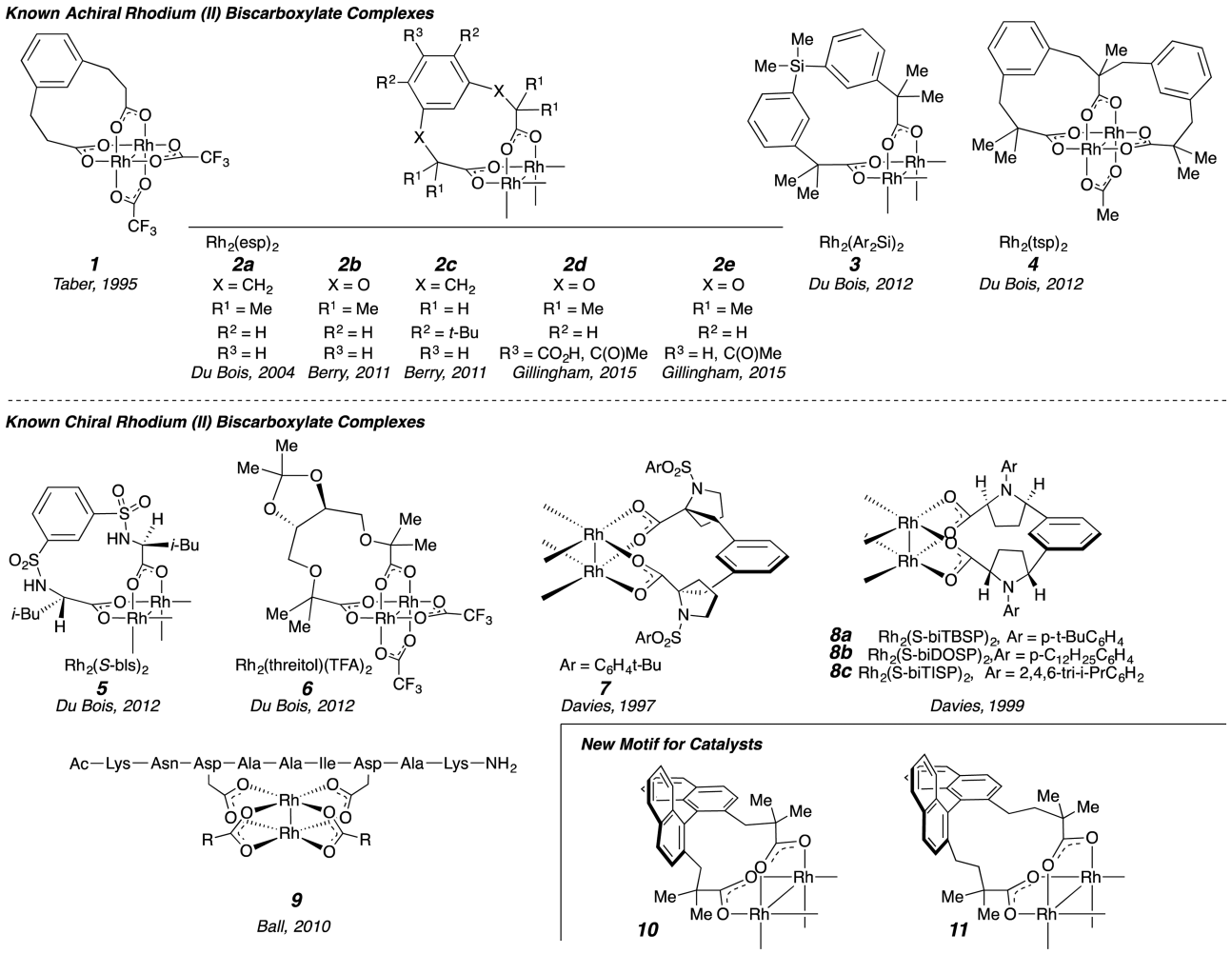


**Figure 1.** Rhodium(II) complexes with biscarboxylate ligands. Undefined ligands are identical to the one illustrated to provide a symmetric complex, with the exception of complexes **2d** and **2e**, which have two different $R^3$ groups.

The shorter linking chain in **16** appeared to create a more structured chiral environment, and so its synthesis was approached first.

A model system for **16**, biphenyl KC3P (**23**),[16] was synthesized initially, since 2−2′-biphenol (**18**) is significantly less expensive than BINOL and would allow the determination of whether the biaryl backbone could access the required geometry for dirhodium binding (Scheme 1). The key transformation was an enolate alkylation using the bis-benzyl bromide **21**, which allowed for the introduction of most of the carboxylate side chain in a single step. Unfortunately, all attempts to exchange **23** for the acetate or trifluoroacetate ligands of $Rh_2(OAc)_4$ or $Rh_2(TFA)_4$, respectively, failed. In a couple of attempts, $Rh_2(KC3P)(TFA)_2$ was inconsistently obtained in small amounts <9% yield, but none of the fully exchanged products were obtained, and oligomers were the major products. None of the corresponding $Rh_2(KC3N)(TFA)_2$ complex could be obtained under the same conditions.[17,18] Apparently, these diacids preferred to coordinate to two different dirhodium centers in a monodentate fashion rather than to a single core in a bidentate fashion.[19] Consequently, the biaryl core with a four-carbon carboxylate chain was next targeted to see if the additional methylene would allow greater conformational freedom for bidentate binding.

The synthesis of the homologous ligand proved to be less facile. Initial strategies of attaching the four-carbon unit to a biaryl bistriflate (**19** or **25**, Scheme 2) via Kumada, Heck, Suzuki, Stille, and Sonogashira couplings failed. The rings could be modified with methyl groups and then brominated for further functionalization. Alkylation strategies were attempted as above but were unsuccessful. On the other hand, transforming the dibromides **21** and **27** into the bisphosphonate **28** via an Arbuzov reaction allowed an aldehyde to be attached in good yields for both the biphenyl and bisnaphthyl substrates. With all the carbons incorporated, hydrogenation and hydrolysis afforded the ligands KC4P (**31**) and KC4N (**17**).[16] More efficient syntheses are still being pursued to enable synthesis of a ligand library, but this route has allowed for evaluation of both ligand incorporation in a dirhodium catalyst and the use of that catalyst in enantioselective transformations.

Ligand exchange to a dirhodium core proved to be somewhat difficult for the homologated biscarboxylates. Using typical conditions[9a−c,f,g] for the exchange of ligands from $Rh_2(OAc)_4$ or $Rh_2(TFA)_4$ with our model biphenyl ligand **31** caused the formation of significant quantities of an insoluble coordination polymer,[20] but also allowed the isolation of complexes with two of the acetate ligands displaced by **31** bound in a bidentate manner (see **32**, Scheme 3A). However, adding additional



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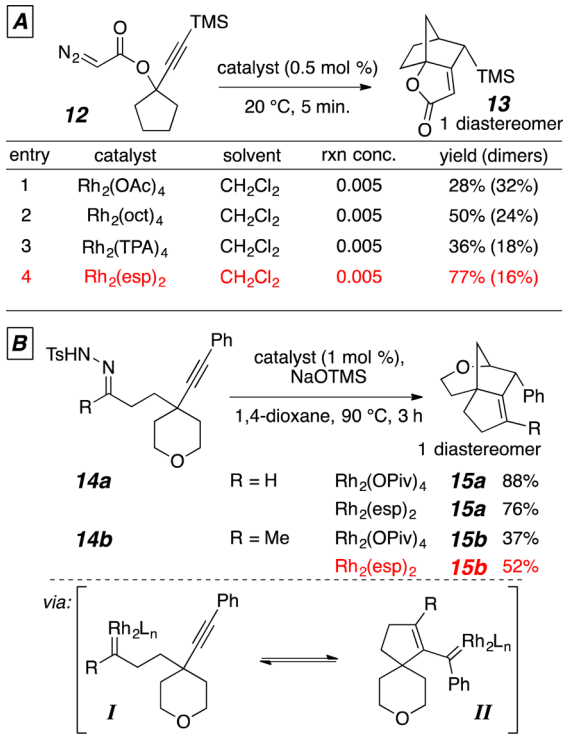



| entry | catalyst | solvent | rxn conc. | yield (dimers) |
|---|---|---|---|---|
| 1 | $Rh_2(OAc)_4$ | $CH_2Cl_2$ | 0.005 | 28% (32%) |
| 2 | $Rh_2(oct)_4$ | $CH_2Cl_2$ | 0.005 | 50% (24%) |
| 3 | $Rh_2(TPA)_4$ | $CH_2Cl_2$ | 0.005 | 36% (18%) |
| 4 | $Rh_2(esp)_2$ | $CH_2Cl_2$ | 0.005 | 77% (16%) |

**Figure 2.** Ligand impact on catalyst efficacy.

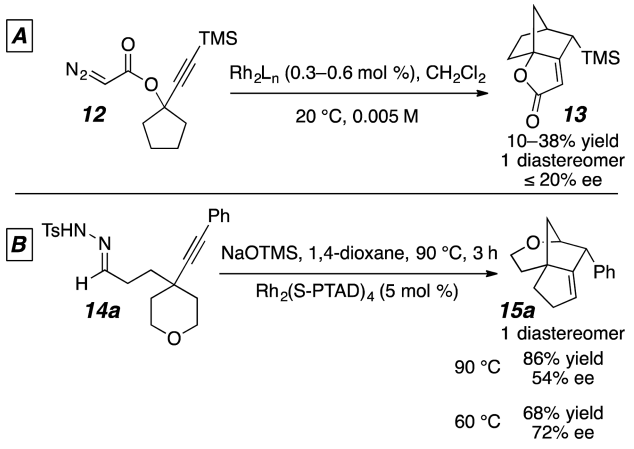



**Figure 3.** Use of known chiral catalysts in the carbene/alkyne cascade.[12]

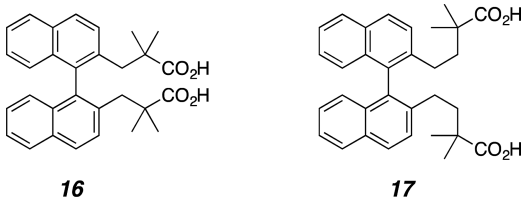
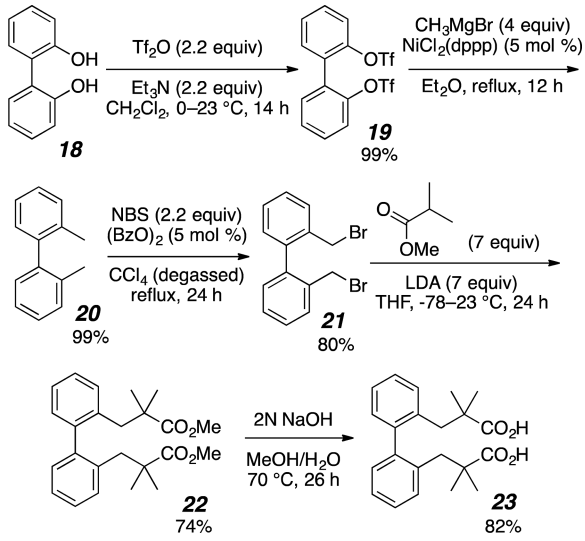



**Figure 4.** Targeted ligands for new Rh(II) catalysts.

equivalents of the ligand produced a lower yield of **32** without any of the completely substituted product **33**. Next, a newer protocol developed by the Ball group that used trifluoroethanol was explored.[9d] While $Rh_2(TFA)_4$ was not productive for the incorporation of **31**, the use of $Rh_2(OAc)_4$ in trifluoroethanol and excess $NEt(i\text{-}Pr)_2$ provided the doubly ligated product **33** in a serviceable yield (Scheme 3B). Moreover, these same

**Scheme 1. Synthesis of a Ligand Model System**




conditions could be used with the chiral binaphthyl ligand **17c** to afford the complex **35** (Scheme 3C).[21] The homochiral complex **35** from enantiopure ligand was a bluish-green (i.e., teal) crystalline solid. As expected, when racemic KC4N (**17b**) was incorporated into the complex, two diastereomers (homo chiral and heterochiral) were observed in equal amounts.

Fortunately, single crystals of the new complexes **33** and homochiral **35** could be grown and analyzed via X-ray diffraction (Figure 5). The structures are remarkably similar, and the bond lengths and angles at rhodium are typical of paddlewheel complexes.[9a,b,f,g] $Rh_2(KC4P)_2$ (**33**) does show a small amount of torsion about the Rh−Rh bond in the solid state so that the O−Rh−Rh-O dihedral angle is between 4.5° and 5° for three of the four carboxylates (see Figure 5A). Those for $Rh_2(R\text{-}KC4N)_2$ (**35**) are all 2.5° or less. A small amount of distortion is seen in the angles between the bound carboxylates in both structures, with the carboxylates from the same ligand splayed slightly apart at an average O−Rh−O angle of 91.9°. Conversely, the O−Rh−O angle between carboxylates of different ligands is an average of 87.9°. This slight distortion from right angles may indicate a small amount of strain in binding that could destabilize the complex in a reaction.[9a,c] The only major difference between the two structures is seen in the dihedral angles between the aromatic rings. For $Rh_2(KC4P)_2$ (**33**), the two sets of phenyl rings were found to be at 71.2° and 77.2° relative to each other (Figure 5A inset). However, the naphthyl rings in $Rh_2(R\text{-}KC4N)_2$ (**35**) were found to be at 86.6° and 93.3°. The wider angle of the latter ligands may introduce additional strain into the system, which would explain the lower yields for the formation of $Rh_2(R\text{-}KC4N)_2$.[22]

The side view of **35** (Figure 5B) would suggest that the two naphthyl rings on the KC4N ligand are not equivalent, with one extending away from the dirhodium core and the other projecting over the apical coordination site. However, both the $^1H$ and $^{13}C$ NMR show that the naphthyl rings are equivalent in solution on an NMR time scale, and thus, the complexes show the anticipated $D_2$ symmetry.[23] Taken together, these solid-state and solution-based observations suggest that the biaryl rings have some conformational freedom through the flexible hydrocarbon chain. Such flexibility would hamper rigorous stereocontrol in reactions. On the other hand, the $\alpha$-methyl groups are not equivalent in either single crystal X-ray



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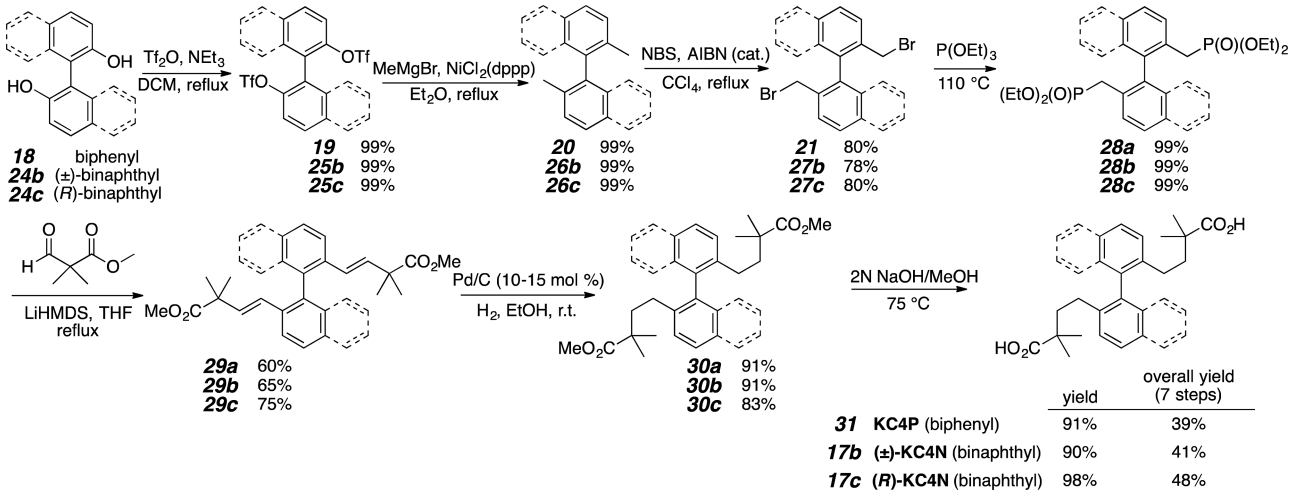
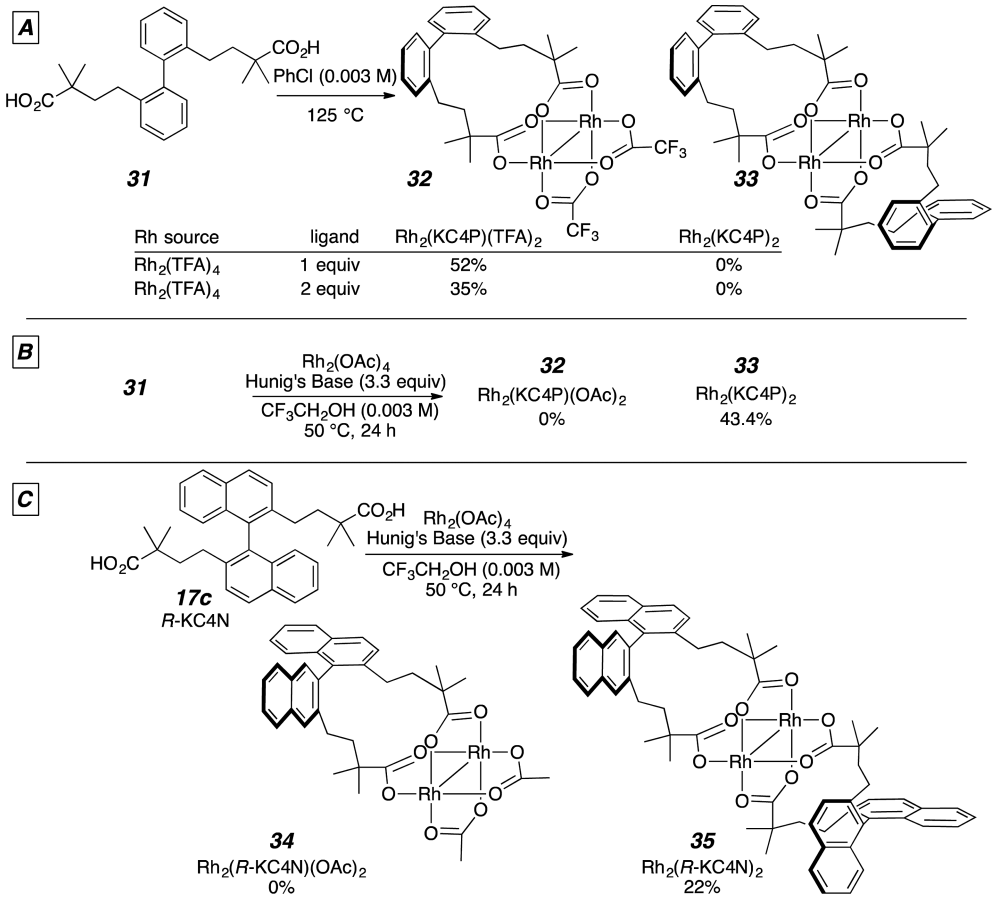
**Scheme 2. Homologated Ligand Synthetic Strategy**




**Scheme 3. Synthesis of Monoligated and Bisligated Complexes**




or NMR spectroscopy. Their orientation near the metal centers is dictated by the chiral binaphthyl backbone. This projection of chirality by a binaphthyl group through a nonstereogenic center to create a chiral environment near a reactive metal center is reminiscent of Noyori's pioneering BINAP ligand.[24] Thus, the ligand does provide a chiral environment at the metal center with $C_2$ symmetry through the axially projecting methyl as seen in the expansion in Figure 5B.

While preliminary tests in intramolecular and intermolecular cyclopropanations and C−H bond insertions did not show superiority to existing chiral catalysts,[25] our most stringent test of the new catalyst was its robustness for the cascade reactions in Figure 3. Tests with existing chiral catalysts did not provide useful catalytic activity for that transformation, and only $Rh_2(esp)_2$ functions in a consistently robust manner. The new ligand contains the $\alpha$-quaternary carbon postulated to be necessary for a productive cascade reaction and also contains a modifiable chiral element. Indeed, the reactivity of $Rh_2(esp)_2$ for hydrazone substrates was significantly recapitulated with the new complex, $Rh_2$(*R*-KC4N)$_2$ (**35**) (Table 1). A high yield was



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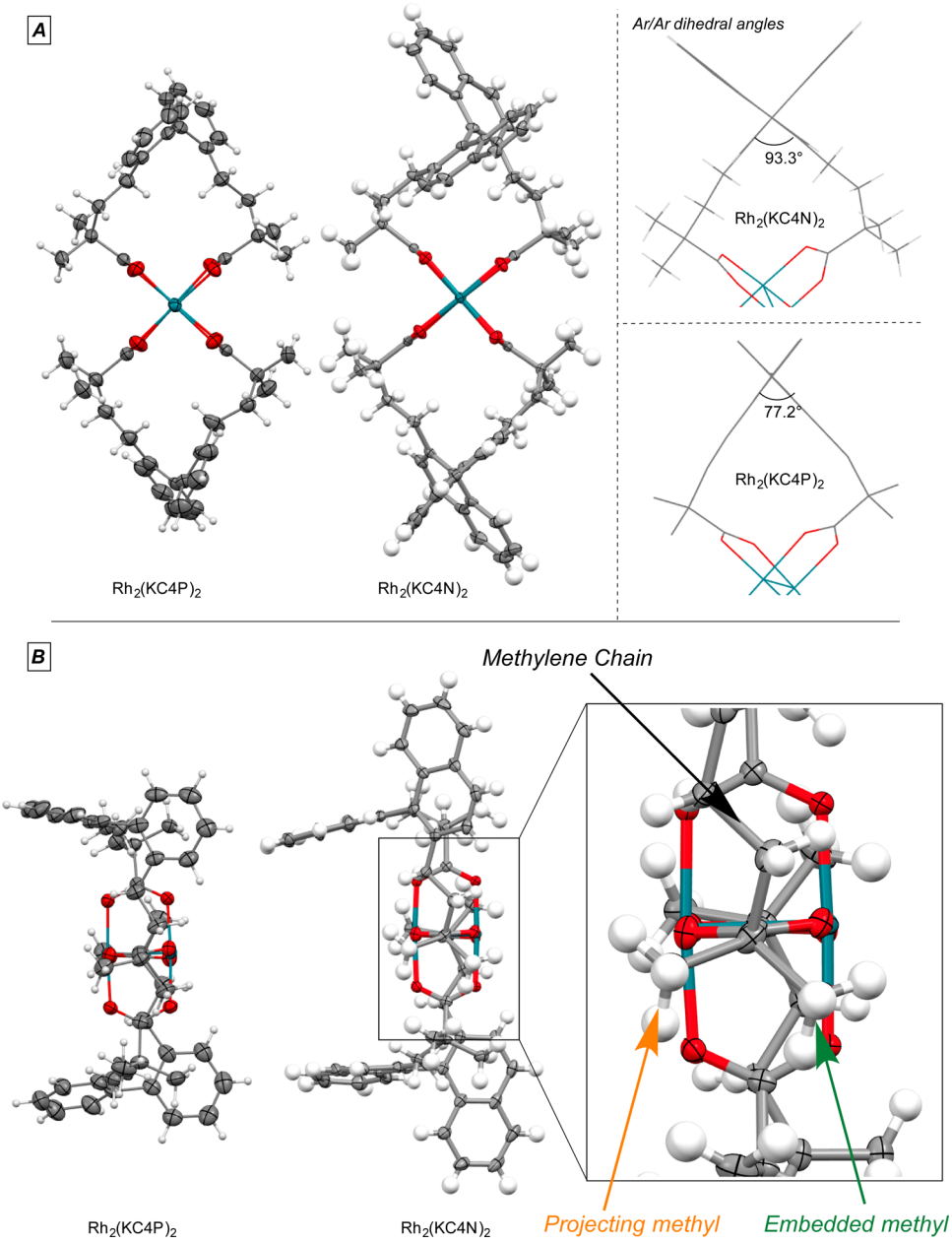


**Figure 5.** $Rh_2(KC4P)_2$ (**33**) and $Rh_2(R\text{-}KC4N)_2$ (**35**). Ellipsoids drawn at 50% probability. Axially coordinated acetones omitted for clarity.

observed of **14a** using **35** (entry 1), giving a similar outcome to $Rh_2(esp)_2$. Impressively, a high level of enantioinduction (96% ee) was also observed with 1 mol % $Rh_2(R\text{-}KC4N)_2$, while $Rh_2(S\text{-}PTAD)_4$ required 5 mol % loading to give 72% ee of the product in only 68% yield (see Figure 3). For the ketone-derived hydrazone **14b**, the isolated yield was much higher than that which had been obtained with either $Rh_2(OPiv)_4$ or $Rh_2(esp)_2$ even though the reaction was at a lower temperature (entry 2), though little enantioinduction was seen. Presumably, differentiation of the *n*-alkyl and methyl substituents of the ketone-derived carbene is significantly more difficult than for the *n*-alkyl and hydrogen substituents of the aldehyde-derived carbenes. Nevertheless, the new chiral catalyst recapitulated or exceeded the catalytic capacity of $Rh_2(esp)_2$ overall and provided promising enantioselectivity for other aldehyde-based substrates (entries 3−5). The dihydropyran-fused products **37**, **39**, and **41** were obtained with lower enantioselectivities than the cyclopentene-fused **15a**, though it is unknown at this time if this is due to electronic or conformational effects. The yields of these latter substrates were in the useful range, though that of **37**, which also proved problematic for $Rh_2(esp)_2$, was lower than desired. Thus, the fact that catalyst **35** gave the highest yields for these products of known carbene catalysts and did so with promising enantioselectivity demonstrates the significant potential of this new ligand type for dirhodium complexes.

In conclusion, a new chiral bidentate carboxylate ligand having $\alpha$-quaternary carbons has been synthesized and incorporated in a dirhodium catalyst. A solid-state structure has been obtained, and the catalytic characteristics have been probed. For the especially difficult to catalyze alkyne/cascade reactions with hydrazone initiation we have recently disclosed, the new catalyst provided products in highest yields obtained to date and induced promising levels of enantioselectivity. The



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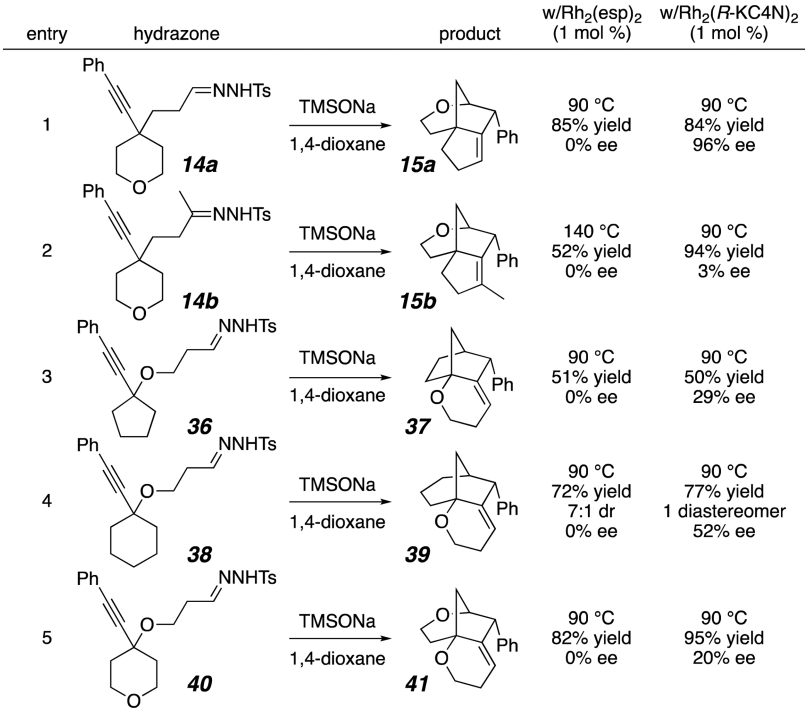
**Table 1. Enantioselective Cascade Reactions**




solid state structure and reactivity will guide the design of future generations of the catalyst based on the biaryl backbone, with a goal of even more effective reactivity and increase stereoselectivity.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b01388.

Data for enantioselective transformations with previously described catalysts, experimental procedures, and compound characterization data(PDF)

Structure of diacetone complex of Rh2(KC4P)2 33 (CIF)

Structure of diacetone complex of Rh2(R-KC4N)2 35 (CIF)

Structure of (1S,2R)-cyclopropanecarboxylate S27 (CIF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: jmay@uh.edu.

### ORCID

Jeremy A. May: 0000-0003-3319-0077

### Author Contributions

‡(P.-A.C., K.S) These authors contributed equally.


### Notes

The authors declare no competing financial interest.

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(12) Catalysts examined for the transformation include: $Rh_2$(*S*-PTAD)$_4$, $Rh_2$(*S*-BTPCP)$_4$, $Rh_2$(*S*-DOSP)$_4$, $Rh_2$(*S*-*t*BuSP)$_4$, **7** and $Rh_2$(*S*-BiTISP)$_2$ (**8c**). Please see the Supporting Information for a detailed table of results for these catalysts.

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(15) Assessments made with a molecular model set and with Spartan 10 on a Mac Pro using molecular mechanics level calculations.

(16) The ligand names are a composite of initials of the chemists who made them (**K**rit Setthakarn and Po-An **C**hen), the number of carbons in the carboxylate chain (**3** or **4**), and the biaryl core (bi**P**henyl or bi**N**aphthyl).

(17) KC3N was synthesized in the same manner as KC3P (see Scheme 1).

(18) In every case, including dilute conditions, either no product was observed by $^1$H NMR or ESI MS, or an insoluble gel was produced.

(19) For examples of biscarboxylate ligands coordinating to two different dirhodium cores, see: Bickley, J.; Bonar-Law, R.; McGrath, T.; Singh, N.; Steiner, A. *New J. Chem.* **2004**, *28*, 425−433.

(20) Short coordination oligomers were observed via electrospray injection mass spectrometry.

(21) When these conditions were used for the metalation of KC3P or KC3N, no ligated dirhodium complex could be isolated.

(22) The different dihedral angles may also be explained by crystal packing forces.

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(25) Please see the Supporting Information for those studies.



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