Synthesis, Structure, and Reactivity of the First Enantiomerically Pure Ortho-Metalated Rhodium(II) Dimer

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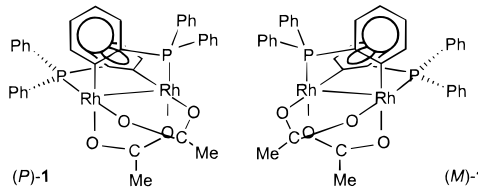
Rhodium(II) complexes have attracted increasing attention as efficient catalysts for the enantioselective transformation of α-diazo carbonyl compounds. Cyclopropanation, C−H insertion, and aromatic cycloaddition are among the reactions that have been investigated.[1] Until now, all approaches to the design of enantiomerically pure Rh(II) catalysts have depended on the attachment of enantiomerically pure ligands to the rhodium core.[2−4] We describe here a complementary strategy, the preparation of Rh(II)-dimers having backbone chirality.

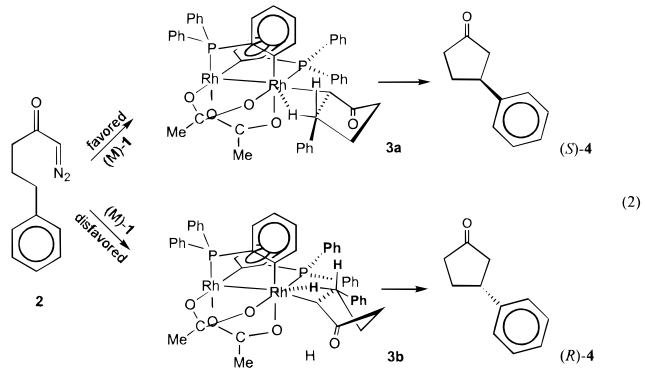
Complexes derived from the ortho-metalated arylphosphines $Rh_2(O_2CR)_2(PC)_2L_2$ (PC = ortho-metalated phosphine) appeared to be particularly interesting candidates for testing this new approach, as the doubly metalated products with head-to-tail arrangement are inherently chiral[5] (e.g., **(*P*)-1** and **(*M*)-1** eq 1)



(1)

and are readily prepared by the reaction of $Rh_2(O_2CCH_3)_4$ and PPh_3.[5] Apart from being a focus of interest in basic research, in some racemic cases these complexes had been shown to be more selective C−H insertion catalysts than the widely used carboxylate or amidate systems.[6]

It was especially intriguing that the proposed transition state[7] for Rh-mediated C−H insertion seemed to fit the chiral twist of complexes **(*P*)-1** and **(*M*)-1** particularly well. Thus, transition state **3a** (eq 2) appeared to be easily accessible, whereas transition state



(2)

3b seemed to be more encumbered.

Motivated by this possibility, we considered several strategies by which complexes such as **(*P*)-1** and **(*M*)-1** might be obtained as single enantiomers. The first approach, separation of the diastereoisomers resulting from addition of chiral ligands to the axial positions of the dimers $[Rh_2(O_2CR)_2(PC)_2L^*_2]$, turned out not to be practical, due to the high kinetic lability of those adducts. We therefore turned to an alternate strategy, separation of the diastereomers derived from the attachment of chiral carboxylate groups $[Rh_2(O_2CR^*)_2(PC)_2L_2]$.

As a chiral auxiliary (Scheme 1) the inexpensive *N*-(4-methylphenylsulfonyl-(L)-proline), (ProtosH (**5**)) was used.[8] Re-

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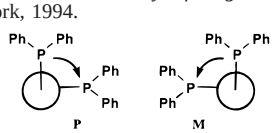

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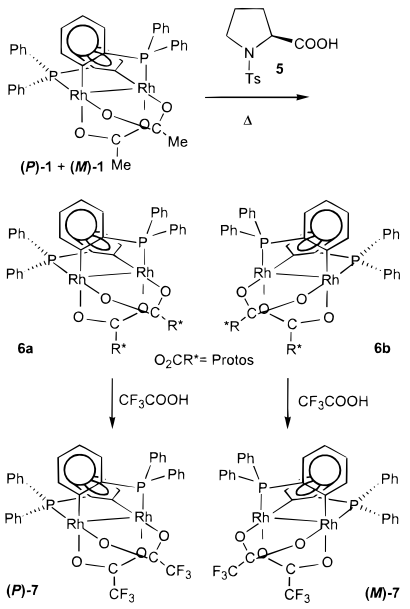
Scheme 1



placement of acetate by Protos in the orthometalated acetate mixture **(*P*)-1** and **(*M*)-1** yielded the expected 1:1 mixture of the desired diastereomers **6a** and **6b**. These were separable by silica gel chromatography.[9]

The two enantiomerically enriched complexes **(*P*)-7** and **(*M*)-7** were obtained via ligand exchange of **6a** and **6b** (separately) with trifluoroacetic acid. The enantiomeric purities **(*P*)-7** and **(*M*)-7** (>98%) were checked by ^{31}P NMR in the presence of (−)-1-(1-naphthyl)ethylamine. Validating this method with the racemic mixture revealed that the signals for the resulting diastereomers coalesced at room temperature (25 °C). Clear spectra could be recorded at higher or lower temperatures. The absolute configurations of **(*P*)-7** and **(*M*)-7** were established by X-ray diffraction methods,[10] using crystals grown from solutions containing pyridine [**8**, from the levorotatory enantiomer (−)-**(*P*)-7**[11]] and trifluoroacetic acid [**9**, from the dextrorotatory enantiomer (+)-**(*M*)-7**[11]]. The two structures are shown in Figure 1 and Figure 2.

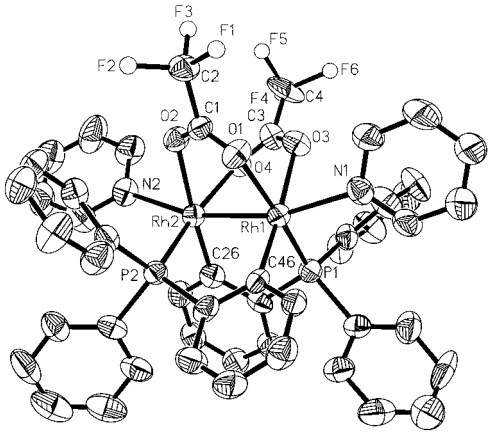


Figure 1.

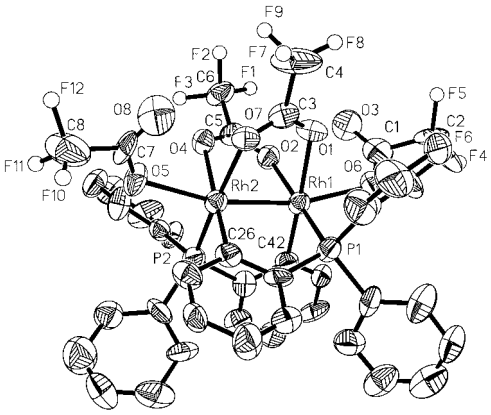


Figure 2.

To explore the possibility of diastereoselectivity in the synthesis of $[Rh_2(O_2CR^*)_2(PC)_2L_2]$ **6a** and **6b**, the metalation of PPh_3 with $Rh_2(Protos)_4$ was also carried out. Under standard conditions, this did indeed lead to a modest (2:1) preference for **6a** over **6b**.

With **(*M*)-7** and **(*P*)-7** in hand, we effected cyclization of the diazoketone **2** to give the cyclopentanones (***S*)-4** and (***R*)-4**. Both enantiomers induced identical enantiocontrol {$[\alpha]_D$= 30° (c = 0.78, $CHCl_3$), 36% ee, 70% yield}[12] in the transformation of this diazoketone, but with opposite ee's.[13] These results support the generally accepted idea that the catalytic reaction occurs via a dirhodium−carbenoid species and also confirm that degradation to an achiral rhodium catalyst is not a major competing pathway.

The ortho-metalated Rh(II) complexes **(*M*)-7** and **(*P*)-7**, having backbone asymmetry, are intriguing lead structures for an interesting new series of chiral catalysts. Studies are in progress to determine the scope and limitations of these complexes as enantioselective catalysts for carbenoid transformations.[14]

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Supporting Information Available: Tables of crystal data and structure refinement for **1** (PDF). An X-ray crystallographic file, in CIF format, for **8** and **9** is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(9) The separation of the diastereoisomer was performed in a 2.5 × 100 cm column using flash silica gel as support and 50:2 methylene chloride/ethyl ether as eluent. Compound **6a** was the first eluted isomer.

(10) X-ray data: Purple crystals of **8**. $C_{50}F_6H_{38}N_2O_4P_2Rh_2$, M_r = 1112.61, orthorhombic, $P2_12_12_1$, a = 12.4918(8) Å, b = 18.3734(12) Å, c = 20.2615(14) Å, V = 4650.4(5) Å^3, Z = 4, R = 0.048, GOF = 0.864. Purple-red crystals of **9**. $C_{44}F_{12}H_{30}O_8P_2Rh_2$, M_r = 1182.44, orthorhombic, $P2_12_12_1$, a = 12.5406(12) Å, b = 18.696(2) Å, c = 20.273(2) Å, V = 4753.1(8) Å^3, Z = 4, R = 0.0832, GOF = 1.062.

(11) **(−)-(*P*)-7**: $[\alpha]_D$ = −83° (c = 0.1, CH_3CN); **(+)−(*M*)-7**: $[\alpha]_D$ = +83°(c = 0.1, CH_3CN).

(12) The absolute configuration of ketone **4** was determined by correlation of the sign of the rotation of polarized light with that of the known enantiomer (ref 13). The major isomer was (*S*)-**4** when **(*M*)-7** was used, which was consistent with the outcome predicted in eq 2.

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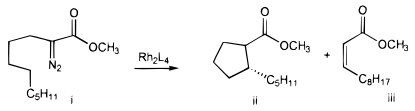
(14) The carbene derived from **(*M*)-7** (or **(*P*)-7**) is very reactive, as evidenced by the observation that attempted cyclization of i (ref 15) gives not the cyclized product ii, but only the eliminated product iii. This suggests that the carbene derived from **(*M*)-7** would have a very early transition state (long C−C distance at the point of commitment to cyclization). While the three-dimensional shape of **(*M*)-7** is intriguing, it will be necessary to significantly attenuate the reactivity of the derived carbene if a highly selective catalyst is to be achieved.



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