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A New Rhodium(II) Phosphate Catalyst for Diazocarbonyl Reactions Including Asymmetric Synthesis

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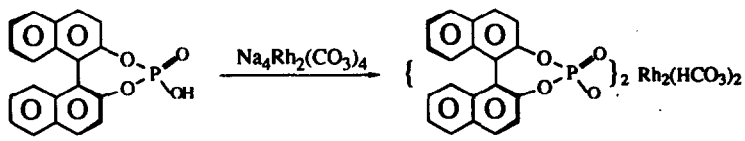
Abstract: *A new homochiral Rh(II) complex, $Rh\{HCO_3\}_2\{(+)\text{-phos}\}_2\cdot 5H_2O$, where (+)phosH represents (S)-(+)-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate, has been prepared and used as a catalyst for reactions of diazocarbonyl compounds leading to enantioselective 2,3-sigmatropic rearrangement (first example), C-H insertion and aromatic cycloaddition*

Much of the success achieved in recent years with α-diazocarbonyls as intermediates in synthesis can be attributed to the use of rhodium(II) catalysts.[1,2] Prior to the introduction of rhodium(II) acetates, copper or copper salts were the catalysts of choice for a range of α-diazocarbonyl reactions, e.g. cyclopropanation. However, there is now substantial evidence to suggest that over the broad range of α-diazocarbonyl reactions, particularly cyclopropanation, C-H, N-H, O-H and S-H insertion, and aromatic cycloaddition, rhodium catalysts are superior to their copper counterparts in both efficiency and chemoselectivity.

Almost all studies with rhodium catalysts employ rhodium(II) carboxylates, notably acetate, trifluoroacetate, pivalate, octanoate. Chiral Rh(II) carboxylates[3] have also been employed in cyclopropanation, aromatic cycloaddition and C-H insertion. In some cases only moderate e.e. values were achieved. It has become apparent that one class of chiral Rh(II) complex is unlikely to produce high levels of asymmetric synthesis across the whole range of carbenoid transformations. It is therefore desirable to investigate other potential chiral Rh(II) catalysts. For example, Doyle has introduced rhodium(II) carboxamides which, though less active catalytically than the carboxylates, do possess the ability to generate high levels of enantioselectivity in asymmetric synthesis when used in homochiral form[4]. We now report a new addition to the range of catalytically active and homochiral rhodium(II) complexes suitable for diazocarbonyl decomposition, namely $Rh_2\{HCO_3\}_2\{(+)\text{-Phos}\}_2\cdot 5H_2O$ **1**, where (+)-PhosH represents (S)-(+)-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate **2**. PhosH (±) **2** was prepared by treatment of (±)-1,1'-bi-2-naphthol with $POCl_3$, followed by aqueous workup. This was then resolved by crystallisation of the salt of (±) **2** with cinchonine to furnish (S)-(+) phosH **2**[5]. Reaction of $Na_4Rh_2(CO_3)_4\cdot 2.5H_2O$ [6] with an excess of (S)-(+)-PhosH gave a complex which formulates as **1**.

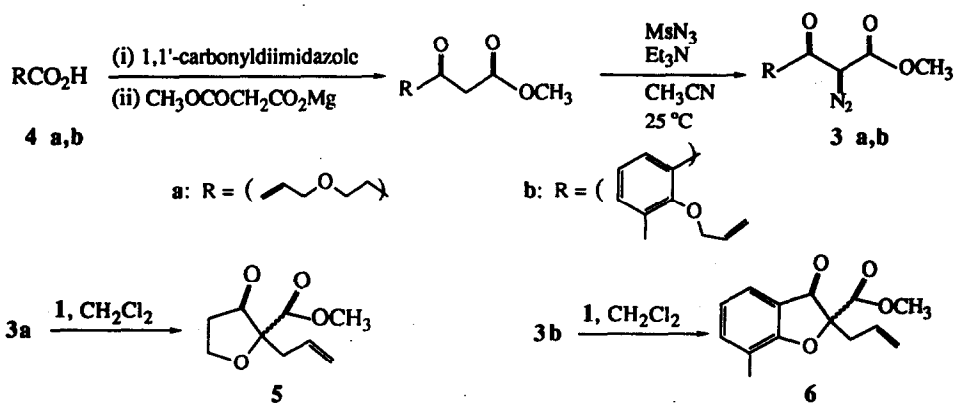


2 **1**

The catalytic efficiency of **1** in the decomposition of several diazocarbonyl compounds and the possibility of asymmetric synthesis were examined in the following areas.

(*i*) 2,3-Sigmatropic rearrangement

Diazocarbonyl intermediates **3a** and **3b** were prepared as outlined in **Scheme 1.** Acids **4a** and **4b**[7] were first converted into the corresponding acyl imidazoles which were treated with the chelated enolate, magnesium monomalonate[8] to form β-ketoesters. Diazo transfer with mesyl azide completed the preparation of the diazocarbonyls (overall yields, 61% **3a**; 68% **3b**)

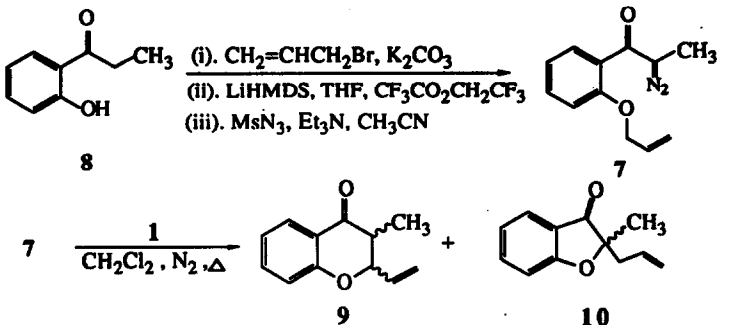


Scheme 1

Treatment of **3a** and **3b** with **1** (0.5mol %) in dichloromethane at reflux under N_2 afforded the 2,3-sigmatropic rearrangement products **5** {88% yield, $[\alpha]_D^{20}$ -4.8° (c 1.85, CH_2Cl_2)} and **6** {92% yield, $[\alpha]_D^{20}$ -39° (c 1.80, CH_2Cl_2)}, respectively. ^{1}HNMR analysis employing the shift reagent Eu(hfc)$_3$ {Tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] europium(III)} revealed that the enantiomeric excess of **5** was 9% while that of **6** was 30%. These represent the first examples of asymmetric induction *via* 2,3-sigmatropic rearrangement of diazocarbonyl intermediates under homochiral Rh(II) catalysis and shed new light on the extent of involvement of the metal in such rearrangements.

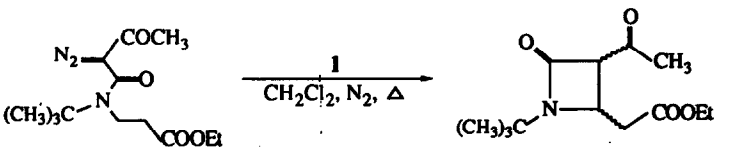
(*ii*) C-H insertion

Diazoketone **7** was prepared from ortho-hydroxypropiophenone **8** by alkylation with allyl bromide followed by diazo transfer using Danheiser's procedure[9](overall yield 48%). Cyclisation of **7** using **1** catalytically (0.5mol %) proceeded quantitatively in dichloromethane to furnish the C-H insertion product **9** (90% by ^{1}HNMR) along with a small amount(ca. 10%) of sigmatropic rearrangement product **10**. The C-H insertion product **9** was predominantly in the *cis* form (93.5%) which had an e.e. value of 33% [from ^{1}HNMR using Eu(hfc)$_3$]. (**Scheme 2**)



Scheme 2

Yet another example of the catalytic activity of **1** was uncovered when it was used to decompose diazocarbonyl **11**[10] in dichloromethane. The sole product was β-lactam **12** {93% yield, $[\alpha]_D^{20}$ -6.38° (c 0.47, CH_2Cl_2)} which was shown by ^{1}HNMR analysis to be the *trans* isomer exclusively. Chiral shift studies using the Pirkle solvent [(R)-(-)-2,2,2-Trifluoro-1-(9-anthryl)ethanol] revealed that **12** had an e.e. value of 26%. **(Scheme 3)**

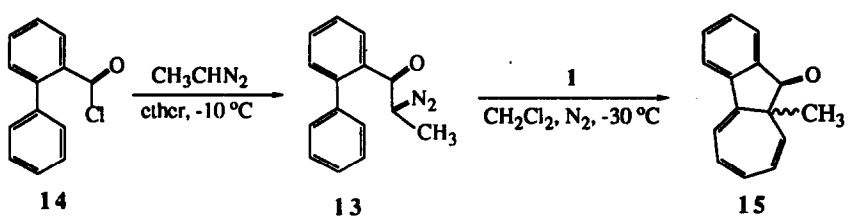


Scheme 3

Thus catalyst **1** is applicable to 4- and 6-membered ring formation *via* C-H insertion reactions.

(*iii*) Aromatic cycloaddition

Diazoketone **13** was prepared from commercially available biphenyl carboxylic acid *via* acid chloride **14** formation followed by exposure to ethereal diazoethane. Decomposition of **13** using **1** (0.5mol %) led to the aromatic cycloaddition product **15** in 80% yield, $[\alpha]_D^{20}$ -22.7° (c 1.94, CH_2Cl_2). Optical resolution on a Chiralcel OD column revealed that the enantiomeric excess was 60%[11]. This result was confirmed by chiral NMR studies using Eu(hfc)$_3$. **(Scheme 4)**



Scheme 4

Since both enantiomers of catalyst **1** are available, the absolute configuration of the above products can be controlled.

In conclusion, $Rh_2\{HCO_3\}_2\{(+)\text{-Phos}\}_2{\cdot}5H_2O$ **1** has emerged as an efficient catalyst for a number of carbenoid transformations. Also moderate to good e.e. values were achieved. The first observation of asymmetric induction in the sigmatropic rearrangement of carbenoids derived from diazocarbonyls is significant.

Preparation of **1**. To a suspension of $Na_4[Rh_2(CO_3)_4]{\cdot}2.5H_2O$ [6] (0.103g, 0.18mmol) in ethanol (50cm^3) was added portionwise (S)-(+)-phosH [5] (0.495g, 1.42mmol). The resulting deep blue solution was filtered to remove a small amount of undissolved phosphate and the filtrate was stirred at room temperature for one week during which time the colour changed to light green. The solution was then concentrated under vacuum at 20 °C to ca. 20 cm^3. An ethanol : water mixture (2:1) was very slowly added to precipitate the product as a light-green microcrystalline solid which was isolated by filtration, washed with 2 portions (1cm^3) of ice-cold ethanol and dried *in vacuo* (0.03g, 15%) (Found: C, 45.4; H, 3.1. Calcd. for $C_{42}H_{34}O_{19}P_2Rh_2{\cdot}5H_2O$. C, 45.3; H, 3.3%; IR(KBr), 1400-1500(CO) and 1230, 1085(PO) cm^{-1}; $[\alpha]_D^{20}$ +367° (c, 0.147, CH_3OH). The FAB mass spectrum of **1** showed a strong peak at m/z 1022 for $Rh_2(HCO_3)_2(+)\text{-(phos)}_2^+$. Other green solids which subsequently precipitate from the mother liquors showing different infrared spectra have not been characterised.

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11. Column: Chiralcel OD (250mm x 4.6mm i.d.); flow rate, 0.5ml/minute; detection,UV 254nm; mobile phase, *n*-hexane : 2-PrOH (90:10). Retention times: 14.60 and 16.50 mins

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