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Enantioselective Si–H insertion of methyl phenyldiazoacetate catalyzed by dirhodium(II) carboxylates incorporating *N*-phthaloyl-(*S*)-amino acids as chiral bridging ligands

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Abstract

Enantioselective insertion reactions of methyl phenyldiazoacetate into the Si–H bond of silanes were effected by employing dirhodium(II) carboxylates incorporating *N*-phthaloyl-(*S*)-amino acids as chiral bridging ligands. The use of dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-phenylalaninate] as a catalyst produced methyl (2*S*)-(dimethylphenylsilyl)phenylacetate in 74% ee, whereas catalysis with dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-phenylglycinate] afforded its enantiomer in 72% ee.

Among transition metal complexes to catalyze a broad spectrum of transformations involving α-diazo carbonyl compounds, it has been well documented that dirhodium(II) complexes distinguish themselves by their superiority in C–H and X–H (X = heteroatom) insertion reactions.[1] While exceptionally high levels of enantiocontrol in C–H insertions have already been achieved by the device of well-defined dirhodium(II) carboxylates and carboxamidates as chiral catalysts, the goal for X–H insertions remains elusive.[2] The poor enantioselectivity in insertions of a chiral rhodium(II) carbene complex into polar bonds (N–H, O–H and S–H) has been speculated to be due to a stepwise process which begins with attack of the heteroatom on the electrophilic carbene to form an ylide followed by proton transfer at the catalyst-free stage.[2,3] Unlike insertion to polar bonds, it has been suggested by Doyle and Moody through Rh(II)-catalyzed enantioselective Si–H insertions (up to 47% ee) that Si–H insertions proceed in the same concerted manner as well-demonstrated C–H insertions.[4] More recently, Landais and co-workers have demonstrated through kinetic investigations that the insertion of a rhodium(II) carbene complex into the Si–H bond proceeds through an early transition state where a small positive charge is developed at the silicon center.[5] Thus, the higher reactivity of the Si–H bond relative

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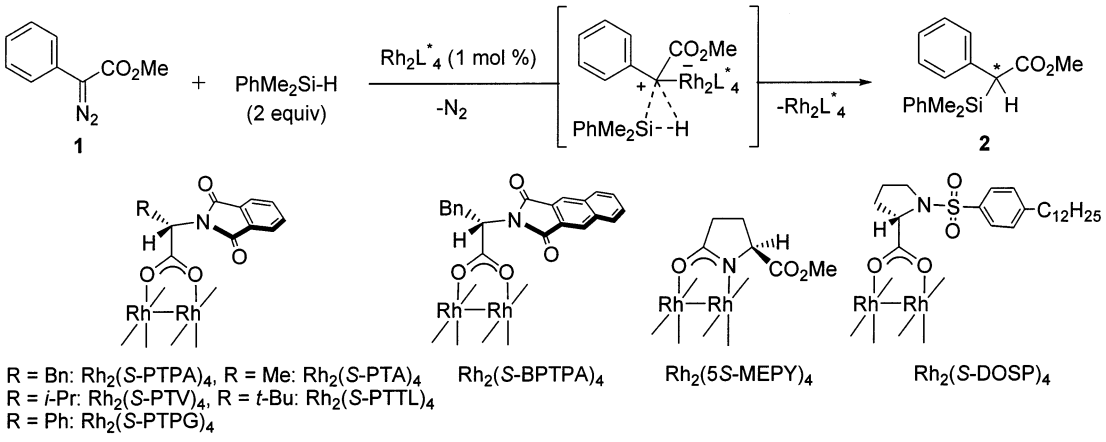
to the C–H bond is one of the barriers to generally high enantiocontrol. As a logical extension of our studies on enantioselective C–H insertions,[6] we now addressed the issue of enantiocontrol in Si–H insertions, focusing on the assessment of our dirhodium(II) catalysts in these systems.

The Si–H insertion of methyl phenyldiazoacetate **1** with $PhMe_2SiH$ under the influence of chiral catalysts represents the bench mark reaction in this field (Scheme 1). As touched on above, Doyle, Moody and co-workers were the first to demonstrate asymmetric induction (4–47% ee) in this reaction using a wide range of dirhodium(II) carboxylate and carboxamidate catalysts, in which $Rh_2(5S\text{-MEPY})_4$ gave the highest % ee value.[4] Davies et al. subsequently reported that a dramatic enhancement of up to 85% ee could be achieved by the combinational use of $Rh_2(S\text{-DOSP})_4$ as a catalyst and pentane as a solvent at −78°C, though the product yield was modest (50%).[7–9] Jacobsen, Panek and co-workers examined copper(I) catalysts associated with chiral, C_2-symmetric Schiff base ligands, and attained 83% ee.[10]



Scheme 1.

At the outset, the Si–H insertion of **1** was carried out with 2 equiv. of $PhMe_2SiH$ in the presence of 1 mol% of dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-phenylalaninate], $Rh_2(S\text{-PTPA})_4$. After experimentation focusing mostly on the solvent effects, the use of dichloromethane was found to be the superior choice for allowing smooth reaction at −78°C, which gave benzylsilane **2**, $[\alpha]_D^{25}$ −20.3 (*c* 1.30, $CHCl_3$), in 86% yield with 65% ee (Table 1, entry 2). The preferred absolute configuration of **2** was established as *S* by its conversion to the known 1-phenyl-1,2-ethanediol **3**, $[\alpha]_D^{25}$ +24.8 (*c* 0.65, EtOH) [lit.,[11] $[\alpha]_D^{20}$ +38.6 (*c* 1, EtOH) for (*S*)-**3**], by the procedure of Landais.[9] It was also found that the enantioselectivity was highly dependent on the reaction temperature (entries 1–3). Further enhancement of up to 74% ee was possible by conducting the reaction at −90°C. While toluene provided (*S*)-**2** in 80% yield with 52% ee at −78°C, the reaction required much longer time to reach completion (entry 4). The use of ether resulted in the formation of (*S*)-**2** in only 12% ee, in which −40°C was the limit temperature to allow for the smooth insertion (entry 5). In stark contrast to Davies' result,[7] pentane was not suitable at all for this case due chiefly to the very limited solubility of this family of catalysts in a hydrocarbon solvent (entry 6).

Table 1
Enantioselective intermolecular Si–H insertion of **1** catalyzed by chiral Rh(II) complexes[a]

Entry	Rh(II) catalyst	Solvent	Temp,°C	Time, h[b]	Yield, %[c]	Ee, %[d]	Config[e]
1	Rh_2(*S*-PTPA)$_4$	CH_2Cl_2	−45	0.5	61	38	*S*
2	Rh_2(*S*-PTPA)$_4$	CH_2Cl_2	−78	1	86	65	*S*
3	Rh_2(*S*-PTPA)$_4$	CH_2Cl_2	−90	3	85	74	*S*
4	Rh_2(*S*-PTPA)$_4$	Toluene	−78	1.5	80	52	*S*
5	Rh_2(*S*-PTPA)$_4$	Et_2O	−45	4	46	12	*S*
6	Rh_2(*S*-PTPA)$_4$	Pentane	23	1.5	77	<1	–
7	Rh_2(*S*-PTA)$_4$	CH_2Cl_2	−78	1	79	49	*S*
8	Rh_2(*S*-PTV)$_4$	CH_2Cl_2	−78	2	83	31	*S*
9	Rh_2(*S*-PTTL)$_4$	CH_2Cl_2	−78	2	82	46	*R*
10	Rh_2(*S*-PTPG)$_4$	CH_2Cl_2	−78	1.5	80	72	*R*
11	Rh_2(*S*-BPTPA)$_4$	CH_2Cl_2	−78	1	78	67	*S*

[a] The following procedure is representative (entry 2): a solution of diazo ester **1** (50.0 mg, 0.284 mmol) in CH_2Cl_2 (0.7 mL) was added dropwise over 30 min to a stirred solution of dimethylphenylsilane (77 mg, 0.57 mmol) and bis(ethyl acetate) adduct of Rh_2(*S*-PTPA)$_4$ (2.2 mg, 1 mol%) in CH_2Cl_2 (2.1 mL) at −78°C. After 30 min, the mixture was concentrated in vacuo and chromatographed on silica gel to afford **2** (69.7 mg, 86%) as a colorless oil.

[b] Total reaction time including the addition time.

[c] Isolated yield.

[d] Determined by HPLC (column, Daicel Chiralcel OD; eluent, 1% 2-propanol in hexane; flow rate, 1.0 mL/min; detection, 254 nm).

[e] See the text.

Using dichloromethane as the solvent, we next screened other chiral dirhodium(II) carboxylates, Rh_2(*S*-PTA)$_4$, Rh_2(*S*-PTV)$_4$, Rh_2(*S*-PTTL)$_4$, and Rh_2(*S*-PTPG)$_4$, derived from *N*-phthaloyl-(*S*)-alanine, -valine, -*tert*-leucine, and -phenylglycine, respectively.[6] It was found that Si–H insertion of **1** with Rh_2(*S*-PTA)$_4$ and Rh_2(*S*-PTV)$_4$ provided (*S*)-**2** as with the case of Rh_2(*S*-PTPA)$_4$ in 49% and 31% ee, respectively, whereas Rh_2(*S*-PTTL)$_4$ and Rh_2(*S*-PTPG)$_4$ brought about a reversal in enantioselection to give (*R*)-**2** in 46% and 72% ee, respectively (entries 7 and 8 versus 9 and 10). Unlike Rh_2(*S*-PTPA)$_4$, the reaction with the other dirhodium(II) complexes did not work at –90°C. While the effect of the bridging ligands on the sense and magnitude of enantioselection as well as the reactivity of dirhodium(II) catalysts is presently not clear, it is noteworthy that the choice of Rh_2(*S*-PTPA)$_4$ or Rh_2(*S*-PTPG)$_4$ could produce either enantiomer of **2** in high yields and with enantioselectivities comparable to those reported by Davies,[7] Jacobsen and Panek.[10] Disappointingly, switching the catalyst to Rh_2(*S*-BPTPA)$_4$ characterized by an extension of the phthalimido wall with one more benzene ring[12] had little beneficial effect in this system, exhibiting virtually the same enantioselectivity as Rh_2(*S*-PTPA)$_4$ (entry 11).[13]

Finally, we examined the effects of silicon substituents on enantiocontrol. The results are summarized in Table 2.[14] It is noteworthy that Rh_2(*S*-PTPA)$_4$-catalyzed Si–H insertions of **1** with Et_3SiH, $PhMe_2SiH$, and Ph_3SiH with different levels of reactivity (Et_3SiH>$PhMe_2SiH$>Ph_3SiH)[5] gave equally good enantioselectivities (65–72% ee, entries 1–3), since Jacobsen and Panek reported a considerable decrease in enantioselectivity with the most reactive Et_3SiH.[10] These results can be understood by the concerted mechanism through a relatively early transition state, in which the steric interaction between the substituents on the silicon center and the bridging ligands on the rhodium is not severe. However, no explanation for a significant decrease in enantioselectivity (35% ee) with the least reactive $ClMe_2SiH$ can be offered at present (entry 4).

Table 2
Enantioselective Si–H insertion of **1** catalyzed by $Rh_2(S\text{-PTPA})_4$: effects of silicon substituents[a]

Entry	R_3Si–H	Time, h[b]	Yield, %[c]	Ee, %[d]	$[\alpha]_D$ (c, $CHCl_3$)
1	Et_3Si–H	1.5	73	72[e]	−28.4 (1.13)
2	$PhMe_2Si$–H	1	86	65	−20.3 (1.30)
3	Ph_3Si–H	1.5	73	71[e]	−23.4 (2.34)
4	$ClMe_2Si$–H	1.5	67[f]	35[e,f]	−11.6 (1.58)[f]

[a] All reactions were performed in CH_2Cl_2 at −78°C as described in Table 1.
[b] Total reaction time including the addition time.
[c] Isolated yield.
[d] Determined by HPLC (column, Daicel Chiralcel OD; eluent, 1% 2-propanol in hexane; flow rate, 1.0 mL/min; detection, 254 nm).
[e] Absolute configuration of the major isomer was not determined.
[f] The values after conversion to methyl (isopropyloxydimethylsilyl)phenylacetate. See Ref. 15.

In summary, we have demonstrated the effective use of $Rh_2(S\text{-PTPA})_4$ and $Rh_2(S\text{-PTPG})_4$ as catalysts for enantioselective Si–H insertions of **1**. While the mechanistic profile is presently unclear, $Rh_2(S\text{-PTPA})_4$ has proven to be the best of our chiral dirhodium(II) carboxylates in terms of selectivity as well as reactivity even at −90°C. Further extension of the present method to vinyldiazoacetates is currently in progress.

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