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Asymmetric Rhodium Carbenoid Insertion into the Si-H Bond

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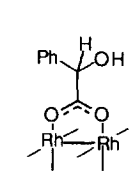
Abstract: Decomposition of methyl 2-diazophenylacetate in the presence of dimethylphenylsilane and a chiral dirhodium(II) catalyst results in Si-H insertion of the intermediate carbenoid with varying degrees of enantioselectivity (up to 47% ee). Copyright © 1996 Elsevier Science Ltd

The development of chiral catalysts for asymmetric reactions of metal carbenoids has been widely studied[1] since the first report by Nozaki and co-workers that decomposition of ethyl diazoacetate in the presence of a copper(II) chiral Schiff base complex resulted in enantioselective cyclopropanation of styrene.[2] Although copper based catalysts are extremely effective in cyclopropanation reactions, dirhodium(II) compounds, first introduced by Teyssié and co-workers,[3] are generally superior catalysts for diazo compound decomposition since they mediate a wider range of carbenoid processes such as insertion.[4] Although enantioselective C–H insertion reactions using chiral dirhodium(II) carboxylates and carboxamidates as catalysts have been widely reported of late,[5] very few attempts to effect enantioselective carbenoid X–H (X = heteroatom) insertion have been described. Thus Brunner *et al.* observed up to 12% ee in the S–H insertion reaction of 3-diazo-2-butanone with thiophenol,[6] and McKervey has very recently described an intramolecular N–H insertion reaction which proceeds in 45% ee using dirhodium(II) mandelate as catalyst.[7] We have recently described some new chiral rhodium(II) carboxylates, and although our attempts to carry out asymmetric O–H insertion reactions have so far proven unsuccessful,[8] we now report that these same catalysts do effect asymmetric insertions into the Si–H bond, but that chiral dirhodium(II) carboxamidates give the highest level of enantiocontrol.

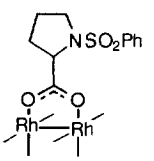
The rhodium(II) catalysed reaction of diazoesters with silanes resulting in the formation of α-silylcarbonyl compounds by Si–H insertion, was first reported in 1988,[9] although examples of copper catalysed processes had been described earlier.[10] The reaction has recently been the subject of renewed interest,[11] and diastereoselective Si–H insertion was achieved by using diazoesters of chiral alcohols with de's approaching 50%.[11b,12] We now find that enantioselective Si–H insertions can be effected by using chiral dirhodium(II) catalysts. Thus a dichloromethane solution of methyl diazophenylacetate and dimethylphenylsilane was treated with the catalyst to give the Si–H insertion product, methyl 2-(dimethylphenylsilyl)phenylacetate in good yield and in ee's that approached 50% (Table). A wide range of dirhodium(II) carboxylate and carboxamidate catalysts **1** - **12** was used (Figure): the known catalysts based on mandelic acid[13] and 1-benzenesulfonylproline, Rh_2(BSPRO)$_4$,[14] gave *ca.* 8 and 12% ee respectively, and our recently described catalysts based on phthalate half esters and 1-substituted pyrroles[8] also gave ee's in a similar range. Dirhodium(II) camphanate gave 15% ee, whereas the related camphenate ligand gave a poorer result.[15] The best results with a carboxylate ligand were obtained with a new catalyst, Rh_2(MTPA)$_4$, prepared from 2-methoxy-2-(trifluoromethyl)phenylacetic acid.[16]

In general carboxamidate ligands gave better results, although the reaction was considerably slower, the reaction mixture needing heating under reflux to produce slightly lower yields. The best catalyst was $Rh_2(MEPY)_4$[17] which gave ee's in the range 45-50%. The related MEOX[18] and MPPIM[19] carboxamidate ligands gave poorer results, though a significant improvement in ee was noted with the new azetidinone-4-carboxylate based catalyst, $Rh_2(IBAZ)_4$.[20] Noteworthy is the general pattern of enantiocontrol whereby dirhodium(II) catalysts whose ligands have the R-configuration yield the B-enantiomer predominantly while those whose ligands have the S-configuration produce the A-enantiomer in excess, although there are some exceptions to this.

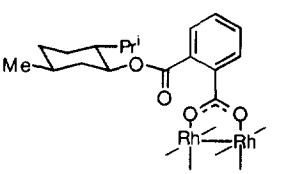
The achievement of catalytic asymmetric Si–H insertion using these diverse sets of chiral dirhodium(II) catalysts belies the mechanism for Si–H insertion that has been proposed by Landais.[11b] Cleavage of two Rh–ligand bonds, as has been suggested, would severely limit, if not eliminate, enantiocontrol that is maintained by chiral ligands on Rh(II). Instead, we suggest that Si–H insertion occurs in the same concerted fashion as has been demonstrated for C–H insertion reactions.[21] The higher reactivity of the Si–H bond towards insertion makes possible intermolecular insertion that is uncharacteristic of C–H insertion using the same catalysts, but this higher reactivity dictates an earlier transition state that limits catalyst control of enantioselectivity. That enantiomeric excesses approaching 50% are achieved encourages us to continue these studies with the expectation that barriers to highly enantioselective Si–H insertion can be overcome.



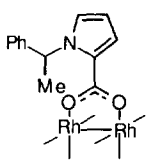
Rh_2(mandelate)$_4$
1



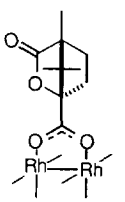
Rh_2(BSPRO)$_4$
2



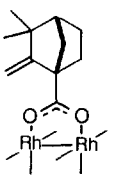
Rh_2(menthyl phthalate)$_4$
3



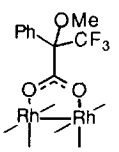
Rh_2[1-(1-phenylethyl)-pyrrole-2-carboxylate]$_4$
4



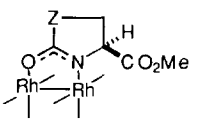
Rh_2(camphanate)$_4$
5



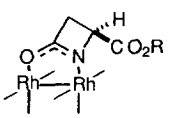
Rh_2(camphene-1-carboxylate)$_4$
6



Rh_2(MTPA)$_4$
7



8 Z = CH_2; Rh_2(5*S*-MEPY)$_4$
9 Z = O; Rh_2(4*S*-MEOX)$_4$
10 Z = $NCOCH_2CH_2Ph$; Rh_2(4*S*-MPPIM)$_4$



11 R = CH_2Ph; Rh_2(4*S*-BNAZ)$_4$
12 R = CH_2CHMe_2; Rh_2(4*S*-IBAZ)$_4$

Figure. Chiral dirhodium(II) catalysts (only one of the 4 bridging ligands is shown in each case).

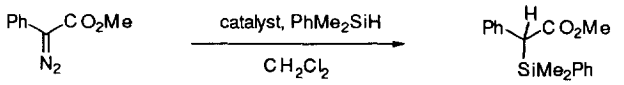


Table. Dirhodium(II) catalysed asymmetric Si–H insertion reactions of methyl 2-diazophenylacetate[a]

Catalyst	Yield / %	HPLC[b] ee / %	Major isomer[c]	Catalyst	Yield / %	HPLC[b] ee / %	Major isomer[c]
$Rh_2(OAc)_4$	93	-	-	**6**	89	6	B
(R)-**1**	86	8	B	(R)-**7**	80	31	B
(S)-**1**	88	7	A	(S)-**7**	73	23	A
(R)-**2**	77	12	B	(R)-**8**	70	45	B
(S)-**2**	75	9	A	(S)-**8**	69	47	A
(+)-**3**	91	10	B	(R)-**9**	67	28	B
(-)-**3**	90	10	A	(S)-**9**	65	25	A
(R)-**4**	88	8	A	(S)-**10**	31	9	B
(S)-**4**	87	8	B	(S)-**11**	38	14	A
5	84	15	A	(S)-**12**	71	30	B

[a]Reactions with carboxylate catalysts were performed at rt; those with carboxamidates occurred under reflux.
[b]HPLC Analysis carried out on a Chiralpak AD column using 0.1% 2-propanol in hexane at 0.5 mL/min, or on a WHELK-O column using 2% 2-propanol in hexane at 1.0 mL/min. Values for ee were confirmed by NMR spectroscopy using chiral shift reagents.
[c]Major isomer refers to the relative retention times on HPLC on the Chiralpak or WHELK-O columns: "A" is the first eluted peak on Chiralpak AD (t_R = 11.37 min) corresponding to the second eluted peak on WHELK-O (t_R = 7.48 min); "B" is the second eluted peak on Chiralpak AD (t_R = 12.36 min) corresponding to the first eluted peak on WHELK-O (t_R = 6.24 min).

Experimental Procedure

To a stirred solution of methyl 2-diazophenylacetate (100 mg, 0.57 mmol) in dry dichloromethane (2 mL) was added dimethylphenylsilane (85 mg, 0.63 mmol) followed by the chiral dirhodium(II) catalyst (2 mol%). The reaction mixture was stirred at room temperature or heated under reflux (see Table), the solvent was removed under reduced pressure to yield a green oil. This crude product was subjected to chromatography using light petroleum and ethyl acetate (19 : 1) as eluant to yield methyl 2-(dimethylphenylsilyl)phenylacetate as a colourless oil; (Found: M^+ 284.1235. $C_{17}H_{20}O_2Si$ requires 284.1232); ν_{max} (film)/cm^{-1} 3025, 2951, 2360, 1719, 1496, 1453, 1198 and 736; δ_H (400 MHz; $CDCl_3$) 7.39-7.35 (5H, m), 7.21-7.13 (5H, m), 3.60 (1H, s), 3.54 (3H, s), 0.35 (3H, s) and 0.32 (3H, s); δ_C (100.6 MHz, $CDCl_3$) 173.08, 135.97, 135.54, 134.01, 129.62, 128.37, 128.03, 127.68, 125.67, 51.26, 46.06, -4.10 and -4.50; *m/z* 284 (M^+, 13%), 151 (10), 135 (60), 118 (100), 105 (8), 90 (14), 77(4) and 43 (10).

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