

The Stereochemistry of the Oxidative Addition of Methyl Iodide to Rhodium(I) Complexes containing Chiral Diphosphines

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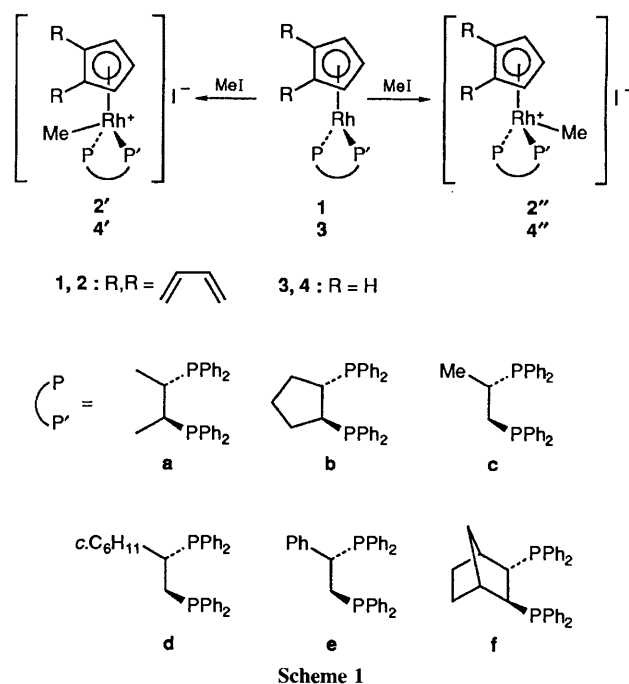
Complexes of the type [(L)Rh(Ph₂PCHR¹CHR²PPh₂)] (L = η⁵-cyclopentadienyl or η⁵-indenyl) rapidly react with methyl iodide to give the pseudotetrahedrally coordinated compounds [(L)Rh(Ph₂PCHR¹CHR²PPh₂)Me]I, in which the metal is a stereogenic centre; the extent of diastereoselectivity is complete in some cases and seems to be mostly dependent on steric factors due to the diphosphine ligand, not being substantially influenced by the η⁵-substituent.

Complexes of rhodium(I) of the type (η⁵-L')Rh(L₂) (L' = η⁵-cyclopentadienyl or η⁵-indenyl; L₂ = chiral diphosphine) have potential interest as chiral organometallic bases.¹ We have synthesized some chiral complexes of the general formula (η⁵-C₉H₇)Rh(Ph₂PCHR¹CHR²PPh₂)₂ (Scheme 1, **1**) and studied their dynamic behaviour by ³¹P NMR spectroscopy. When the chiral diphosphine lacks C₂ symmetry (R¹ ≠ R²) the complexes exist in two diastereoisomeric conformations; the relative concentration of the two conformers seems to be influenced by both the electronic and steric factors. Owing to their basic character the above compounds show an enhanced reactivity towards electrophiles, e.g. they react smoothly with methyl iodide.¹ In this reaction the geometry of the system is changed from formally planar³ to pseudotetrahedral (Scheme 1). Therefore, when a C₁ chiral diphosphine is the ligand two diastereoisomeric complexes may form depending on the direction of the attack of the incoming electrophile. This reaction can be considered to be the organometallic counterpart of the diastereoface differentiating reactions which can take place at trigonal carbon atoms.⁴ We report herein the first examples of asymmetric induction phenomena which can take place in such reactions.

The addition reaction of methyl iodide[†] was first tested on compounds **1a** and **1b** (Scheme 1), which contain the chiral C₂ diphosphines 1,2-dimethylethane-1,2-diylbis(diphenylphosphine)⁵ and *trans*-cyclopentane-1,2-diylbis(diphenylphosphine).⁶ The optical stability at the metal centre (at least on the NMR time scale) for the resulting complexes **2a** and **2b** may be inferred from the ³¹P NMR spectrum (room temperature, 81 MHz). Both complexes give a spectrum of eight lines corresponding to the two diastereotopic phosphorus atoms coupled with each other and with the ¹⁰³Rh nuclei. In the case of the compounds containing the C₁ diphosphines renorphos⁷ **1f** and phenphos⁸ **1e** the two expected diastereoisomeric complexes are formed in a molar ratio of 55:45 (**2'f**:**2''f**) and 80:20 (**2'e**:**2''e**), respectively; for **2e** the diastereoisomer with the larger difference in the ³¹P NMR chemical shift prevails (Table 1 and Scheme 1). By contrast, for the complexes of the

other C₁ ligands propfos⁹ and cycphos¹⁰ (**2c** and **2d**, respectively) only one eight-line system is visible in the ³¹P NMR spectrum, thus indicating that only one of the two possible diastereoisomers is formed. The largest difference in the population for the two conformers of the starting materials **1** (Table 1) was observed in the case of complex **1e**² (11:89 molar ratio at ca. 190 K, Table 1).

The oxidative addition reaction of methyl iodide to **1** (Scheme 1) appears to be irreversible. The product formed from **1f** and C²H₃I (labelled **2'f** and **2''f**) was dissolved in the presence of an excess of unlabelled methyl iodide. After 3 days no signal corresponding to the formation of the unlabelled diastereoisomeric methyl derivatives (δ 0.21 and 0.77) was identified in the ¹H NMR spectrum. Furthermore, we have been unable either to change the molar ratio between the diastereoisomers for **2e** and **2f** or to see the formation of the alternative diastereoisomer for **2c** and **2d** by thermal and reductive or oxidative means.¹¹



[†] Satisfactory elemental analyses were obtained for all new compounds. ³¹P NMR, δ (CD₂Cl₂): **2a**: 83.1 and 67.7 (dd, *J*_{PP} 39, *J*_{PRh} 146 Hz); **2b**: 60.8 and 40.1 (dd, *J*_{PP} 40, *J*_{PRh} 144 and 151 Hz); **2c**: 82.5 and 54.0 (dd, *J*_{PP} 32, *J*_{PRh} 144 and 149 Hz); **2d**: 83.1 and 52.2 (dd, *J*_{PP} 32, *J*_{PRh} 144 and 147 Hz); **2'e** (predominant diastereoisomer): 84.4 and 48.9 (dd, *J*_{PP} 34, *J*_{PRh} 144 and 149 Hz); **2''e** (less abundant diastereoisomer): 73.3 and 64.4 (dd, *J*_{PP} 34, *J*_{PRh} 144 and 149 Hz); **2'f** (predominant diastereoisomer): 59.2 and 37.3 (dd, *J*_{PP} 42, *J*_{PRh} 144 and 151 Hz); **2''f** (less abundant diastereoisomer): 50.2 and 44.7 (dd, *J*_{PP} 39, *J*_{PRh} 146 and 151 Hz); **4a**: 82.8 and 73.7 (dd, *J*_{PP} 34, *J*_{PRh} 139 and 142 Hz); **4b**: 61.7 and 44.2 (dd, *J*_{PP} 44, *J*_{PRh} 142 and 147 Hz); **4c**: 85.3 and 59.3 (dd, *J*_{PP} 34, *J*_{PRh} 142 and 144 Hz); **4d**: 85.2 and 57.5 (dd, *J*_{PP} 36, *J*_{PRh} 142 and 146 Hz); **4'e** (predominant diastereoisomer): 87.4 and 54.0 (dd, *J*_{PP} 36, *J*_{PRh} 142 Hz); **4''e** (less abundant diastereoisomer): 75.7 and 66.1 (dd, *J*_{PP} 37, *J*_{PRh} 144 Hz); **4'f** (predominant diastereoisomer): 53.4 and 49.3 (dd, *J*_{PP} 44, *J*_{PRh} 144 and 149 Hz); **2'f** (less abundant diastereoisomer): 64.6 and 38.5 (dd, *J*_{PP} 44, *J*_{PRh} 144 and 149 Hz).

Table 1 Diastereoisomeric ratio^a for complexes **1**, **2** and **4**

	c	d	e	f
1b	37:63	45:55	89:11	36:64
2	~100:0	~100:0	80:20	55:45
4	~100:0	~100:0	85:15	41:59

^a Ratio of diastereoisomers having the larger difference in the chemical shifts of the ³¹P NMR signal to diastereoisomers with the smaller difference. ^b Thermodynamic equilibrium at ca. 190 K.

The analogous cyclopentadienyl compounds **3** give the same oxidative addition reaction, as expected.¹ The diastereoselectivity of the reaction appears to be very similar to that observed in the indenyl case (Table 1). Only one diastereoisomer is formed for **4c** and **4d**; for **4f** the diastereoisomeric ratio is close to 1 : 1, whereas for **4e** again the diastereoisomer with the largest difference in the ³¹P NMR chemical shift prevails (*ca.* 85 : 15).

The non-reversibility observed for the oxidative addition of methyl iodide most probably implies that the diastereoselectivity observed during the reaction is kinetically controlled, unless strange mechanisms are involved in the epimerization at the metal atom. The very similar stereochemical outcome observed both for the cyclopentadienyl and for the indenyl derivatives suggests that the diastereoselectivity is overwhelmingly determined by the properties of the diphosphine ligand and does not seem to be consistently influenced by the η⁵-ligand.

Previous investigations on the structurally related cyclopentadienyl ruthenium diphosphine complexes [(η⁵-C₅H₅)Ru(Ph₂PCHR¹CHR²PPh₂)X] (X = Cl, Me, CH₂CH₂Ph *etc.*) have shown that the differences in the chemical shift of the phosphorus atoms for a pair of diastereoisomers could be related to the geometry at the metal atom,¹² the larger difference (*ca.* 20–30 ppm) corresponding to the *ul*-diastereoisomer³ (based on the X-ray crystal structure determination of some compounds for which R¹ = H, R² = Me). If this regularity is maintained for the complexes under examination, then the diastereoisomer prevailing formed for **2c**, **2d**, **2e** and for **4c**, **4d**, **4e** is the same (possibly also in these cases the *ul*-diastereoisomer). This geometry would arise from an attack at the metal by the electrophile from the direction opposite to that of the substituent on the chelate ring of the diphosphine ligand and would be understandable on the basis of steric considerations. In fact, the very low diastereoselectiv-

ity in the formation of **2f** and **4f** can also be understood in the same way. The smaller diastereoselectivity observed for the complexes containing phenphos ligand with respect to that observed for the analogous prophos and cycphos containing compounds, however, shows that electronic factors as well as steric ones influence the stereochemical outcome of this oxidative addition. Attempts to produce crystals suitable for a X-ray structure determination leading to an unambiguous assignment of the geometry at the metal are underway.

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