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Preliminary communication

On the stereochemistry of chiral (η^5-C_9H_7)Rh(diphosphine) complexes

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Abstract

The dynamic behaviour of some indenyl complexes of the type (η^5-C_9H_7)Rh($Ph_2PCHRCHR'PPh_2$) (R = or ≠ R′) has been investigated, and the relevant energy barrier involved evaluated (10–11 kcal/mol). For the complexes in which the diphosphine has a C_1 symmetry (R ≠ R′), the energy differences between the two diastereomeric conformations seem to depend on both steric and electronic factors.

Asymmetric induction phenomena in chiral transition metal complexes containing poly-hapto ligands and having Lewis acid properties have recently attracted much interest [1]. These compounds can be used as template for stereospecific transformation of organic ligands [2,3] and have potential as chiral catalysts [4–6]. Despite the growing interest in the chemistry of half-sandwich electron-rich organotransition metal compounds [7] the potential of their optically active counterparts as asymmetric base catalysts has never been investigated. Very little attention, if any, has been given to the stereochemistry of these compounds [7].

We report here the synthesis, NMR characterization, and extent of asymmetric induction for some complexes containing chiral diphosphines of the type (η^5-C_9H_7)Rh($Ph_2PCHRCHR'PPh_2$), **1** (C_9H_7 = indenyl). Homologous achiral (or racemic) complexes have been found to be very basic [7] and to show a marked propensity to ring slippage (allyl-ene structure) [8–13] which holds promise for rate enhancement [14,15] of both stoichiometric and catalytic reactions. The chiral complexes **1** have been synthesized, as previously described [16], through exchange reactions of the parent bisethylene complex with the appropriate diphosphine, **2**

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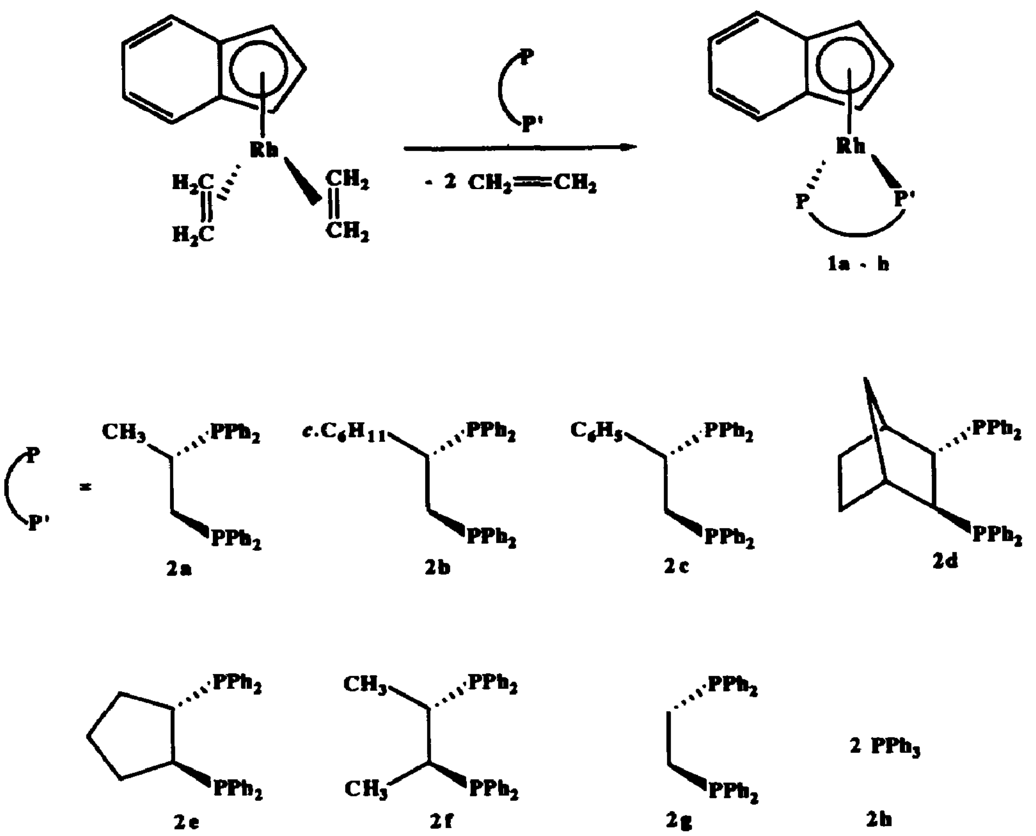

Scheme 1

(Scheme 1) [17*]. For purposes of comparison, the known compounds containing 1,2-ethanediyl-bis(diphenylphosphine), **1g**, [16,18] and triphenylphosphine, **1h**, [16] were also investigated. The complexes were characterized by multinuclear NMR spectroscopy, and, their dynamic behaviour investigated by variable temperature ^{31}P-NMR spectroscopy [19*]. The ^{31}P spectra of complexes **1g** and **1h** show a doublet arising from the two equivalent phosphorus atoms coupled with ^{103}Rh. The spectrum does not show any change when the temperature is lowered from ambient to 173 K, as would be expected [20] in terms of the assumption of a ground state structure in which the RhL_2 unit straddles the symmetry plane of the rhodium-indenyl unit. A pyramidal geometry (Fig. 1, **3** or **4**) can be assumed only if either of the diastereomeric conformations (**3** or **4**) is strongly predominant. The asymmetry of the complexes **1e** and **1f**, which contain ligands having C_2 symmetry, is clearly reflected in the anisochronicity of C^1 and C^3 (Fig. 2) in the ^{13}C-NMR spectrum at room temperature. However, under these conditions the ^{31}P-NMR spectrum shows only a doublet arising from coupling with ^{103}Rh. Lowering of the temperature to about 173 K reveals the expected anisochronicity of the two phosphorus atoms, which now give rise to an 8-line system for both compounds. The coalescence temperature is 237 K for **1f** and 244 K for **1e** at 81 MHz. The activation barrier for

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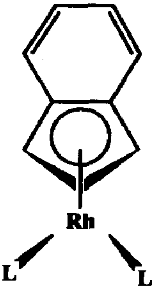
* Reference number with asterisk indicates a note in the list of references.



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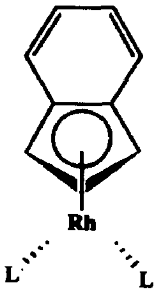

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Fig. 1. Structural formulas of **3** and **4**.

the fluxional phenomenon observed is in the range of 10–11 kcal/mol and therefore fully comparable with values found for the chiral racemic complexes of the type (η^5-1-CH_3-Ind)RhL_2 (L = phosphine ligand) [20]. The ^{31}P-NMR spectra of compounds **1a–d** at room temperature consist of 8-line patterns arising from non-equivalent phosphorus atoms coupled with ^{103}Rh. These patterns change at low temperature to pairs of 8-line patterns of unequal heights.

Clearly, when the chiral ligand has C_1 symmetry the non-rigid behaviour previously described gives rise to two diastereomeric conformations. The diastereomeric ratio at the thermodynamic equilibrium at ~ 190 K is 63 : 37 ($\Delta G° = 200$ cal/mol) for **1a**, 55 : 45 ($\Delta G° = 75$ cal/mol) for **1b**, 11 : 89 ($\Delta G° = 790$ cal/mol) for **1c** and 64 : 36 ($\Delta G° = 216$ cal/mol) for **1d**. These values are comparable with those found for the pseudotetrahedral complexes of formula (η^5-C_5H_5)Ru(diphosphine)Cl [21] that contain the same chiral diphosphine ligands (**2a–c**) and in which the metal is a chirogenic center, but there are different features. For many ruthenium complexes of this type [4] containing the ligand **2a** it was found that without exception the *ul*-diastereomers [22] exhibit differences in ^{31}P chemical shifts for the two phosphorus atoms that are larger than those for the *l*-diastereomers. For most complexes the resonances of the *l*-diastereomer actually fall between the two resonances arising from to the other diastereomer. A similar feature is also apparent for the rhodium complexes studied in the present work, and might imply that the predominant diastereomer for **1a**, **1b** and **1d** is the opposite of that for **1c**. In any case, the extent of asymmetric induction appears to be influenced by both steric and electronic factors. For the previously mentioned chiral racemic (η^5-1-CH_3-Ind)RhL_2 [20] compounds a ground state geometry was assumed in which the plane bisecting the C^1–C^2–C^3 angle is perpendicular to the chelation plane P–Rh–P. The dynamic behavior of these species was ascribed to the rotation of the indenyl ligand which is slowed down as the temperature is lowered. Our observation of the anisochronicity

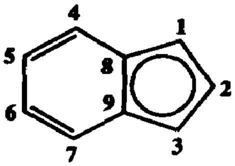

Fig. 2. Numbering scheme of indenyl ligand.

for C^1 and C^3 in the complexes **1e** and **1f** allows us to rule out mechanisms involving dissociation of the indenyl ligand, which might appear improbable but are not impossible [15]. These complexes tend to assume a geometry in which the RhL_2 moiety is displaced from the center of the five-membered ring toward an η^3-bonding mode, as indicated by the chemical shift of the ^{13}C signals [23*] from the five-membered ring of the indenyl ligand [11]. This would imply a "pyramidal" rather than a "planar" geometry [24,25]. Thus an inversion at the pseudotetrahedral rhodium atom (similar to that well known for EX_3 compounds [26]) could also account for the observed non-rigid behaviour. Since the stereochemical consequences of the two possible dynamic processes are the same (i.e., epimerization at the level of the plane of chirality [27], which can be identified with the coordination plane P^1–Rh–P^2), we cannot at present decide between the two alternatives.

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J_{P-Rh} 219, J_{P-P} 48; (minor diastereomer) δ 84.5, J_{P-Rh} 218, J_{P-P} 48 and δ 57.9, J_{P-Rh} 214, J_{P-P} 49. **1a** (in $C_7{}^2H_8$): δ 83.2, J_{P-Rh} 220, J_{P-P} 46 and δ 65.2, J_{P-Rh} 220, J_{P-P} 46; (major diastereomer) δ 78.6, J_{P-Rh} 212, J_{P-P} 49 and δ 63.8, J_{P-Rh} 222, J_{P-P} 49; (minor diastereomer) δ 83.7, J_{P-Rh} 220, J_{P-P} 49 and δ 59.9, J_{P-Rh} 215, J_{P-P} 49.

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