Chiral rhodium complexes as catalysts in Diels–Alder reactions

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The first rhodium enantioselective catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene are described; the molecular structure of the catalyst precursor [(η^5-C_5Me_5)Rh(*R*-Prophos) (H_2O)] [SbF_6]$_2$ is also presented.

The use of asymmetric catalysis in organic synthesis[1] is one of the most interesting topics in organic chemistry. Diels–Alder reactions are classical pattern reactions that play an important role in the construction of complicated molecules with stereochemical control. In this context, very impressive results have recently been reported for enantioselective Diels–Alder reactions catalysed by chiral Lewis acids.[2] Titanium, aluminum and boron based catalysts with chiral ligands have produced the best results to date although, very recently, some transition-metal and lanthanide complexes have been described as promising catalysts for these reactions.[3] In spite of the interest, versatility and excellent results obtained in numerous organic reactions when rhodium complexes are used as catalysts,[4] to the best of our knowledge, rhodium derivatives have never been used in enantioselective Diels–Alder reactions.

Following our studies on transition metal complexes with chiral metal centres,[5] we have prepared the aquo-compounds [(η^5-C_5Me_5)Rh(*R*-Prophos)(H_2O)]A$_2$ [*R*-Prophos = (*R*)-(+)-1,2-bis(diphenylphosphino)propane; A = BF_4 (**1**), SbF_6 (**2**)], in 90% isolated yield, by treating the corresponding solvato-complexes[6] [(η^5-C_5Me_5)Rh(Solvent)$_3$]$^{2+}$ with *R*-Prophos.† The synthetic procedure is diastereoselective. From room temperature to 183 K there is no evidence from either the ^{1}H or ^{31}P NMR spectra for the presence of the two possible diastereoisomers. Fig. 1 shows the molecular structures of the cation of compound **2**, which was determined by diffractometric means.‡ The rhodium atom is pseudo-octahedral being coordinated to an η^5-C_5Me_5 ring, to the two phosphorus atoms of the *R*-Prophos ligand, and to the oxygen of a water molecule. A second water molecule solvated the cation through an O(1)–H···O(2) hydrogen bond. The rhodium atom has *S* absolute configuration[7] and the metallacycle Rh–P–C–C–P presents a slightly twisted envelope conformation [q_2 = 0.500(2) Å, Φ_2 = 111.2(4)°][8] with the C(24) out of the plane. The chirality descriptor of the ring conformation is λ.[9]

NOE difference spectra support that the $S_{Rh}R_C$ configuration of the cationic complex [(η^5-C_5Me_5)Rh(*R*-Prophos)(H_2O)]$^{2+}$ and the λ conformation of the Rh–P–C–C–P metallacycle are retained in solution.

When dissolved in dichloromethane, complexes **1** and **2** catalyse the Diels–Alder reaction between methacrolein and cyclopentadiene (Table 1).§ The reaction occurs rapidly at room temperature (99% conversion in 50 min.), the system operating at low catalyst loading (1 mol%) but with poor enantioselectivity (entries 2 and 3). As can be seen from entries 4 and 5, the stereoselectivity was slightly improved by increasing the catalyst ratio to 5 mol%. Good *exo*:*endo* selectivity (≥93:7) and moderate to good enantioselectivities were observed

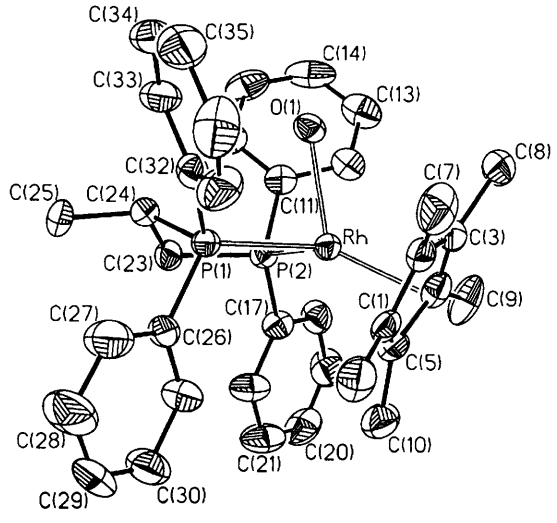
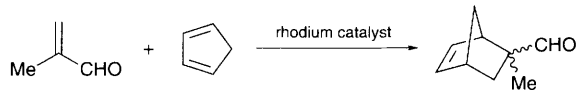


Fig. 1 A perspective drawing of the cation of complex **2** (Thermal ellipsoids at 30% probability). Selected bond distances (Å) and angles (°): Rh–P(1) 2.324(2), Rh–P(2) 2.342(2), Rh–O(1) 2.187(5), Rh–C(C_5Me_5) 2.165(9)–2.232(9), Rh–G(centroid C_5Me_5) 1.854(8); P(1)–Rh–P(2) 84.1(1), P(1)–Rh–O(1) 82.0(1), P(2)–Rh–O(1) 86.9(1), P(1)–Rh–G 131.4(3), P(2)–Rh–G 131.8(3), O(1)–Rh–G 124.1(3).

Table 1 Enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene catalysed by complexes **1** and **2** in dichloromethane



Entry	Catalyst (molar ratio)	H/C_5H_5 Metha-crolein	*T*/°C[a]	*t*/h	Yield (%)	Isomer ratio (*exo*:*endo*)	Ee[b] (%)
1	—	—	RT	1	0.5	—	—
2	**1** (1%)	1/1	RT	1.5	81	82:18	—
3	**1** (1%)	6/1	RT	0.83	99	83:17	5 (*R*)
4	**1** (5%)	1/1	RT	3	78	85:15	9 (*R*)
5	**1** (5%)	6/1	RT	0.83	97	85:15	10 (*R*)
6	**1** (5%)	6/1	−20	144	65	94.5:5.5	28 (*R*)
7	**1** (5%)	20/1	−20	48	88	93:7	27 (*R*)
8	**1** (10%)	6/1	−20	72	77	95:5	46 (*R*)
9	**1** (10%)	6/1	−50	168	49	98:2	52 (*R*)
10	**2** (5%)	6/1	−20	24	87	97.5:2.5	62 (*R*)
11	**2** (10%)	6/1	−20	3	65	97:3	60 (*R*)
12	**2** (10%)	6/1	−50	27	73	98:2	71 (*R*)

[a] RT = room temp. [b] Absolute configuration at C_2.

operating at lower temperatures, the major product being (1*S*, 2*R*, 4*S*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde. Inspection of the entries 6, 8 and 9 *vs.* 10, 11 and 12, respectively, reveals that the Diels–Alder reaction of these substrates were significantly improved, in both rate and enantioselectivity of the major *exo* adduct, by using as catalyst the SbF_6^- derivative **2**, instead of the BF_4^- complex **1**. In this respect, dramatic counterion effects, that improved the rate and the level of asymmetric induction of chiral bis(oxazoline) copper(II) complexes towards enantioselective Diels–Alder reactions, have been recently reported by Evans *et al.*[3c]

The ^{31}P NMR spectrum, in CD_2Cl_2 of freshly prepared 20/1 molar mixtures of methacrolein/**1**, at −60 °C, showed the presence of two 'Rh(*R*-Prophos)' containing compounds, in *ca.* 80/20 molar ratio. The major component of the mixture was complex **1** and we, tentatively, attributed to $[(\eta^5\text{-}C_5Me_5)Rh(R\text{-Prophos})(methacrolein)]^{2+}$ the remaining signals [δ 52.3 (dd, $^1J_{Rh,P}$ 133.8, $^3J_{P,P'}$ 40.7 Hz; the signals due to the P atom closer to the *R*-Prophos Me group[10] are masked by the corresponding peaks of compound **1**]. The subsequent addition of cyclopentadiene (methacrolein : cyclopentadiene, 1 : 2) produced the disappearance of the peaks assigned to the methacrolein complex, in the ^{31}P NMR spectrum. The only observable compound during the catalysis was complex **1**.¶ As catalysis was taking place in these conditions, we assume that the rate of the processes, in which the complexes of the catalytic cycle were involved, avoid their NMR observations in the range of temperatures investigated (from room temperature to 183 K). Comparable results were obtained for **2**, the most important variation being that the molar ratio **2** : methacrolein complex was reduced to 68 : 32, this change probably accounting for the greater rate observed when compound **2** was used as catalyst precursor. According to these data, the real catalyst was present in a very low concentration (0.20[**1**] or 0.32[**2**]) consequently being a very active catalyst for the Diels–Alder process.

The absolute configuration of the major *exo* product suggest that the corresponding transition state resembles the structure depicted in Fig. 2. The dienophile, coordinated to the $S_{Rh}R_C$ diastereoisomer, is in the preferred *S-trans* conformation and the diene approaches the alkene *Si* face. The *Re* face is shielded by the methyl groups of the C_5Me_5 ligand. The attack of the dienophile to the deshielded *Re* face of the conformer formally obtained by a 180 °C rotation of the aldehyde around the M–O bond is desfavored due to the severe steric hindrance of the Ph_3 phenyl ring.

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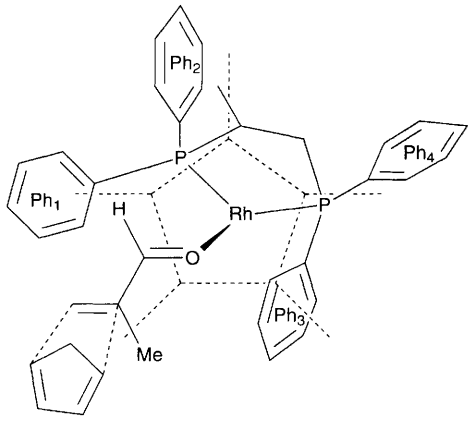

Fig. 2 Model of the transition state

Footnotes

† *Selected spectroscopic data* for **1**: ^1H NMR (300 MHz, CD_2Cl_2, 20 °C, Me_4Si); δ 1.43 (pt, $^4J_{P,H}$ 3.3 Hz, 15 H, C_5Me_5) and 3.5 (br, s, 2 H, H_2O); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C, H_3PO_4): δ 76.4 (dd, $^1J_{Rh,P_1}$ 129.7, J_{P_1,P_2} 40.7 Hz) and 47.1 (dd, $^1J_{Rh,P_2}$ 132.6 Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 20 °C, Me_4Si): δ 9.5 (s, $C_5\mathit{Me}_5$) and 106.4 (bs, C_5Me_5); IR(Nujol): ν cm^{-1} 3550 and 1628 (H_2O). For **2**: ^1H NMR (300 MHz, CD_2Cl_2, 20 °C, Me_4Si): δ 1.40 (pt, $^4J_{P,H}$ 3.2 Hz, 15 H, C_5Me_5) and 3.0 (br, s, 2 H, H_2O); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C, H_3PO_4): δ 78.0 (dd, $^1J_{Rh,P_1}$ 129.7, J_{P_1,P_2} 40.7 Hz) and 49.1 (dd, $^1J_{Rh,P_2}$ 130.6 Hz); IR (Nujol): ν cm^{-1} 3540 and 1610 cm^{-1} (H_2O). Satisfactory elemental analysis (C,H).

‡ *Crystal data* for **2**·H_2O: $C_{37}H_{43}F_{12}OP_2RhSb_2{\cdot}H_2O$, M = 1158.1, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.688(2), b = 16.146(2), c = 25.421(2) Å, U = 4387(1) $Å^3$, Z = 4, D_c = 1.753 g cm^{-3}, μ = 1.75 mm^{-1}, $F(000)$ = 2272, graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collected in a Siemens-Stoe diffractometer. 9499 ref. collected, 8589 unique, 8577 used in the refinement. A psi-scan absorption correction applied. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares on F^2 techniques. Anisotropic displacement parameters used for all atoms except one disordered SbF_6^- group. Hydrogens included in calculated (C_5Me_5, Ph's and diphosphine) or found positions (coordinated H_2O). Final R_1 = 0.0729, wR_2 = 0.1029 (SHELXL93, all data). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/65.

§ Catalytic Diels–Alder reaction of methacrolein with cyclopentadiene: A solution of the corresponding catalyst (0.005, 0.025 or 0.05 mmol) in 2 ml of dry CH_2Cl_2 was prepared under argon at the appropriate temperature. The dienophile (0.5 mmol in 2 ml of CH_2Cl_2) and freshly distilled cyclopentadiene (0.5, 3 or 10 mmol in 2 ml of CH_2Cl_2) were added consecutively by syringe. The resulting solution was stirred, at the reaction temperature, until the dienophile was consumed (GC). Yields and *exo*/*endo* ratios were determined by GC analysis. The reaction mixture was concentrated and filtered through silica gel (AcOEt as eluent for **1**, and $CHCl_3$ for **2**) before the determination of the enantiomeric purity. Enantiomeric excesses were determined by ^1H NMR spectroscopy in the presence of the chiral shift reagent Eu(hfc)$_3$. The configuration of the major adduct was assigned by comparing the sign of $[\alpha]_D$ with that in the literature.[11]

¶ Small amounts of the hydrido complex $[(\eta^5\text{-}C_5Me_5)RhH(R\text{-Prophos})]^{2+}$ were observed: δ −12.2 (dt, $^1J_{Rh,H}$ 36, $^2J_{P,H}$ 24 Hz).

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