Ruthenium(II) Complexes with the Atropisomeric Diphosphine 2,2'-Bis(diphenylphosphino)-6,6'-dimethylbiphenyl in the Enantioselective Hydrogenation of Pentane-2,4-dione†

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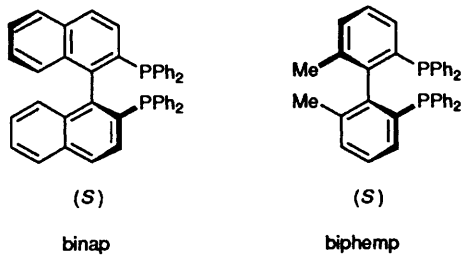
The five-co-ordinate complex $[RuCl_2(PPh_3)\{(S)\text{-biphemp}\}]$ [(*S*)-biphemp = (*S*)-2,2'-bis(diphenylphosphino)-6,6'-dimethylbiphenyl] reacts with pentane-2,4-dione (Hacac) in the presence of NEt_3 to give $[RuCl(acac)(PPh_3)\{(S)\text{-biphemp}\}]$, which has been isolated in the solid state. The reaction of the chlorohydride $[RuHCl(PPh_3)\{(S)\text{-biphemp}\}]$ with Hacac gives $[RuH(acac)(PPh_3)\{(S)\text{-biphemp}\}]$ and eventually $[Ru(acac)_2\{(S)\text{-biphemp}\}]$, which were identified spectroscopically. The relevance of the formation of these new species to the enantioselective hydrogenation of 2,4-diketones to the corresponding diols has been studied by testing $[RuCl_2(PPh_3)\{(S)\text{-biphemp}\}]$ and some of its derivatives as catalyst precursors, also in connection with the use of modifiers such as anhydrous HCl, PPh_3, chloride ions, NEt_3 and HBF_4. The hydrogenation reaction has also been followed under ambient conditions by means of ^{31}P and ^1H NMR spectroscopy. The activity and selectivity data confirm that for optimum efficiency two chloride ligands must be present in the catalyst precursor. These data are discussed in view of the assessment of a possible reaction pathway for the catalytic reaction.

In recent years the development of ruthenium(II) complexes based on the atropisomeric diphosphine 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap)[1] has given a strong impulse to the field of enantioselective catalysis. As some of the first reported syntheses of the catalyst precursors[2] have been found to be either troublesome or not generally applicable,[3b] much effort has been directed both to improving the published procedures[4a,b] and to preparing new catalyst precursors containing either binap[4c-g] or similar atropisomeric ligands,[3,5] also in order to enlarge the scope of the reactions. The hydrogenation of a large number of functionalized olefins and ketones has been achieved by using the carboxylato complexes $[Ru(O_2CMe)_2(P\text{–}P)]$, where P–P is binap[1] or 2,2'-bis(diphenylphosphino)-6,6'-dimethylbiphenyl (biphemp).[3a,b] However, it has been recognized that halogen-containing ruthenium complexes are necessary in order to achieve efficient enantioselective reduction of the less basic ketones with oxygen-containing groups such as diketones, hydroxy ketones or keto esters.[4b-f,6] A convenient catalytic system has been obtained from the *in situ* reaction of the acetato species $[Ru(O_2CMe)_2(P\text{–}P)]$ (P–P = biphemp[3] **1a** or binap[6a,b] **1b**) with methanolic HCl. Also, the solvento complex $[RuCl_2(MeCN)_2(binap)]$ has been prepared by displacement of the benzene ligand from $[RuCl(\eta^6\text{-}C_6H_6)(binap)]Cl$ with an excess of acetonitrile, and tested in the hydrogenation of methyl 3-oxobutanoate.[6e]

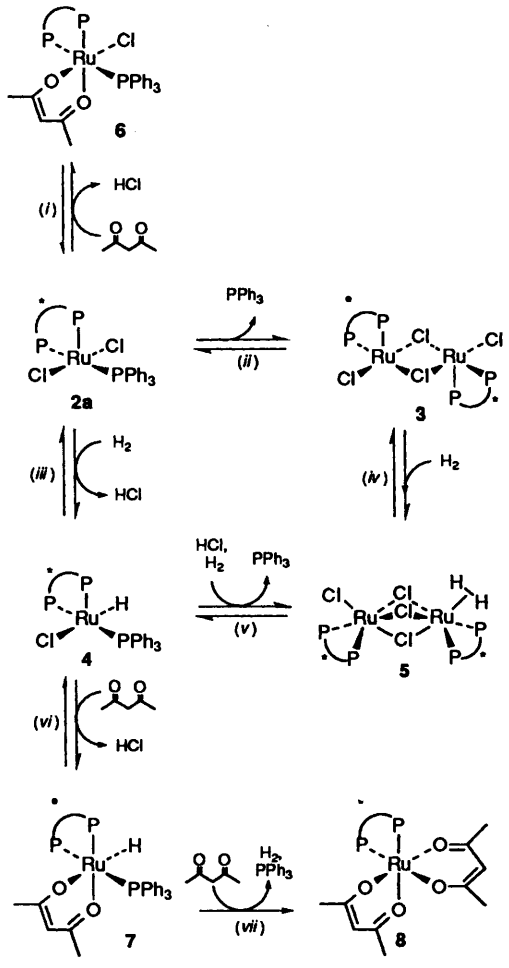
We succeeded in isolating the dichloro complex $[RuCl_2(PPh_3)\{(S)\text{-biphemp}\}]$ **2a**[3c,7] and its binap analogue $[RuCl_2(PPh_3)\{(S)\text{-binap}\}]$ **2b** in high yield.[7] Both species have a five-co-ordinate, square-pyramidal structure with a meridional arrangement of the P atoms. Complex **2a** partially dissociates the PPh_3 ligand yielding the binuclear species $[\{(S)\text{-biphemp}\}ClRu(\mu\text{-}Cl)_2RuCl\{(S)\text{-biphemp}\}]$ **3** [(*ii*), Scheme 1]. A DANTE (delays alternating with nutation for tailored excitation) experiment furnished evidence of fast exchange between free and co-ordinated PPh_3, which probably occurs *via* the non-detectable four-co-ordinate species $[RuCl_2\{(S)\text{-biphemp}\}]$.[7] Recently, James and co-workers[8] reported the synthesis of complex **2b**. Although ruthenium(II) complexes containing both an unidentate phosphine and a bidentate diphosphine are still relatively uncommon,[9] it is widely recognized that the size of the chelate ring is pivotal in stabilizing five-co-ordinate species.[10] Five-co-ordination is achieved with diphosphines which form a seven-membered chelate ring, such as 1,4-bis(diphenylphosphino)butane (dppb) or 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop). The resulting complexes can be either monomers such as $[RuCl_2(PPh_3)(dppb)]$,[10c] or binuclear species as in the case of $[(P\text{–}P)Cl_2Ru(\mu\text{-}P\text{–}P)RuCl_2(P\text{–}P)]$ (P–P = dppb[10a] or diop[10b]). Also, the size of the halide ligand has been shown to play a significant role in stabilizing five-co-ordinate species in co-operation with the steric hindrance due to the diphosphine ligand.[11]



(*S*) binap (*S*) biphemp

Preliminary results showed that complex **2a** catalyses the enantioselective hydrogenation of pentane-2,4-dione (Hacac) with efficiency and selectivity comparable to those of the system prepared *in situ* from **1b** and HCl.[6a,c] Moreover, the system based on **2a** allows the isolation of the monohydrogenated product 4-hydroxypentan-2-one in good yield.[3c] This prompted us to investigate the solution chemistry of **2a** further, and we

† *Non-SI units employed:* bar = 10^5 Pa, atm = 101 325 Pa.



Scheme 1

found out that it splits molecular hydrogen heterolytically yielding the chlorohydride [RuHCl(PPh$_3$){(*S*)-biphemp}] **4** (Scheme 1). The formation of **4** is quantitative when a base such as NEt$_3$ is added.[7] Under hydrogen pressure (300 bar), complex **2a** forms the binuclear, molecular hydrogen complex [{(*S*)-biphemp}ClRu(μ-Cl)$_3$Ru(η^2-H$_2$){(*S*)-biphemp}] **5** with loss of PPh$_3$. In an attempt to cast some light on the species which are possibly involved in the catalytic hydrogenation of 1,3-diketones, we have been investigating the reactivity of **2a**, isolated some of its derivatives and tested them in the reduction of Hacac. Moreover, the catalytic reaction was followed by ^{1}H and ^{31}P NMR spectroscopy. In this paper we report on the results of these investigations.

Results

Reactivity of Complexes **2a** *and* **4** *with Pentane-2,4-dione.*— When complex **2a** is dissolved in MeOH–CD$_2$Cl$_2$ (1:1) in the presence of an excess of Hacac, equilibrium (*i*) (Scheme 1) is established, as can be observed by variable-temperature ^{1}H and ^{31}P NMR spectroscopy (see below). In CD$_2$Cl$_2$ or in C$_6$D$_6$, equilibrium (*i*) is shifted to the left, as can be inferred from the ^{31}P NMR spectrum which shows only the signals of **2a**. Addition of a base (NEt$_3$) to the solution shifts the equilibrium quantitatively toward the formation of the acetylacetonato species [RuCl(acac)(PPh$_3$){(*S*)-biphemp}] **6**. No further reaction is observed over 24 h after saturating the solution with hydrogen under ambient conditions. It has been proposed that the chelation of the substrate plays an important role in the stereochemical outcome of the catalytic hydrogenation of 1,3-diketones.[6a,c] As the formation of β-diketonato complexes of ruthenium(II) is facile,[12] the role of the acetylacetonato species **6** in the catalytic hydrogenation of Hacac remained to be elucidated.[13] Treatment of **2a** with excesses of Hacac and NEt$_3$ in ethanol yielded an air-stable, yellow precipitate analysing as [RuCl(acac)(PPh$_3$){(*S*)-biphemp}] **6**. The formulation of **6** is supported by its FAB mass spectrum, which displays peaks at *m/z* 1013 and 786. The presence of an *O,O'*-co-ordinated, bidentate acac ligand is suggested by the IR spectrum (KBr). The carbonyl modes ν(C···O) are assigned at 1580 and 1403 cm^{-1}, and a strong band at 1514 cm^{-1} is attributed to the C···C stretching coupled with δ(C–H).[14] No bands are present in the non-co-ordinated carbonyl region (1690–1620 cm^{-1}), ruling out the possibility of a *C*-bonded acac ligand.

The ^{1}H, ^{13}C and ^{31}P NMR spectra of complex **6** (0.1 mol dm^{-3} CD$_2$Cl$_2$ solution) are temperature dependent. At room temperature, the methyl groups of the acac ligand appear as two resolved, broad singlets at δ 1.11 and 1.40, and the internal proton appears at δ 4.22 as a broad signal. A single signal at δ 0.64 is observed for the methyl groups of (*S*)-biphemp, which is split up into two singlets (δ 0.60 and 0.47) by lowering the temperature to −40 °C. The acac signals also sharpen up at low temperature. The presence of an acac ligand is confirmed by the ^{13}C-{^{1}H} spectrum at −40 °C, which displays two signals at δ 185.0 and 185.5, attributed to the two inequivalent carbonyl C atoms, and a signal at δ 99.7 for the methine C atom. The acac methyl groups are observed at δ 18.4 and 21.3. In agreement with the dynamic process suggested by the ^{1}H and ^{13}C NMR spectra, the room-temperature ^{31}P NMR spectrum indicates that **6** (broadened ABC system in the range δ 20–40) dissociates PPh$_3$ (broad signal centred at δ −5.0), albeit to a very low extent, at a rate detectable on the NMR time-scale. An additional, low-intensity ABCD system can be attributed to the chloro-bridged dimer [{(*S*)-biphemp}(acac)Ru(μ-Cl)$_2$Ru(acac){(*S*)-biphemp}],* which has a precedent in the literature as the PPh$_3$ analogue [{RuCl(acac)(PPh$_3$)$_2$}$_2$].[12c] All the signals sharpen up by lowering the temperature as the exchange between free and co-ordinated PPh$_3$ becomes slower. A resolved ABC system is obtained at −40 °C, whose large ^2J(PP) of 353.9 Hz indicates a meridional arrangement of the P atoms.[15] As the metal centre in **6** is stereogenic, the presence of a single ABC pattern shows that only one diastereoisomer is present. Also, the intensity of the signal corresponding to that of free PPh$_3$ decreases at low temperature since the dissociation of PPh$_3$ is depressed. Similar processes involving dissociation of the bulky PPh$_3$ ligand have been observed both for five- and six-co-ordinate complexes with biphemp.[7] In all these instances one diastereoisomer is overwhelmingly preferred over the other one, which causes the reversible addition of PPh$_3$ to occur stereoselectively.

As for the dichloro species **2a**, the reactivity of the chlorohydride **4** with Hacac was briefly investigated in view of its relevance to catalysis. When a CD$_2$Cl$_2$ solution of complex **4** is treated with equimolecular amounts of Hacac and NEt$_3$, [RuH(acac)(PPh$_3$)(biphemp)] **7** is initially formed [(*vi*), Scheme 1].† As for **6**, the presence of a single ABX pattern in the ^{31}P NMR spectrum indicates that only one diastereoisomer is formed. The presence of a hydride ligand is confirmed by a pseudo-quartet at δ −16.81 in the high-field ^{1}H NMR spectrum. The *J*(PH) coupling constants of about 25 Hz indicate that the hydride ligand is *cis* to all three P atoms, which supports the meridional geometry of the complex. However, attempts to isolate pure **7** failed, as it reacts further with Hacac according to (*vii*), probably by the elimination of molecular hydrogen (and PPh$_3$). Two singlets at δ 54.7 and 53.9 appear in

* ^{31}P NMR data (101 MHz, solvent C$_6$D$_6$, 293 K): ABCD system, δ$_A$ 42.6, δ$_B$ 51.7, δ$_C$ 59.7, δ$_D$ 60.1, J_{AD} 42.7, J_{BC} 41.2 Hz, J_{AB}, J_{AC}, J_{BD} and J_{CD} not resolved.

† The NMR studies were done in CD$_2$Cl$_2$ due to the insufficient solubility of the complexes in CD$_3$CD$_2$OD.

the ^{31}P NMR spectra of the reaction solutions (intensity ratio about 3:1), which are assigned to the Λ and Δ diastereoisomers of [Ru(acac)$_2${(*S*)-biphemp}] **8a**, **8b** by comparison with the ^1H and ^{31}P NMR data of [Ru(acac)$_2$(binap)].[13] These singlets remain sharp in the ^{31}P NMR spectrum obtained with selective decoupling of the phenyl protons, in keeping with no hydride ligand being present. A further, low-intensity singlet at δ 51.3 is attributed to [Ru(acac)$_2$(PPh$_3$)$_2$],[12a,b] which is apparently formed by ligand scrambling with free PPh$_3$ from reaction (*vii*). Reactions (*vi*) and (*vii*) occur even in the absence of NEt$_3$. The ^1H and ^{31}P NMR spectra show that a CD_2Cl_2 solution of **4** reacts with a three-fold excess of Hacac forming about 9% of **8** (diastereoisomeric ratio 2:1) within 30 min. Both **7** and **8** form the dichloro derivative **2a** by reaction with aqueous, concentrated hydrochloric acid and with PPh$_3$ present in solution. Interestingly, neither **7** nor **8** reacts with dihydrogen under ambient conditions over 24 h. Also, none of the attempted reactions furnished any evidence either of alcohol formation or of carbonyl insertion into the metal–hydride bond.

Activation of H_2 *by Complex* **2a**.—We have previously reported that complex **2a** reacts with H_2 in the presence of a base to yield the chlorohydride **4**.[7] Due to its relevance to catalysis, we have examined this reaction more closely. Even if no base is present, complex **4** is partially formed (*ca.* 5% of starting **2a**, 293 K) when a 0.05 mol dm^{-3} CD_2Cl_2 solution of **2a** is saturated with hydrogen at room pressure [(*iii*), Scheme 1]. Under such conditions we did not detect any classical hydrides of higher nuclearity, such as *e.g.* the trinuclear [{RuHCl(P–P)}$_3$] isolated by James and co-workers[16] [P–P = dppb or (2*S*,3*S*)-bis(diphenylphosphino)butane, chiraphos]. However, about 35% of the starting dichloro species **2a** is converted into the binuclear dihydrogen complex [{(*S*)-biphemp}ClRu(μ-Cl)$_3$-Ru(η^2-H$_2$){(*S*)-biphemp}] **5**.[7] It has been suggested that the analogous five-co-ordinate [RuCl$_2$(PPh$_3$)$_3$] could activate H_2 heterolytically *via* the hypothetical dihydrogen complex [RuCl$_2$(η^2-H$_2$)(PPh$_3$)$_3$] with elimination of HCl.[17] Although no evidence has been found to corroborate this hypothesis, the formation of such a species could be a consequence of the facility with which many five-co-ordinate complexes of ruthenium(II) form molecular hydrogen complexes.[18] Reactions of the type **2a** to **4** are documented in the older[10b,19] and recent literature.[20] It should be noted that the heterolytic splitting of dihydrogen is also of relevance in view of the transition metal-catalysed disproportionation between H_2 and D_2.[21] A high acidity of the postulated dihydrogen ligand[22] would be required for the elimination of HCl, particularly if the low basicity of the dichloromethane solvent is taken into account. However, the free PPh$_3$ arising from the equilibrium might act as a HCl acceptor, although its basicity is rather low (pK_a 2.7).[23] The protonation of PPh$_3$ might also promote the formation of binuclear **5** according to (*v*) in Scheme 1. In fact, after saturating a CD_2Cl_2 solution of **2a** with H_2 we do not observe any signal which could be assigned to the phosphonium salt PPh$_3$H$^+$. However, the ^{31}P NMR signal of free PPh$_3$ dramatically broadens (linewidth increases from 7 to 32 Hz) and shifts slightly toward the protonated PPh$_3$ (*ca.* δ 5) from δ −4.97 to −4.82.*

In an attempt to detect an intermediate of the reaction of **2a** to **4**, such as the hypothetical dihydrogen complex '[RuCl$_2$(η^2-H$_2$)(PPh$_3$){(*S*)-biphemp}]', protonation of the chlorohydride **4** was carried out with anhydrous HCl at low temperature and monitored by means of ^{31}P and ^1H NMR spectroscopy. However, when a stoichiometric amount of HCl (MeOH solution) is added to **4** in CD_2Cl_2 under argon at −80 °C, a mixture of products is formed. Besides a small amount of unreacted **4** (*ca.* 20%), the dichloro species **2a** and [{(*S*)-biphemp}ClRu(μ-Cl)$_3$Ru(η^2-H$_2$){(*S*)-biphemp}][7] **5** are present as the main products in an approximate 1:1 molar ratio, as can be judged from ^1H NMR integration. Besides the signal of free PPh$_3$, a low-intensity, slightly broadened singlet centred at δ 4.7 is attributed to PPh$_3$H$^+$ arising from its partial protonation. By contrast, if the same reaction is performed under H_2, the binuclear dihydrogen complex **5** is formed as the main product according to (*v*) in Scheme 1, together with a minor amount (*ca.* 20%) of the dichloro derivative **2a**. Also in this case, a mononuclear dihydrogen species cannot be detected even at low temperature (−80 °C). In fact, six-co-ordinate ruthenium(II) complexes with biphemp show a high lability. The binuclear species **5** might arise from the fast reaction of two hypothetical species of the type '[RuCl$_2$(η^2-H$_2$)(PPh$_3$){(*S*)-biphemp}]', in which both the dihydrogen ligand and PPh$_3$ are potentially labile. Interestingly, the signals of **4** reappear when water (8 μl) is added. Together with the H/D exchange reaction in the presence of D_2O (see below), this suggests either a high acidity of the dihydrogen ligand in the binuclear complex **5**, or that **5** is in fast equilibrium with a highly acidic dihydrogen species.

When the protonation of **4** is carried out using DCl (concentrated D_2O solution), the ^{31}P NMR pattern is identical with that observed in the corresponding reaction with HCl. The ^1H NMR spectrum of [{(*S*)-biphemp}ClRu(μ-Cl)$_3$Ru(η^2-HD){(*S*)-biphemp}] displays a 1:1:1 triplet of binomial triplets centred at δ −9.8 with ^1J(HD) 29.0 Hz which is indicative of a molecular hydrogen complex.[22] A clearly resolved ^2J(HP) coupling of 8.6 Hz is observed in this spectrum. The corresponding signal of the η^2-H$_2$ analogue is broad and featureless. Its short T_1(min) of 8 ms (233 K, 200 MHz) also supports the presence of a dihydrogen ligand.[7] Although the ^{31}P NMR pattern remains unchanged, the intensity of the hydride signal of the η^2-HD derivative rapidly decreases with time, apparently due to fast H/D exchange between co-ordinated HD and D_2O.[24]

Catalytic Hydrogenation of Pentane-2,4-dione.—With the aim of gaining some insight into the species involved in the catalytic cycle, complex **2a**, its derivatives **4** and **6**, as well as the system formed *in situ* from **1a** and 2 equivalents of anhydrous HCl were tested in the catalytic hydrogenation of Hacac using ethanol as the solvent. The reactions were performed in a steel autoclave equipped with a pressure gauge. Since the solutions of all the complexes used are air-sensitive, the catalytic runs were prepared in a glove-box under purified nitrogen. As deactivation of the catalyst was observed after prolonged contact with the steel surface of the autoclave, the reaction solutions were placed in a glass insert. Attempts to follow the reaction progress by taking samples also led to deactivation. Therefore the progress of the hydrogenation reaction was monitored by the loss of the hydrogen pressure as measured on the pressure gauge. As most reactions went to completion within the total reaction time (24 h), reaction rates were evaluated as initial rates $\{-d[P(H_2)]/dt\}_{initial}$ based on plots of hydrogen pressure *vs.* time, and then converted to relative rates by taking the value of run 1 as the reference (see Experimental section). The experimental details and results are listed in Table 1.

Complex **2a**. The dichloro derivative **2a** catalyses the reduction of Hacac to **10** (Scheme 2) with very high diastereo- (*lk*:*ul* ratio 99.4:0.6) and enantio-selectivity [99.5% enantiomeric excess (e.e.)] under relatively mild conditions (Table 1, run 1). The reaction goes to completion in less than 24 h at 50 °C when an initial H_2 pressure of 100 bar is used. If the reaction is stopped after 6 h at 85% conversion of Hacac, the monohydrogenated **9** is recovered from the reaction solution in 88% yield and with an e.e. as high as 99.3% (run 2), confirming that the formation of the diol **10** occurs stepwise. The effect of the initial pressure of hydrogen on the reaction rate has been

* It should be noted that HCl behaves as a relatively weak acid in CH_2Cl_2, and does not react quantitatively with PPh$_3$ when bubbled through a 0.1 mol dm^{-3} CD_2Cl_2 solution of the phosphine. The ^{31}P NMR spectrum of the resulting solution shows a very broad signal, whose position and linewidth depend on the concentration of HCl.

Table 1 Enantioselective hydrogenation of pentane-2,4-dione[a]

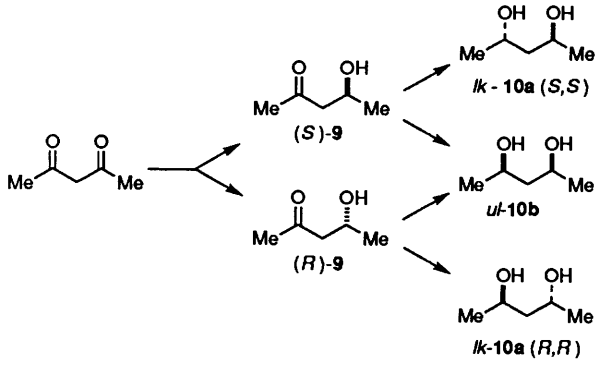
Run	Catalyst precursor	Remarks	Relative initial rate (×100)[b]	**9** (%)	*lk*-**10a** (%)	*ul*-**10b** (%)	e.e.[c]
1	**2a**		100	0	99.4	0.6	99.5
2	**2a**	Conv. = 85%, 6 h	100	88	12[d]		99.3
3	**2a**	+1 equiv. PPh_3, conv. = 45%	7	97	3[d]		91.8
4	**2a**	+1 equiv. NEt_3, conv. = 41%	8	99	1[d]		89.6
5	**2a**	+1 equiv. HCl	141	0	99	1	99.9
6	**2a**	+1 equiv. $[AsPh_4]Cl$	95	0	99.9	0.1	99.3
7	**1a**	+2 equiv. HCl	260	0	99.7	0.3	99.8
8	**1a**	+2 equiv. HCl + 1 equiv. PPh_3	180	0	98	2	99.2
9	**4**	Conv. = 22%	5	99	1[d]		74
10	**4**	+1 equiv. HCl	71	0	99	1	>99.9[e]
11	**6**	Conv. = 55%	12	99	1[d]		93.4
12	**6**	Reaction time = 96 h	12	0	93	7	99.0
13	**6**	+1 equiv. HCl	150	0	97	3	99.4
14	**6**	+1 equiv. HBF_4, conv. = 60%	13	98	2[d]		97.6

[a] Other conditions (unless otherwise stated): EtOH as solvent, [catalyst precursor] = 4.26 mmol dm^{-3}, [Hacac] = 8.52 mol dm^{-3}, substrate:catalyst = 2000:1, T = 50 °C, initial pressure of H_2 = 100 bar, total reaction time = 24 h, Hacac final conversion = 100%. [b] Run 1 is taken as the reference (see Experimental section). [c] Referred to major product. Major enantiomer has either (*S*) or (*S*,*S*) configuration. [d] Total value of *lk* and *ul* diastereoisomers. Diastereoisomeric ratio not determined. [e] Only one enantiomer detected.

Table 2 Dependence of initial rates on the initial dihydrogen pressure[a]

Run	Initial pressure/bar	Relative initial rate (×100)[b]
15	50	68
16	75	86
1	100	100
17	125	91
18	150	64

[a] Other reaction conditions: see Table 1, footnote *a*. [b] See Experimental section.



Scheme 2

examined (Table 2). The maximum initial rate is obtained with an initial hydrogen pressure of 100 bar. Both lower (runs 15, 16) and higher (runs 17, 18) initial pressures give rise to slower reactions. Some reactions have been performed by adding modifiers to the reaction mixture. In particular, the effects of added PPh_3, base (NEt_3), acid (HCl) and chloride ions on the reaction (runs 3–6) were studied. The addition of PPh_3 or NEt_3 causes definite decreases both of the rate and of the selectivity (runs 3 and 4, respectively). The reaction rate is affected to a limited extent by the addition of HCl (methanol solution) (run 5), and not at all by chloride ions (run 6).

The system obtained *in situ* from the reaction of $[Ru(O_2CMe)_2(binap)]$ **1b** with 2 equivalents of methanolic HCl has been used as a catalyst precursor for the hydrogenation of functionalized ketones.[6a–c] We now find that the analogous **1a**–HCl system, which has been successfully applied to the enantioselective reduction of 3-oxo-esters,[3b] also reduces Hacac (run 7) with activity and selectivity which are similar to those reported for the binap system.[6a,c] The results are similar to those of run 1 confirming that **2a** is a convenient catalyst precursor for this reaction. A brief ^{31}P NMR investigation of the nature of the metal-containing species formed in solution when **1a** and anhydrous HCl are mixed in CD_2Cl_2 in a 1:2 ratio shows that a complex mixture of products is present, whose main components are presumably the oligomeric species of composition $[(RuCl_2\{(S)\text{-biphemp}\})_x]$. A broad signal at δ 47.0 is attributed to trimer $[Ru_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3\{(S)\text{-biphemp}\}_3]Cl$.[25] Addition of PPh_3 (1 equivalent) to solutions of the **1a**–HCl system converts the mixture to complex **2a**, as inferred by ^{31}P NMR spectroscopy. The resulting solution displays the same catalytic behaviour as **2a** (run 8).

Complex **4**. Although the chlorohydride **4** is highly reactive toward dioxygen, the reactions performed with the usual precautions gave reproducible results. Both the activity and selectivity achieved with complex **4** are much lower than those of dichloro derivative **2a** (run 9). However, when HCl (methanol solution) is added to the reaction solution in a 1:1 molar ratio to the metal (run 10), the reaction rate is comparable to that found with **2a** (run 1) and the enantioselectivity is restored. As discussed above, complex **2a** is the predominant species formed under these conditions.

Complex **6**. The acetylacetonato derivative **6** affords a lower reaction rate and optical yield in the reduction of Hacac when compared with **2a**, only 55% Hacac conversions being attained after 24 h (run 11). Quantitative conversion to **10** can be obtained by running the reaction for 4 d (run 12). A substantial improvement of the performance of the system is obtained by adding HCl to the reaction solutions (methanol solution, 1:1 molar ratio) (run 13), which is known to convert **6** to the dichloro complex **2a**. If HBF_4 is used, hardly any improvement in the rate is noticed (run 14). Interestingly, under these conditions the monohydrogenated ketoalcohol can be recovered (98% selectivity at 60% conversion) with good enantioselectivity. In fact, the most active species in the asymmetric hydrogenation of Hacac is the dichloro derivative **2a**.

NMR Investigations of the Hydrogenation Reactions.—The hydrogenation of Hacac was performed in an NMR tube under ambient conditions (1 atm H_2, 20 °C) and monitored by means of ^1H and ^{31}P NMR spectroscopy. A CD_2Cl_2 solution of **2a** (*ca.* 0.05 mol dm^{-3}) was saturated with H_2 and Hacac was added in a 1:1 ratio. The ^1H and ^{31}P NMR spectra were

recorded during 3 d. As observed in the analogous experiment without Hacac, the signal of the chlorohydride **4** and of the binuclear dihydrogen complex **5** appear in the high-field ^1H NMR spectrum after saturating the solution with H_2. The signals of the monohydrogenated product **9** appear just after adding Hacac confirming that the reaction occurs stepwise with **9** as intermediate. After 24 h the conversion of Hacac is as high as 70% with a **9**:**10** molar ratio close to 3:2, and is 100% after 48 h (**9**:**10** molar ratio 3:7). Quantitative conversion into the diol **12** is observed after 72 h.

The ^{31}P NMR spectrum confirms that **2a** is partially converted into **4** and **5** after saturating with H_2. No new species besides compounds **2a**, **4** and **5** are detected after addition of Hacac. Upon addition of Hacac, more of **2a** is converted into **4** (from *ca.* 5% to *ca.* 10% of starting **2a**, 293 K). A further increase in the concentration of **4** takes place during the reaction, and after 72 h **4** and **5** are the only metal-containing species. The increase in the concentration of the binuclear complex **5** during the reaction might be due to oxidation of PPh_3 by traces of oxygen, as a signal at δ 28.5, attributed to Ph_3PO, grows during this time. If the NMR tube is not constantly refilled with hydrogen during the reaction, the formation of the dimer **3** at the expense of **5** is observed as hydrogen is consumed according to (*iv*) in Scheme 1. Reversible addition of H_2 to the dimeric species [(dppb)ClRu(μ-Cl)$_2$Cl(dppb)] has already been reported.[26] A control of the enantioselectivity of the hydrogenation reaction in CD_2Cl_2 (GC on chiral column) showed that **10a** is formed in 99.6% e.e., while **10b** is 0.7% of the dihydrogenated product. This suggests that the reaction pathway, operative in CD_2Cl_2 under ambient conditions, should not be significantly different from that followed by the catalysis in EtOH as solvent under 100 bar H_2 at 50 °C.

As these experiments still left open the question about the role of the heterolytic splitting of H_2, we tried to substantiate a reaction pathway involving the chlorohydride **4** by monitoring a solution of **4** and Hacac (1:1 molar ratio, H_2 atmosphere) using ^1H and ^{31}P NMR spectroscopy over 24 h. The spectra failed to reveal any insertion product being formed under these conditions. However, the signals of the hydrogenated products **9** and **10** appear, albeit the reaction being much slower than with **2a** (about 10% Hacac conversion to **9** after 24 h). Complex **4** is partially converted (*ca.* 14%) into **8a** and **8b** (in 1:1 ratio), and also some ligand scrambling takes place, leading to [Ru(acac)$_2$(PPh$_3$)$_2$] (*ca.* 11%), which was identified spectroscopically by comparison with literature data.[12a,b]

Discussion

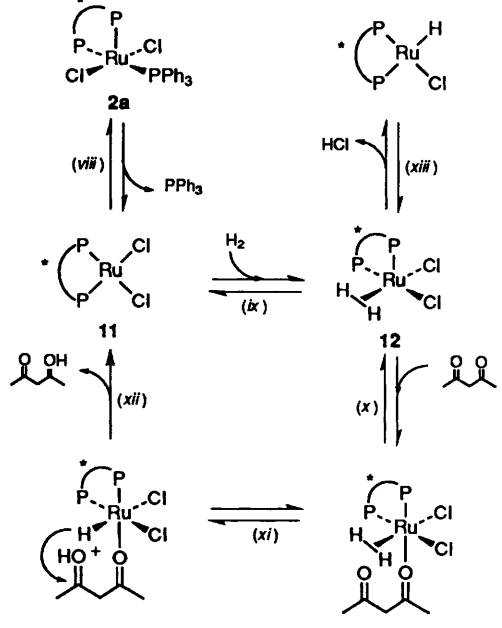
Both the catalytic reaction (runs 2–4, 11, 14) and the NMR investigations indicate that the double reduction of Hacac proceeds stepwise *via* the monohydrogenated keto alcohol 4-hydroxypentan-2-one **9**. With all catalyst precursors the sense of induction is the same, (*S*)-biphemp giving rise to (*S*) chiral centres in the substrate. The second reduction step produces the diastereoisomeric diols *lk*-pentane-2,4-diol **10a** or *ul*-pentane-2,4-diol **10b** (Scheme 2). The effect of a double stereodifferentiation process[27] is evident from the selectivity values for the reactions run to different endpoints (runs 1, 2 and 11, 12): the e.e. of **10** is always higher than that of **9**, as the minor enantiomer (*R*)-**9** is mostly converted to *ul*-**10b** in the second hydrogenation step.

Although a thorough kinetic investigation has not been attempted, comparison between the catalysis data and the overall reactivity of **2a**, which is summed up in Scheme 1, allows some consideration about the species that are possibly involved in the enantioselective reduction of Hacac. As it has been proposed that some kind of chelating interaction between the carbonyl groups of the substrate and the metal centre plays a crucial role both in the catalytic cycle and in the stereochemical outcome of the hydrogenation reaction,[6a,c] we suspected that a β-diketonato species might be involved in the hydrogenation reaction. In fact, the acetylacetonato species **6** is both less active and less selective than **2a**, suggesting that the reaction does not proceed *via* enolato species. As for the hydrogenation of β-keto esters with the **1b**–HCl system,[28] this conclusion is supported by the reduction of the 3,3-dimethyl-substituted substrate being catalysed by **2a**.[29] The inhibiting effect of added base in the reaction catalysed by **2a** (run 4) can be explained by equilibrium (*i*) being shifted toward the formation of the acetylacetonato complex **6**.

On the basis of the NMR results reported above, the role of the chlorohydride **4** remained to be assessed, as well as that of the binuclear dihydrogen complex **5**. Though monohydride species have been shown to be plausible intermediates in the catalytic hydrogenation of olefins with [Ru(O$_2$CMe)$_2$(binap)],[30] a low rate and e.e. are obtained with **4** (run 9). Also under ambient conditions the hydrogenation of Hacac (1:1 molar ratio) is much slower with the chlorohydride **4** than with **2a**. This might be due to the formation of **7** and **8** according to (*vi*) and (*vii*) in the presence of an excess of Hacac (Scheme 1). As compound **4** displays the same catalytic activity as **2a** when treated with 1 equivalent of HCl (run 10), the presence of two chloride ions in the catalyst precursor appears to be a prerequisite for optimal catalytic activity (Scheme 3). This is also confirmed by the different effects of the addition of HCl and HBF_4 to **6** (runs 13, 14).

The inhibition due to PPh_3 when using **2a** as the precursor (run 3) could be explained by the involvement of the binuclear complexes **3** and **5** in the catalytic cycle. However, the formation of **5** appears to be non-productive, as the hydrogenation rate drops at high hydrogen pressures (Table 2, runs 17, 18) at which complex **5** predominates.[7] Other well defined, polynuclear species such as the trimer [Ru$_3$(μ$_3$-Cl)$_2$(μ-Cl)$_3$(binap)$_3$]Cl, which is formed by prolonged heating of [RuCl(binap)(η^6-C$_6$H$_6$)]Cl in the presence of methanol or acetone, have been found to be ineffective as catalysts.[6e,f] Their formation under catalysis conditions might explain the low activity of [RuCl$_2$(MeCN)$_2$(binap)] in the hydrogenation of β-keto esters.[6f] By contrast, the presence of PPh_3 as ancillary ligand in the solutions of **2a** and of its derivatives probably inhibits the formation of species with nuclearity higher than two.

The above results suggest that the key species in the catalytic cycle is a mononuclear complex containing two chloride ligands, probably the 14 electron species [RuCl$_2${(*S*)-biphemp}] **11**. The formation of the highly unsaturated species **11** is supported by the fast exchange between free and co-ordinated



Scheme 3

PPh_3 observed in the solutions of **2a**,[7] as an associative mechanism is not probable in view of steric crowding considerations.[31] It should be noted that in the $[RhCl(PPh_3)_3]$-catalysed hydrogenation of cyclohexene the dissociation of PPh_3 leads to the 14 electron rhodium(I) fragment $[RhCl(PPh_3)_2]$, which is responsible for the fast activation of dihydrogen.[32] Analogously, we suggest that the optimal activity of **2a** as the catalyst precursor is related to the easy activation of dihydrogen by **2a** or by the strictly related 14 electron species **11**. Consistently, neither **4** nor **6** reacts with H_2 under ambient conditions and shows lower catalytic activity.

Finally, the possible mechanism of dihydrogen activation deserves some comment. The NMR studies of the hydrogenation reaction, showing that the chlorohydride **4** is always present during the reaction, indicate that the heterolytic splitting of H_2 according to reaction (*iii*) in Scheme 1 is faster than the hydrogenation reaction. Thus, one might expect reaction (*iii*), or its analogous (*xiii*), to be responsible for H_2 activation either before or in an early stage of the catalytic cycle (*i.e.*, before the rate-limiting step). Then, both HCl and chloride ions should slow down the catalytic reaction. This is clearly not the case with **2a**. The initial rate is not affected by the addition of chloride to the reaction solution (run 6), while an acceleration, albeit hardly significant, occurs with HCl (run 5). The addition of HCl has been shown to inhibit a catalytic cycle in which the active species is formed by H_2 addition to a chloro-containing complex, followed by elimination of HCl.[20] Therefore, we suggest that the activation of H_2 in the catalytic cycle does not occur according to (*xiii*), but probably involves the formation of a dihydrogen complex of the type $[Ru(\eta^2\text{-}H_2)Cl_2\{(S)\text{-biphemp}\}]$ **12** (Scheme 3). Complex **12** is also a possible intermediate in the reaction of **2a** with H_2 to give **4**. The slight acceleration observed upon the addition of HCl (run 5) could be thus explained with the shift of equilibrium (*xiii*) toward the formation of **12**.

The hypothetical species **12** could evolve in the presence of the substrate by transferring a proton from the acidic dihydrogen ligand to a carbonyl oxygen atom, followed by hydride transfer to the carbon atom, as in steps (*xi*) and (*xii*), respectively (Scheme 3). It should be noted that the addition of a strong acid speeds up the rate of reaction of β-keto esters hydrogenation catalysed by $[\{RuCl_2(binap)_2\}_2]\cdot NEt_3$ and $[RuCl(binap)(\eta^6\text{-}C_6H_6)]Cl$,[4b] while the opposite effect has been observed for the asymmetric hydrogenation of α,β-unsaturated carboxylic acids by **1b**.[30a] Stoichiometric reductions based on successive H^+/H^- transfer are documented both for C=O[33] and for C=C double bonds.[34] A H^+/H^- transfer from a dihydrogen complex has been proposed for the *stoichiometric* reduction of acetone[35] in the presence of $[Os(\eta^2\text{-}H_2)(NH_3)_5]^{3+}$ and for the *catalytic* hydrogenation of dimethyl maleate by $[Rh\{P(CH_2CH_2PPh_2)_3\}]^+$.[36] In the case of carbonyl compounds, protonation of the carbonyl oxygen of the substrate would assist the nucleophilic attack of the hydride onto the carbonyl group.[37] However, in the absence of a detailed kinetic study, the reaction sequence in Scheme 3 has to be regarded as a mere working hypothesis for further studies directed to a conclusive elucidation of the reaction mechanism.

Conclusion

The investigation of the catalytic properties of complex **2a** and of some of its derivatives confirms that the presence of two chloride ligands in the catalyst precursor affords optimal activity and selectivity. The easy heterolytic splitting of dihydrogen by **2a** suggests that the catalytic reaction involves facile heterolytic activation of dihydrogen by a dichloro-containing species as a key step. The proton transfer onto the carbonyl oxygen might assist the hydride attack, as already observed in the stoichiometric reductions of various carbonyl compounds.

Experimental

All manipulations involving solutions of the complexes were performed either under argon with the use of Schlenk-line techniques or in a Braun AG glove-box under purified nitrogen. The air-sensitive complex **4** was manipulated under an inert atmosphere in the solid state. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The salt $RuCl_3\cdot H_2O$ was purchased from Aldrich, PPh_3 from Janssen. The (*S*)-biphemp and $[Ru(O_2CMe)_2\{(S)\text{-biphemp}\}]$ were a gift of F. Hoffman–La Roche; $[RuCl_2(PPh_3)\{(S)\text{-biphemp}\}]$ and $[RuHCl(PPh_3)\{(S)\text{-biphemp}\}]$ were prepared by published methods.[7] Yields are based on ruthenium. Infrared spectra were recorded on a Mattson Instruments 6020 Galaxy Series FT-IR spectrophotometer as KBr pellets. Positive-ion FAB mass spectra were carried out on a ZAB VSEQ instrument by the MS service at Laboratorium für Organische Chemie (ETH Zürich) in a 3-nitrobenzyl alcohol matrix using a Xe-atom beam with a translational energy of 8 keV. Microanalyses were performed by the Microanalytical Laboratory of the Dipartimento di Scienze e Tecnologie Chimiche (Università di Udine).

NMR Investigations.—The reactions were performed in NMR tubes closed with serum septa, which allowed the addition of solvent and reactants *via* syringe or microsyringe under argon supplied by a standard Schlenk-line system *via* a needle. When necessary a hydrogen atmosphere was kept in the tube *via* a hypodermic needle connected to a hydrogen reservoir at ambient pressure. The ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were obtained with AMX 500, AMX 400, AM 300 or AC 200 Bruker spectrometers. Spectral simulations were performed with PANIC (Bruker Spectrospin AG). Positive *trans*-^2J(PP) and negative *cis*-^2J(PP) were used for the ABX spin systems.[38]

Synthesis of Complex **6**.—Complex **2a** (0.49 g, 0.50 mmol) was suspended in an ethanol solution (10 cm^3) of Hacac (57 μl, 0.55 mmol) and NEt_3 (84 μl, 0.60 mmol) and stirred at room temperature. After 2 h, yellow *microcrystals* of $[RuCl(acac)(PPh_3)\{(S)\text{-biphemp}\}]$ **6** were filtered off, washed with ethanol (2 cm^3) and vacuum-dried (0.45 g, 86%) (Found: C, 69.4; H, 5.20. $C_{61}H_{54}ClO_2P_3Ru$ requires C, 69.9; H, 5.2%); $\tilde{\nu}_{max}/cm^{-1}$ 3048 (=C–H), 1580m and 1403m (C···O), 1514m (C···C + C–H) (KBr); δ_H(400 MHz, solvent CD_2Cl_2, standard $SiMe_4$, 233 K) 0.47 and 0.60 (2 × 3 H, s, aromatic CH_3), 1.03 and 1.26 [2 × 3 H, s, $H_3C(O)C{=}CHC(O)CH_3$], 4.07 [1 H, s, $H_3C(O)C{=}CHC(O)CH_3$]; δ_C(100 MHz, solvent CD_2Cl_2, standard $SiMe_4$, 233 K) 18.4 and 21.3 [2 × 1 C, $H_3C(O)C{=}CHC(O)CH_3$], 99.7 [1 C, $H_3C(O)C{=}CHC(O)CH_3$)], 185.0 and 185.5 (2 × 1 C, C···O); δ_P(solvent CD_2Cl_2, standard 85% H_3PO_4, 233 K) 21.47 [1 P, dd, $J(P_AP_B)$ 23.7, $J(P_AP_C)$ 353.9], 30.65 [1 P, dd, $J(P_BP_C)$ 34.2 Hz] and 34.03 (1 P, dd); *m/z* 1013 (M^+ − Cl, 13), 786 (M^+ − PPh_3, 35) and 751 (M^+ − Cl − PPh_3, 100%).

Reaction of Complex **4** *with Hacac.*—A CD_2Cl_2 solution (0.7 cm^3) of **4** (48 mg, 0.050 mmol) was treated with Hacac (5 μl, 0.050 mmol) and NEt_3 (14 μl, 0.10 mmol) in a NMR tube under argon. The ^{31}P and ^1H NMR spectra of the reaction solution indicate that **4**, **7** and **8** are simultaneously present just after mixing. After 12 h only **8** and unreacted **4** are present. Addition of an excess of Hacac (10 μl, 0.10 mmol) and NEt_3 (14 μl, 0.10 mmol) to this solution results in further conversion to **7** and eventually to **8**. However, the formation of **8** is not quantitative even after 24 h. NMR data for **7**: δ_H(250 MHz, solvent CD_2Cl_2, 293 K) −16.81 [1 H, dt, J(PH) = J(P′H) = 24.1, J(P″H) = 24.7 Hz, Ru–H], 0.38, 0.99 (2 × 3 H, s, aromatic CH_3), 1.25, 1.81 [2 × 3 H, s, $H_3C(O)C{=}CHC(O)CH_3$], 4.31 [1 H, s, $H_3C(O)C{=}CHC(O)CH_3$]; δ_P(101 MHz, solvent CD_2Cl_2, 293 K), 40.29 [1 P, dd, $J(P_AP_B)$ 322.0, $J(P_AP_X)$ 25.9], 43.63 [1 P, dd, $J(P_BP_X)$ = 36.7 Hz], 69.20 (1 P, dd). Complex **8a**: δ_H 1.54 (6 H, s, aromatic CH_3), 1.60 and 1.64 [2 × 6 H, s, $H_3C(O)C{=}CHC(O)CH_3$], 4.83 [2 H, s, $H_3C(O)C{=}CHC(O)CH_3$]; δ_P 54.7

(2 P, s). Complex **8b**: δ_H 1.16 (6 H, s, aromatic CH_3), 1.45 and 1.91 [2 × 6 H, s, $H_3C(O)C{=}CHC(O)CH_3$], 5.04 [2 H, s, $H_3C(O)C{=}CHC(O)CH_3$]; δ_P 53.9 (2 P, s).

Catalytic Reactions.—A typical procedure consisted in transferring the catalyst, weighed in a glass inert, into a glove-box. After adding Hacac (10.0 g, 99.9 mmol) and solvent (10.0 g), the vessel was inserted into a 250 cm^3 steel autoclave (equipped with a pressure gauge), which was closed and taken out of the box. The lines were flushed several times with hydrogen before connecting the autoclave to the hydrogen source (99.9999%). The nitrogen in the autoclave was then replaced by three cycles of pressurisation with 50 bar of hydrogen and careful venting. After pressurisation, the autoclave was transferred into a thermostatted oil-bath equipped for mechanical stirring and the hydrogen pressure *vs.* time data collection was started. After initial equilibration of the system (about 15–30 min), the progress of the reaction was monitored by the loss of H_2 pressure by visual measurements on the pressure gauge. No side-products were detected by GC and the total hydrogen uptake was always in fairly good agreement (± 5%) with the value expected on the basis of the total conversion as determined by GC and of the measured volume of the system. Repeated controls showed that the apparatus experienced no pressure loss over 24 h or more. Most reactions (runs 1–4, 6, 9, 11, 12, 15–18) were repeated at least twice, giving initial rates which were reproducible to within ± 10%.

The initial rates $\{-d[P(H_2)]/dt\}_{initial}$ in bar H_2 h^{-1} were obtained from the slope of the linear part of the hydrogen uptake *vs.* time curve (conversion interval 5–15%, based on H_2), and then converted to relative rates by taking the value of run 1 as the reference. Recovery of the reaction products was performed in air. The yellow to red, clear reaction solutions were analysed by GC on a Hewlett Packard GC 5890 II instrument equipped with a 50 m cross-linked methyl silicon gum capillary column to check the final conversion. For reactions which did not go to completion, the Hacac conversion and product distribution corresponded to the total H_2 conversion within ± 5%. Pure products could be isolated by distillation under reduced pressure (isolated yields between 90 and 80%). The enantiomeric excesses were determined by direct GC analysis of the distilled products on a Fisons GC 8000 instrument equipped with a 50 m Lipodex C chiral column. The absolute configuration of the hydrogenation products was determined by comparison of the sign of optical rotation (Perkin-Elmer 241 polarimeter) with literature data.

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