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'Diopium', a chiral phosphoniophosphine derived from Kagan's diop. Rhodium complexes and reducing catalytic properties

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Abstract

Cationic chiral monophosphines are devised as a novel type of ligands for catalytic transformations of polar substrates with polar reagents. A phosphonio-phosphine derived from (*R*,*R*)-diop ('methyldiopium') proved to act as a chiral version of Baird's ω-phosphonio-phosphine ligands ('phophos') in Rh(I) complexes in both 1:1 and 2:1 P:Rh stoichiometry. Their versatile structure in $CDCl_3$ solution has been studied by NMR spectroscopy in the presence of various anions (Cl^-, I^-, BF_4^-, PF_6^-). The in situ 2.5:1 methyldiopium–Rh catalytic system slowly hydrogenated (*Z*)-α-acetamidocinnamic acid in 63% conversion and 5% ee. This system was, however, specifically active in a novel hydrogen transfer procedure by a 1:1 $HCOOH:NEt_3$ mixture under mild conditions (40 °C, in the absence of DMSO), for which the corresponding diop–Rh system was not active. Itaconic acid was thus quantitatively reduced to racemic methylsuccinic acid. (*Z*)-α-acetamidocinnamic acid was reduced in up to 85% conversion to *N*-acetylphenylalanine in various solvents. Though still moderate, the ee's depend on the solvent: 10% in (*R*) product in THF, 14% in (*S*) product in acetonitrile. © 2002 Published by Elsevier Science B.V.

Keywords: Diop; Phosphoniophosphines; Rhodium complexes; Hydrogen transfer; Asymmetric catalysis

1. Introduction

Thirty years after its discovery by Kagan [1], diop stands as a historical benchmark amongst chiral diphosphines [2], while the chemical simplicity of its chiral skeleton is still inspiring the search for new ligands of asymmetric hydrogenation catalysts [3]. As a further example, 'methyldiopium' **1** [4], a monophosphonium salt of diop (Scheme 1), is proposed here as a tentative prototype to examine the scope of hybrid dative-electrostatic interactions in the rhodium-catalyzed reduction of acrylic acid derivatives.

After the early discoveries of chiral monophosphine–rhodium catalysts [5], a rigid chelation of the transition metal center by diphosphine ligands was recognized as a desirable feature for the design of highly enantioselective hydrogenation catalysts [6]. A further conceptual advance aimed at improving the diphosphine catalysts' performances consisted in the introduction of functional groups enabling secondary ligand–metal interactions [7,3d,3e]. In particular, chelating dative–dative-electrostatic interactions have been invoked to account for high ee's obtained in rhodium-catalyzed hydrogenation of acrylic acid derivatives in the presence of chiral amino-*di*phosphines ligands [8]. Keeping in mind recent observations that certain monophosph(on)ite-rhodium catalysts also exhibit high enantioselectivity in catalytic hydrogenation [9], we may devise new ligands susceptible to be engaged in a simple dative-electrostatic interaction with a metal center. A single P→Rh dative bond might be sufficient to ensure a chiral organization, which would simply result from a formal cationic charge on a monophosphine backbone. In most of the chiral quaternary ammonium-diphosphine ligands reported so far, the positive charges are rigidly repelled at the periphery of the complex in order to ensure water-solubilty [10]. By contrast, the present prospect requires the possibility of back folding of the cationic charge onto an electron-rich metal center or to its polar ligands [11]. The metal would thus be embedded in a enzyme-like chiral electrostatic pocket where a 'chiral zwitter-

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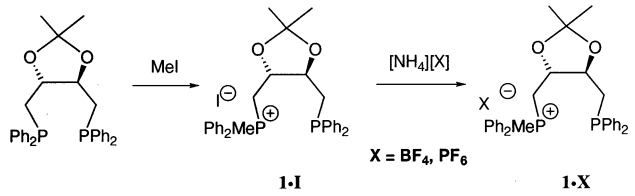


Scheme 1. (*R*,*R*)-methyldiopium salts from (*R*,*R*)-diop.

ionic control' of the reaction could take place [12]. A related strategy has been envisioned by Brunner with chiral pyridinium–oxazolidine–rhodium catalysts for the hydrosilylation of ketones [13].

Baird et al. have designed achiral phosphonium–phosphine ligands $PPh_2(CH_2)_nP^+Me_3$ ($n = 2$, 3, 6, 10) for which they coined the generic term '*n*-phophos' [14]. Phophos–rhodium complexes (2:1) were shown to be catalytic precursors for the hydrogenation of alkenes in biphasic media [15]. A chiral version of IV-phophos ($n = 4$) is here investigated through the diopium ligand **1**.

2. Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenk tube and vacuum line technics. THF and diethylether were distilled over Na–benzophenone. Dichloromethane and acetonitrile were distilled over P_2O_5. Triethylamine was distilled over KOH. Commercial synthesis grade methanol (SDS) was degassed by bubbling argon. (−)-(*R*,*R*)-diop, (*Z*)-α-acetamidocinnamic acid and methyl iodide were purchased from Fluka. Formic acid was purchased from Riedel-de-Haën. Ammonium tetrafluoroborate was purchased from Aldrich. $[RhCl(cod)]_2$ was prepared from cyclooctadiene and $RhCl_3 \cdot 3H_2O$ (Johnson–Mattey) according to a modified described procedure (no carbonate was added) [16]. NMR spectra were recorded in $CDCl_3$ solution, on Brucker AC 200, AM250 and AMX 400 spectrometers. Positive chemical shifts at low field are expressed in ppm by internal reference to TMS for ^1H and ^{13}C, and by external reference to 85% H_3PO_4 in D_2O for ^{31}P. Optical rotations were measured in a 1 dm cell with a Perkin–Elmer 241 polarimeter.

2.1. (*R*,*R*)-Methyldiopium

1·I was prepared from (*R*,*R*)-diop and methyl iodide according to a described procedure in 97% yield according to stoichiometry [4]. Complementary analytical data: melting point (m.p.): 106–109 °C; FAB (< 0) *m*/*z*: 127 ($[I]^-$); FAB (> 0) *m*/*z*: 513 ($[\mathbf{1}]^+$). Tetrafluoroborate and hexafluorophosphate of **1** were obtained by anion metathesis. For instance: diopium iodide **1·I** (0.076 g, 0.2 mmol) was treated with $[NH_4][PF_6]$ (0.150 g, 1.6 mmol) in dichloromethane (5 ml) and water (5 ml) for 6 h. The organic phase was then separated, washed with water (3 × 10 ml), dried over $MgSO_4$, filtered and dried under vacuum, affording **1·PF$_6$** as a white powder (0.056 g, 72%). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 81 MHz) δ: −143.95 (sept, $^1J_{PF} = 713.3$ Hz, 1P; PF_6^-); −24.87 (s, 1P; CH_2PPh_2); 23.21 (s, 1P; P^+Me).

2.2. Characterization of complex 2·BF$_4$

A solution of $[NH_4][BF_4]$ (0.022 g, 0.21 mmol) in water (1 ml) was added to diopium iodide **1·I** (0.067 g, 0.10 mmol) in dichloromethane (5 ml). After stirring for 2 h, the organic phase was separated, washed with water (2 × 5 ml), and concentrated. The product (**1·BF$_4$**) was dissolved in methanol (3 ml), and added to a solution of $[Rh(cod)Cl]_2$ (0.026 g, 0,032 mmol) in a 1:1 methanol–dichloromethane mixture (1 ml). The mixture was stirred for 9 h at room temperature (r.t.). The solvents were evaporated to dryness, giving the single complex **2·BF$_4$** as a light brown solid which could be characterized without further purification. ^1H-NMR (200 MHz) δ: 1.35, 1.41 (2 s, 6H; $C(CH_3)_2$); 1.91–2.56 (m, 8H; CH_2(cod)); 2.67 (d, $^2J_{PH} = 14$ Hz, 3H; CH_3P^+); 2.80–3.02 (m, 2H; CH_2P); 3.13 (broad, 2H; $CH{=}CH$(cod) *trans* to Cl); 3.20–3.61 (m, 3H; P^+CH_2CHO); 4.20 (m, ^1H; $RhPCH_2CHO$); 5.15–5.55 (broad, 2H; $CH{=}CH$(cod) *cis* to Cl [19a,19]); 7.2–8.0 (m, 20H; aromatic *CH*). $^{31}P\{^1H\}$-NMR (81 MHz) δ: 23.16 (s, 1P; P^+CH_3); 29.41 (d, $^1J_{PRh} = 149.4$ Hz, 1P; *P*Rh). $^{13}C\{^1H\}$-NMR (62.9 MHz) δ: 8.41 (d, $^2J_{PC} = 55.7$ Hz; P^+CH_3); 26.16, 26.41 (2 s; $C(CH_3)_2$); 25.30–27.03 (broad m; CH_2P, CH_2P^+ and CH_2(cod) [19a]); 75.32 (m; *C*HO); 110.02 (s; CMe_2); 118.77, 120.15 (2 d, $^1J_{PC} = 86.6$, 87.3 Hz; (*ipso*-*C*)$_2P^+$); 128.68–134.76 (m; aromatic *C*). As reported for [RhCl(nbd)(II-phophos)], the olefinic carbons of the diene ligand did not give observable ^{13}C-NMR signals [15a].

2.3. VTP ^{31}P-NMR analysis of complexes 2·I and 3·Cl

Methyldiopium iodide **1·I** (0.026 g, 0.04 mmol) and $[Rh(cod)Cl]_2$ (0.010 g, 0.02 mmol) were dissolved in $CDCl_3$ (0.5 ml) in an NMR tube. Heating of the sample for 10 min at 50 °C was required to observe the disappearance of the free $^{31}P^{III}$ signal of **1**. NMR spectra were recorded at 162 MHz, at 293 K and 233 K. $^{31}P\{^1H\}$-NMR (293 K) δ: 25.78 (s; P^+CH_3); 28–32 (residual coalescence signal; *P*Rh). $^{31}P\{^1H\}$-NMR (233 K) δ: 25.87 (broad s, 1P; CH_3P^+); 34.27 (d, $^1J_{PRh} =$ 144.1 Hz, 0.7P; *P*Rh of **3·Cl**); 35.47 (d, $^1J_{PRh} = 149.3$ Hz, 0.3P; *P*Rh of **2·I**). Diopium oxide impurities were also observed at δ: 26.04 (CH_3P^+), 32.57 (*P*=O), and assigned by comparison with an authentic sample

prepared by controled oxidation of **1·I** with H_2O_2 in acetone.

2.4. Characterization of complex **4**

[RhCl(cod)]$_2$ (0.016 g, 0.032 mmol) and methyldiopium iodide **1·I** (0.084 g, 0.13 mmol) were dissolved in CH_2Cl_2 (3 ml). A solution of [NH_4][BF_4] (0.010 g, 0.096 mmol) in water (3 ml) was added, and the mixture was stirred for 2 h at r.t., and the organic phase was separated, then concentrated. Crude complex **4·Y$_2$** (Y = BF_4, I) was obtained as an orange oil and characterized as such, exactly as described for [Rh(nbd)(*n*-phophos)$_2$]$^+$ complexes [15a]. ^{1}H-NMR (250 MHz) δ: 1.34, 1.44 (2 s, 12H; C(CH_3)$_2$); 2.00–2.50 (m, 8H; CH_2(cod)); 2.67 (d, $^2J_{PH}$ = 14 Hz, 6H; CH_3P$^+$); 2.80–3.22 (m, 4H; CH_2P); 2.35–3.65 (m, 4H; CH_2P$^+$); 3.59, 4.20 (2 m, 2 × 2H; (C*H*O)$_2$); 5.60–5.70 (m, 4H; C*H*=C*H*); 7.20–8.00 (m, 40H; aromatic C*H*). Secondary signals at δ = 5.37 (m) and 1.5–2.5 (m) might be assigned to a side-product of general formula [Rh(cod)$_2$]X. ^{31}P{^{1}H}-NMR (81 MHz) δ: 23.11 (s, 2P; CH_3*P*$^+$); 31.87 (d, $^1J_{PRh}$ = 144.9 Hz, 2P; *P*Rh). ^{13}C{^{1}H}-NMR (62.9 MHz) δ: 8.26 (d, $^1J_{PC}$ = 56 Hz; *C*H$_3$P$^+$); 25.96 (d, $^1J_{PC}$ = 55 Hz, *C*H$_2$P$^+$); 26.90, 27.23 (2 s; C(*C*H$_3$)$_2$); 29.38, 30.10, 32.29, 32.89 (4 s; *C*H$_2$(cod)); 32.40 (d, J_{PC} = 27.5 Hz; *C*H$_2$PRh); 74.07–75.48, 81.05 (2 m; (*C*HO)$_2$); 103.35 (very broad; =*C*H(cod)); 110.44 (s; *C*(CH$_3$)$_2$); 120.22 and 120.40 (2 d, $^1J_{CP}$ = 86.2 Hz; (*ipso*-*C*)$_2$P$^+$); 127.83–135.68 (m; other aromatic *C*). (+)ESMS *m/e*: 851.1 ([RhI(cod)(**1**)]$^+$) with consistent isotopic pattern).

2.5. Characterization of complex **5**

RhCl(cod)]$_2$ (0.010 g, 0.021 mmol) and methyldiopium hexafluorophosphate **1·PF$_6$** (0.054 g, 0.082 mmol) were dissolved in CH_2Cl_2 (3 ml). A solution of [NH_4][PF_6] (0.037 g, 0.227 mmol) in water (3 ml) was added. The mixture was stirred for 2 h at r.t. while the color turned from yellow to orange. The organic phase was separated, washed with water (3 × 6 ml) and then concentrated. Complex **5·(PF$_6$)$_3$** was obtained as a light orange solid (0.050 g, 73%). ^{31}P{^{1}H}-NMR (81 MHz) δ: 22.05 (s, 2P; *P*$^+$Me);16.45 (d, $^1J_{RhP}$ = 144.0 Hz, 2P; *P*Rh); −143.87 (sept, $^1J_{PF}$ = 713.9 Hz, 3 P; *P*F_6^-). ^{1}H-NMR (200 MHz) δ: 0.63, 1.10 (2 s, 12H; C(CH_3)$_2$); 1.90–2.15 (m, 8H; CH_2(cod)); 2.44 (d, $^2J_{PH}$ = 13.7 Hz, 6H; CH_3P$^+$); 2.25–3.15 (m, 8H; CH_2P and CH_2P$^+$); 3.62–3.82 (m, 4H; OC*H*–C*H*O) 4.46 (m, 2H; =C*H* cod); 4.92 (m, 2H; C*H* = cod); 6.87 (broad t, $^3J_{HH}$ = 7.3 Hz, 2H; *p*-C*H* *Ph*PRh) 7.18–7.31 (m, 10H; aromatic C*H* *Ph*′PRh); 7.46 (broad t, $^3J_{HH}$ ≈ 7.4 Hz, 4 H; *m*-C*H* *Ph*PRh); 7.64–7.78 (m, 20H; aromatic C*H* Ph$_2$P$^+$); 8.25 (broad td, $^3J_{HH}$ ≈ 7.3 Hz, $J_{(RhP)H}$ ≈ 10.2 Hz, 4 H; *o*-C*H* *Ph*PRh) (assignment of the diastereotopic Ph and Ph′ protons of the PhPh′PRh units by ^{1}H–^{1}H selective decoupling). ^{13}C-NMR (62.9 MHz) δ: 7.78 (dq, $^1J_{PC}$ = 56.7 Hz, $^1J_{CH}$ = 135.8 Hz; *C*H$_3$P$^+$); 26.42 (dm, $^1J_{PC}$ = 55.3 Hz, *C*H$_2$P$^+$); 25.86, 26.39 (2 s; C(*C*H$_3$)$_2$); 28.28 (broad m, *C*H$_2$PRh); 30.03, 31.32 (2 m; *C*H$_2$ cod); 74.61 (broad d, $^1J_{CH}$ = 148.4 Hz; *C*H–O); 78.80 (broad d, $^1J_{CH}$ = 150.9 Hz; *C*H–O); 97.51 (d; $^1J_{CH}$ = 151.1 Hz; =*C*H cod); 99.30 (d; $^1J_{CH}$ = 157.7 Hz; =*C*H cod); 109.81 (s; *C*(CH$_3$)$_2$); 119.54 (d, $^1J_{CP}$ = 86.2 Hz; (*ipso*-*C*)P$^+$); 119.82 (d, $^1J_{CP}$ = 88.2 Hz; (*ipso*-*C*)P$^+$); 127.41–136.88 (m; aromatic *C*). (+)ESMS and (+)FAB *m/e*: 1527.4 ([Rh(cod)(**1**)$_2$(PF$_6$)$_2$]$^+$) minor peak with consistent isotopic pattern); 513.2 ([**1**]$^+$).

2.6. Procedure for the catalytic reduction of (*Z*)-α-acetamidocinnamic acid with 1:1 HCOOH:NEt$_3$

[RhCl(cod)]$_2$ (0.005 g, 0.1 μmol), methyldiopium iodide **1·I** (0.032 g, 50 μmol) and acetamidocinnamic acid **5** (0.148 g, 0.72 mmol) were dissolved in THF (5 ml). The mixture was stirred for 15 min. at 20 °C. Triethylamine (0.5 ml, 3.6 mmol) and formic acid (0.129 ml, 3.6 mmol) were then added, and the medium was stirred for 9 h at 40 °C. After cooling to r.t., 2 M aqueous (aq.) NaOH was added, and the aqueous phase was washed with ether (3 × 10 ml), then acified with 10 N HCl, and filtered through celite. The filtrate was extracted with ether (3 × 20 ml), dried over $MgSO_4$ and concentrated. The resulting grey solid was analyzed by ^{1}H-NMR in DMSO-d_6 solution showing the signals of the starting material **5** and those of the *N*-acetylphenylalanine **6** only: the calculated conversion was 54%. The enantiomeric excess in (*R*)-**6** (10%) was estimated from the optical rotation of a diluted solution of the product: $[\alpha]_D^{25} = -5.5°$ (c = 0.297, absolute EtOH).

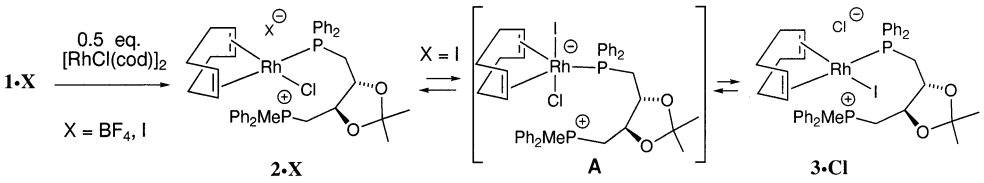
3. Results and discussion

3.1. Solution structure of diopium–rhodium complexes

In continuation of previous reports on the coordination chemistry of phosphonium derivatives of diop (isodiop in a chlororhenium cluster [17], methyldiopium **1** in carbonyliron complexes [4]), the solution structure of **1**–Rh(I) complexes in 1:1 and 2:1 stoichiometry has been investigated.

3.1.1. Diopium:rhodium stoichiometry = 1:1

Reaction of **1·BF$_4$** with [Rh(cod)Cl]$_2$ lead to the formation of the complex **2·BF$_4$** (Scheme 2). It is a chiral homologue of Baird's square–planar complex [RhCl(nbd)(II-phophos)]$^+$, with similar spectroscopic characteristics: $\delta_{^{31}P}$ = 29.41 (d, $^1J_{PRh}$ = 149.4 Hz) and 23.16 (s) [15a].



Scheme 2. 1:1 Diopium–rhodium complexes in the presence of various anions.

The iodide analog **1·I** exhibits a different behavior. After heating the $CDCl_3$ solution of **1·I** and $[Rh(cod)Cl]_2$ for 10 min at 50 °C, the ^{31}P-NMR spectrum at 293 K and 162 MHz displays a sharp signal for the phosphonium center at $\delta = 25.78$, and a very broad signal at $\delta = 28$–32. Decoalescence starts at 273 K, and finally gives rise to two sharp doublets at 233 K: $\delta = 34.27$ (70%, $^1J_{RhP} = 149.3$ Hz) and 35.47 (30%, $^1J_{RhP} = 144.1$ Hz). These PRh units can be assigned to those of isomers **2·I** and **3·Cl**, respectively. Indeed, the $^1J_{RhP}$ coupling constant of the *cis*-*X*–Rh–P unit in square–planar $RhXP_2L$ complexes with similar $\delta_{^{31}P}$ and $^1J_{PRh}$ values (*ca.* 35 ppm and 140 Hz, respectively), were found to be a few Hz greater for X = Cl than for X = I [18]. The integration is thus also in accordance with a greater stability of the Rh–Cl bond with respect to the Rh–I bond. The interconversion of these species by a fast chloride–iodide exchange at r.t., could occur via an association–dissociation mechanism, involving a 18-electron zwitterionic rhodate intermediate **A** [12]. Similar elusive $[RhCl_2(cod)P_2]^-$ species have been previously mentionned [19a]. Within this hypothesis, the free enthalpy of activation $\Delta G^{\neq}$ for the **2·I**⇄**3·Cl** interconversion can be estimated from the Eyring equation [19b]:

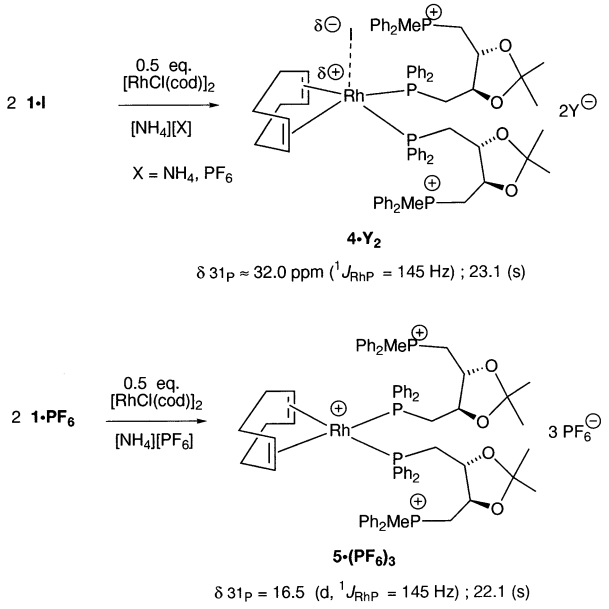
$$\Delta G^{\neq} = RT_c\left(10.32 + \log\frac{T_c}{K_c}\right) \text{ cal. mol}^{-1}, \quad k_c = \frac{\pi\Delta\nu}{\sqrt{2}},$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

where T_c (≈ 293 K) is the coalescence temperature, and $\Delta\nu$ ($= 194$ Hz at 233 K) is the separation in Hertz of the ^{31}PRh signals at the slow exchange limit. Thus, $\Delta G^{\neq} \approx$ 14 kcal mol^{-1}. This value is greater than the average activation barrier (10 ± 2 kcal mol^{-1}) for Berry pseudorotation in related five-coordinated d_8 rhodium complexes [19c]. The putative intermediate **A**, in equilibrium with **2·I** or **3·Cl** via a Berry transition state, should therefore lie *ca.* 4 kcal mol^{-1} higher in energy than **2·I** and **3·Cl**.

3.1.2. Diopium:rhodium stoichiometry = 2:1

In biphasic CH_2Cl_2–H_2O mixture in the presence of a slight excess tetrafluoroborate, a single diopium complex was formed from $[RhCl(cod)]_2$ and four equivalent of **1·I**. It can be formulated as **4** on the basis of ^{31}P-NMR: $\delta = 23.11$ (s); 31.87 (d, $^1J_{PRh} = 144.9$ Hz) (Scheme 3). A complex with similar spectroscopic



Scheme 3. 2:1 Diopium–rhodium complexes in the presence of iodide, tetrafluoroborate and hexafluorophosphate anions.

characteristics was formed even from a large excess $[NH_4][PF_6]$: integration of the ^{31}P-NMR spectrum showed that the PF_6^- anions compensate the charges of the phosphonium groups but not that of the Rh(I) center: $\delta_{^{31}P} = 23.08$ (s, 2P); 32.35 (d, $^1J_{PRh} = 145.2$ Hz, 2P); −143.99 (sept, $^1J_{PF} = 713.3$ Hz, 2P). The rhodium–iodide association is thus rather strong and is revealed in the positive electrospray mass spectrum by the main monocationic fragment $[RhI(cod)(\mathbf{1})]^+$ at $m/z = 851.1$. The $^1J_{PRh}$ coupling constant has the order of magnitude (145 ± 5 Hz) reported for equivalent P atom(s) in related square–planar complexes: RhX(diene)P [15a], $RhXP'P_2$ [18], or $[Rh(diene)P_2]^+$ [3d,3e,6b,15a,20]. This suggests that the geometry of the $Rh(cod)P_2$ unit in **4** is close to square–planar as well. However, the unusual deshielding of the ^{31}P and olefinic ^{1}H chemical shifts for a $(RCH_2Ph_2P)_2Rh^I(cod)$ unit beyond 30 and 5.5 ppm, respectively, could also be indicative of a non dissociated Rh···I center [3d,3e,6b,20], with a halide *cis* to the cod ligand and *trans* to the PPh_2 termini [6b]. NMR and MS analyses thus support a flattened square-pyramidal structure for **4** in a solvent of low polarity such as $CDCl_3$, with a bulky iodide anion associated in an apical position.

This interpretation was confirmed by the preparation of the analogous complex in the absence of iodide ion. Diopium hexafluoroposphate **1·PF$_6$** was prepared by metathesis of **1·I** with an excess [NH$_4$][PF$_6$], and then reacted with [RhCl(cod)]$_2$ in the presence of [NH$_4$][PF$_6$]. A novel cationic rhodium complex **5** was formed which exhibited spectroscopic characteristics different to those of **4**: the olefinic ^{1}H (<5 ppm) and ^{31}P chemical shifts of **5** (<20 ppm) now lye in the classical range for a cationic (RCH$_2$Ph$_2$*P*)$_2$Rh^I(cod) unit [3d,3e,6b,20]: $\delta_{^1H} = 4.46$ (2 H), 4.92 (2 H). $\delta_{^{31}P} = 22.05$ (s);16.45 (d, $^1J_{RhP} = 144.0$ Hz). NMR data show a perfect C_2 symmetry of the complex, with characteristic well resolved ^{1}H-NMR pattern for one of the two diastereotopic types of phenyl rings of the Ph′(Ph)P–Rh units (Section 2). This pattern is not observed in **4** and suggests here a frozen orientation of the corresponding Rh–P–Ph′ sequence.

3.2. Catalytic properties

Both the preformed complex **5** and the in situ 5:1 **1·I**:[Rh(cod)Cl]$_2$ system were tested in catalytic hydrogenation of (*Z*)-α-acetamidocinnamic acid **6a** under 1 bar H$_2$. Complex **5** was not active, and this is reminiscent of the peculiar inactivity in C=C hydrogenation of the closely related structural analog [Rh(cod)(PMePh$_2$)$_2$][PF$_6$] [21]. The in situ catalyst, however, was more active, and smoothly afforded (−)-*N*-acetyl-(*R*)-phenylalanine **7a** in 63% conversion and 5% ee after 22 h. This rather low ee is similar to those given by many monodentate chiral ligands, but the cationic character of **1** could exhibit specific effects in the presence of polar reducing agents used in transfer hydrogenation.

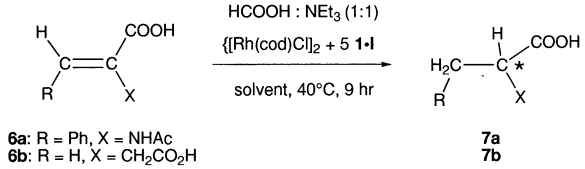
Since early exploratory works on the use of ruthenium–diop catalysts for asymmetric hydrogen transfer from alcohols to itaconic acid [22] and acetophenone [23], ruthenium-catalyzed asymmetric hydrogen transfer to acrylic acid derivatives [24] and ketones [25] has been made highly efficient through the use of a 5:2 formic acid–triethylamine azeotropic mixture. Few applications of this system were also reported with rhodium and iridium catalysts [24a,26]. Rocha Gonsalves and coworkers showed that the 5:2 HCOOH:NEt$_3$ mixture can be used for the reduction of *N*-acetyldehydroaminoacids with chiral diphosphine–rhodium catalysts in DMSO as a specific solvent [27]. For example, with (*R*,*R*)-diop as ligand, (*Z*)-α-acetamidocinnamic acid **6a** was converted to (*R*)-*N*-acetyl-phenylalanine **7a** in 100% conversion (18 h, 3% catalytic ratio) and 50% ee The latter substrates and polar reducing agent are a priori suited for favoring electrostatic interactions around the catalytic center. In order to avoid the use of DMSO, an unconvenient and oxidizing solvent [27], we considered a 1:1 HCOOH:NEt$_3$ mixture in THF at 40 °C, recently described for the stoichiometric reduction of ketones by chromium hydrides [28]. The 1:1 acid–base reducing mixture was also selected in order to lower the acidity of the medium, and thus prevent an eventual acid-catalyzed ring opening of the dioxolane ring of the diopium ligand **1**.

The in situ 5:1 **1·I**:[Rh(cod)Cl]$_2$ system in 3% catalytic ratio [27], and five equivalents of 1:1 HCOOH:NEt$_3$ mixture in THF at 40 °C for 9 h, allowed (*Z*)-α-acetamidocinnamic acid **6a** to be reduced to (*R*)-**7a** in 54% conversion and 10% ee (Scheme 4). A kinetic monitoring showed that in this case, the reaction was completed in 5 h. The use of ten equivalents of the reducing agent did not improve much the conversion (ca. 60%), whatever was overall concentration of the substrate: a competing deactivation of the rhodium catalyst by the formiate mixture with a kinetic order similar to that of the reduction process [29], would account for the leveling of the kinetic curve below complete conversion.

Under the same conditions, itaconic acid **6b** was successfully reduced to methylsuccinic acid **7b** in 100% conversion, but without significant ee By contrast, the α-keto function of pyruvic and phenylglyoxylic acids was not reduced at all.

The effect of the diluting solvent on the reduction of **6a** was studied (Table 1). While low conversion occurred in methanol and DMSO, a better conversion (85%) and a better and reversed enantioselectivity (14% in (*S*)-**7a**) were obtained in acetonitrile.

Surprisingly, the reducing system in THF is specific of the monophosphine ligand: no conversion was observed with diop as ligand. This observation is consistent with Rocha Gonsalves' report that the activity of the diop–rhodium catalyst requires the use of DMSO as solvent [27]. It also suggests that the active species for this reducing system requires a *trans* P–Rh–P arrangement. Although no mechanistic study has been tackled (contrary to the simplicity of the medium in direct hydrogenation procedures, the complexity medium in the hydrogen transfer procedure with excess HCOOH and NEt$_3$, prevents in situ ^{1}H-NMR studies of the rhodium–**6** interaction), the mechanism is therefore surely quite different to those proposed for *chelating* ligands-cod-rhodium catalysts [30]. Despite the remote position of the chirality center of diopium with respect to the catalytic center, the low but significant ee's suggest



Scheme 4. Hydrogen transfer catalysis by the in situ 2.5:1 diopium–rhodium association.

Table 1
Catalytic reduction of (*Z*)-α-acetamidocinnamic acid **6a** and itaconic acid **6b** (0.7–1 mmol) with the in situ 1:5 $[RhCl(cod)]_2$–**1**·**I** system

Substrate	Reducing agent/substrate	Solvent	Conversion (%)	Percent ee of **7**
6a	1 bar H_2 [a]	MeOH	63	5 (S)
	5:5 HCO_2H:NEt_3 [b]	No	41	3 (*R*)
	5:5 HCO_2H:NEt_3 [b]	MeOH	15	–
	5:5 HCO_2H:NEt_3 [b]	MeCN	85	14 (*S*)
	5:5 HCO_2H:NEt_3 [b]	THF	54	10 (*R*)
	10:10 HCO_2H:-NEt_3 [b]	THF	60	10 (*R*)
6b	10:10 HCO_2H:-NEt_3 [b]	THF	100	0

[a] Hydrogenation. $[Rh]_2$/**1**·**I**/**6a** = 1/5/100, concentration of **6a**: 0.13 M in methanol, 20°C, 22 h. Optical rotation of **7a**: $[\alpha]_D = +2.2°$ ($c = 1.0$, EtOH).
[b] Hydrogen transfer. $[Rh]_2$/**1**·**I**/**6** = 1/5/66, concentration of **6**: 0.13 M, 4°C, 9 h.

that the Ph_2P^+Me terminus of the monophosphine **1** could play a role just as does the $R^1R^2P{=}O$ terminus of chiral β-aminophosphine oxide ligands in transfer hydrogenation of ketones by ruthenium catalysts [31]. The efficiency of the putative electrostatic interaction should, however, be enhanced in the more rigid environment of the homologous methylbinapium ligand [4], a Hayashi-type phosphonium-MOP ligands [32]. In preliminary experiments, however, the conditions used for the complexation of **1**–**4** were not suitable for the bulkier binapium ligand, and an ylide strategy can be devised [33].

4. Conclusion

It has been shown that for the cationic chiral phosphine **1**, the use of a suitable polar reducing reagent lead to improved activity and enantioselectivity with respect to the use of molecular hydrogen. These preliminary results pave the way for further explorations of the catalytic properties of chiral cationic monophosphine ligands. Alternatively, instead of rather soft phosphonium group, harder cationic ammonium group could also could also be considered by resorting to chiral ammoniophosphinite ligands (ephosiums, valphosiums) [12,34], or to quaternary ammonium derivatives of Sinou's diop-related amino-monophosphines [3a]. The latters would be chiral versions of Baird's (IV)–amphos ligands [35].

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