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Synthesis and characterisation of a new class of phosphine-phosphonite ferrocenediyl dinuclear rhodium complexes

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Abstract

We previously reported the easy access to mixed ferrocenediyl ligands bearing phosphine and phosphonite moieties. Using this strategy, a new enantiopure phosphine-menthylphosphonite ferrocenediyl has been synthesised. This mixed ligand leads to original unsymmetrical dinuclear rhodium coordination-complexes. One example of this new class of "quasi-close bridging **A** frame" dinuclear rhodium complexes, fully characterised by multinuclear ^{1}H, ^{13}C, ^{31}P and ^{103}Rh NMR and optical rotation measurements, is presented. Preliminary tests have shown an activity improvement in the hydroformylation of oct-1-ene using the phosphine-menthylphosphonite ferrocenediyl auxiliary compared to known phosphine-phosphonite ligands.
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The studies concerning mixed chelating ligands such as phosphine-phosphite, phosphine-phosphinite or phosphine-phosphonite mainly concern non-metallocenic species. With the view to extend the scope of relevant mixed ligands, we recently reported the easy access to unsymmetrical ferrocenediyl ligands bearing both phosphine and phosphonite moieties [1]. It was speculated that these species could constitute accessible catalysis auxiliaries with attractive steric, electronic or chiral properties easy to modulate. The new enantiopure phosphine-menthylphosphonite ferrocenediyl **1** (Scheme 1) is now presented, together with the original dinuclear rhodium complex **2**, fully characterised by multinuclear ^{1}H, ^{13}C, ^{31}P and ^{103}Rh NMR. [1] The ment-

hylphosphonite ferrocenediyl **1** has been found a more active auxiliary in the hydroformylation of oct-1-ene than the previously reported unsymmetrical ferrocenediyl ligands.

The chemical pathways leading to **1** and **2** are summarised in Scheme 1. Compound **1** was obtained as a viscous orange oil in three steps from 1-phenyl-1-phospha[1]-ferrocenophane. Upon reaction of **1** with the dimeric precursor $[Rh(\mu\text{-Cl})(CO)_2]_2$, the complex **2** is obtained in 70% yield after workup procedures. While the purification attempts on **1** using convenient standard chromatography method lead to its decomposition [2], the complex **2** is much more resistant and has been purified by chromatography on neutral silica.

The ^{31}P NMR (C_6D_6) spectra obtained for **1** and **2** attest to the presence of the electronically different phosphine and phosphonite groups: upon coordination to rhodium, the two singlets obtained at $\delta = -15.9$ ppm (PPh$_2$) and $\delta = 163.8$ ppm (P(OMent)$_2$) for the free phosphine-phosphonite ligand are inversely shifted, and two doublets at $\delta = 39.3$ ppm (PPh$_2$, $^{1}J_{\text{P–Rh}} = 178$ Hz) and $\delta = 145.4$ ppm (P(OMent)$_2$, $^{1}J_{\text{P–Rh}} = 234$ Hz) are

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[1] ^{31}P-(121.49 and 161.99 MHz), ^{13}C-(75.47 and 100.62 MHz), ^{103}Rh NMR (12.64 MHz) were performed on Bruker 300 or AMX 400. Different NMR-solvent (C_6D_6, toluene-D$_8$, CDCl$_3$) were used to solve resonances obscured problems. The ^{103}Rh shifts are given relative to Ξ (^{103}Rh) $= 3.16$ MHz. ^{1}H-NMR data are available upon request to the authors.
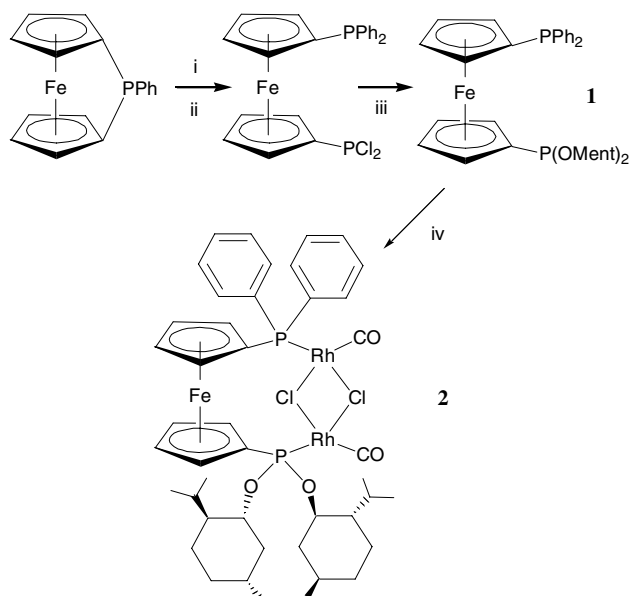
Scheme 1. Syntheses of the asymmetric phosphine-menthylphosphonite **1** and dinuclear rhodium complex **2**. *Reagents and conditions*: (i) 1.1 equiv. PhLi, hexane, −80 °C, 4 h, (ii) 1 equiv. PCl₃, hexane, −80 °C, 4 h, (iii) 2.2 equiv. (1*R*, 2*S*, 5*R*)-(-)-menthol, NEt₃, toluene, r.t., 4 h. (iv) 1 equiv. [Rh(μ-Cl)(CO)₂]₂, toluene, −40 °C, 2 h.

observed. Despite our efforts to obtain single crystals of **2**, recrystallisation only yielded microcrystalline material. A multinuclear ^{1}H, ^{13}C and ^{103}Rh thorough NMR assignment was therefore conducted using *J*-mod ^{13}C, inverse gradient δ^1H–^{13}C HMQC and selective phosphorus decoupling ^{31}P–^{13}C irradiation. This characterisation yields additional information *in solution* about

the symmetry and the electronic environment of the identified nucleus.

As exemplified in the ^{13}C spectrum (toluene-D8, 75.47 MHz) presented in Fig. 1, the NMR study at ambient temperature has revealed a number of interesting and unexpected features for the compound **2**. The asymmetry of **2** is detectable in almost all the NMR resonances: indeed, six different singlets were found for the six methyl groups of the two menthyl rings ($\delta = 14.7, 15.6, 19.8, 20.6, 21.20, 21.22$ ppm, see a̲ Fig. 1). A selective decoupling ^{13}C{^{31}P} NMR experiment focused on the phosphonite, revealed that resonances corresponding to carbon b̲, c̲, d̲, and e̲ are true singlets. Thus, these CH_2 ($\delta = 21.4, 22.0$ and $32.6, 33.5$ ppm, respectively b̲ and e̲) and CH groups ($\delta = 23.6, 24.2$ and $30.3, 30.7$ ppm, respectively c̲ and d̲) of the two menthyl rings are anisochronous, even if they can be assigned as a pair of atoms [3]. The resonances for carbon atoms f̲ and g are detected as a singlet at 43.7 ppm and a doublet centred at 42.5 ppm ($^3J_{C–P} = 7.5$ Hz). The absence of detectable coupling constant for f̲ is confirmed by the ^{13}C{^{31}P} decoupling focused on the phosphonite, which gives two singlets of identical intensity for f̲ and g. The carbon atoms h̲ are also anisochronous but contrary to those of f̲ and g, the resonances exhibit two doublets centred at 47.3 and 49.1 ppm with identical $J_{C–P}$ values ($^3J_{C–P} = 7.4$ Hz). The ^{13}C spectrum is more complex in the Cp area, while the quaternary carbon atoms k̲ and l̲ are easily identified, a careful cross-examination of the δ^1H–^{13}C HMQC and selective phosphorus ^{13}C{^{31}P} decoupling experiments has been necessary to attribute the carbon atoms of type
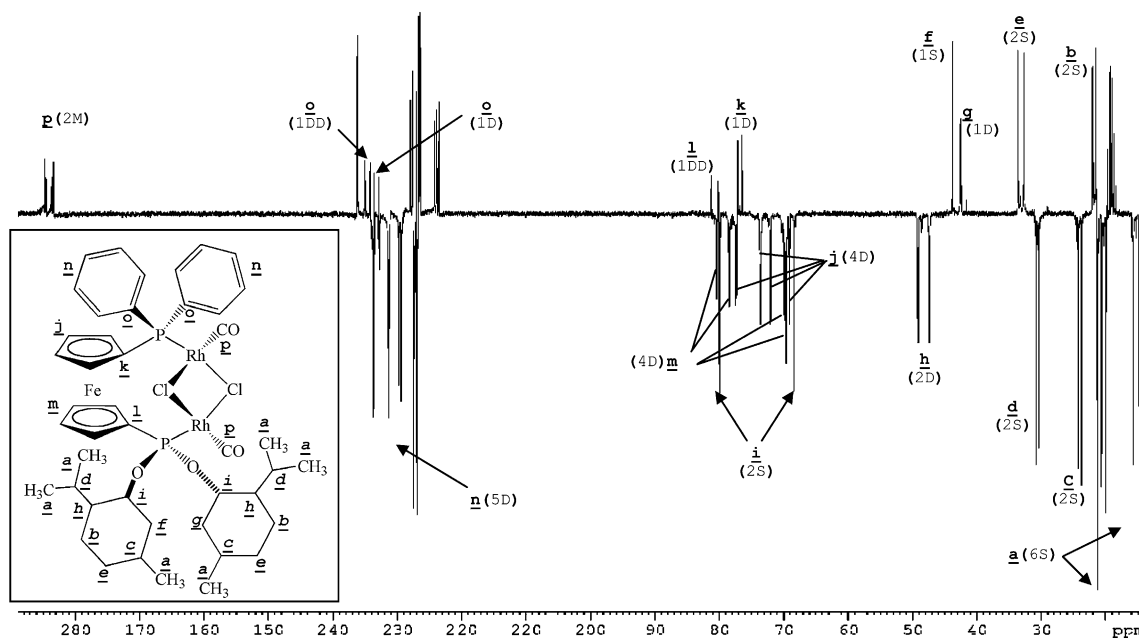

Fig. 1. ^{13}C attribution of complex **2** on a *J*-mod NMR experiment in toluene-D8: S = singlet, D = doublet, DD = doublet of doublet, M = multiplet.

j, m and i. As expected, the electronegative oxygen substituents at the phosphorus atom of the phosphonite group lead to an *increase* in the magnitude of $^1J_{C-P}$ for l compared to those of k [4], which were unambiguously attributed by $^{13}C\{^{31}P\}$ selective decoupling: l, doublet of doublet centred at 76.7 ppm ($^1J_{C-P} = 84.6$ Hz, $^2J_{C-Rh} = 4.5$ Hz) and k, doublet centred at 80.6 ppm ($^1J_{C-P} = 54.4$ Hz, no detectable J_{C-Rh}) [5]. An assignment of the ^{13}C NMR signals for the four j carbon atoms of the Cp ring bearing the –PPh$_2$ moiety was possible using phosphorus selective-decoupling: four doublets centred at 69.0 ($J_{C-P} = 6.0$ Hz), 72.0 ($J_{C-P} = 7.2$ Hz), 73.5 ($J_{C-P} = 4.2$ Hz) and 77.3 ppm ($J_{C-P} = 13.1$ Hz) are distinguished. The asymmetry of the molecule is noticeable, with the four rather different chemical shifts and carbon–phosphorus coupling constants being observed, from which two are $^2J_{C-P}$ and two others are $^3J_{C-P}$. More tenuous was the assignment of carbon atoms m and i using only phosphorus selective-decoupling since two signals were constant singlets, while for all m and i carbon atoms detectable carbon–phosphorus coupling constants were expected. A possible solution to the assignment problem came from the examination of the ^1H–^{13}C HMQC spectrum, indeed one ^1H NMR signal of the complex area corresponding to the C*H* m and i clearly appears as a triplet (4.43 ppm, 1H, $^3J_{H-H} = 10$ Hz) while the other resonances are singlets. The carbon atoms i are the only C*H* group corresponding to this area having a methylene CH$_2$ nearby (f or g). From ^1H–^{13}C HMQC, this ^1H triplet corresponds to one of the ^{13}C singlet ($\delta = 79.9$ ppm) noted i in Fig. 1. Thus, we propose on the basis of these results that the two carbon atoms i give two singlets [6] with a null value for $^2J_{C-P}$ coupling transmitted through the oxygen atom, while $^3J_{C-P}$ for g and h are observed. A wide variation of J(C,P) are known, which range from $(-)50$ to $(+)480$ Hz including values near zero, and organic phosphite compounds have been reported where $^2J_{C-O-P}$ are <3 Hz and $^3J_{C-C-O-P}$ > 5 Hz, and even >13 Hz [4]. Consequently, the four remaining doublets were attributed to the carbon atoms m at 69.6 ($J_{C-P} = 6.6$ Hz), 69.8 ($J_{C-P} = 13.0$ Hz), 78.4 ($J_{C-P} = 15.5$ Hz) and 80.1 ppm ($J_{C-P} = 32.0$ Hz). It is worth noting again, the effect of the electronegative oxygen atoms increasing the magnitude of the J_{C-P} constants, when are compared m and j carbons. The *ipso*-carbons for the phenyl groups correspond to two different signals, a doublet centred at 133.2 ppm ($^1J_{C-P} = 50.1$ Hz) and a doublet of doublet centred at 134.5 ppm ($^1J_{C-P} = 57.4$ Hz, $^2J_{C-Rh} = 2.3$ Hz). Presumably a *trans* and a *cis* position with regard to the rhodium atom are distinguished, since it is well-known that *cis* coupling is of smaller magnitude. Interestingly, the signals for the other carbon atoms from the phenyl were detected as only five doublets, suggesting a fast exchange-rotation not observed for the menthyl moieties: n, $\delta = 127.3$ ($J_{C-P} = 10.7$ Hz), 129.3

($J_{C-P} < 1.4$ Hz), 129.6 ($J_{C-P} = 1.4$ Hz), 131.2 ($J_{C-P} = 11.4$ Hz) and 133.5 ppm ($J_{C-P} = 13.2$ Hz). The quaternary carbon atoms of carbonyl ligands p lead to overlapping signals, which simplify and become understandable using selective phosphorus-decoupling (C$_6$D$_6$, 100.62 MHz): two doublets of doublet centred at 185.62 ($^1J_{C-Rh} = 81.5$ Hz, $^2J_{C-PPh} = 17.1$ Hz) and 185.65 ppm ($^1J_{C-Rh} = 85.5$ Hz, $^2J_{C-P(Oment)} = 14.9$ Hz) are observed. All the others non-assigned signals in Fig. 1 are due to the deuterated toluene solvent. Variable-temperature NMR on compound **2** have been conducted from 20 °C till 70 °C, and show no changes in the ^{31}P NMR and ^1H patterns, demonstrating for the rigidity of the molecule. Finally, a ^{31}P–^{103}Rh INEPT NMR experiment was carried out, where two doublets were observed, one centred at -5.8 ppm ($^1J_{Rh-P} = 178$ Hz) and the other at -46.7 ppm ($^1J_{Rh-P} = 234$ Hz) demonstrating the electronic difference between the two rhodium nucleus. The optical rotations of **1** and **2** were measured and compared to that of the starting product (1R, 2S, 5R)-(−)-menthol: $[\alpha]_{1D}^{25} = -43$, $[\alpha]_{2D}^{25} = -88$, $[\alpha]_{menthol D}^{25} = -54$, $c2$, THF.

Dinuclear rhodium complexes have been subject of interest for use in the important oxo-process [7,8]. Potential cooperating effects between two metal centres have been studied and debated [9–11]. Stanley and co-workers, [7,12] have shown that the dinuclear symmetric rhodium complex *rac*-[Rh$_2$H$_2$(μ-CO)$_2$(CO)$_2$(eLTTP)] [BF$_4$]$_2$ (where eLTTP is the ethyl-substituted linear tetratertiary phosphine Et$_2$P-(CH$_2$)$_2$PPh-(CH$_2$)-PPh-(CH$_2$)$_2$-PEt$_2$) catalyses the hex-1-ene hydroformylation at substrate/catalyst ratio of 900: with 85% conversion and high selectivity in a few hours, while its monometallic analogue only affords poor activity (2% conversion) and selectivity [13]. Diéguez et al. have reported that from dinuclear chloride or dithiolate bridged rhodium complexes, mononuclear species formed under hydroformylation reaction are responsible of the activity [11].

In most of the dinuclear rhodium complexes reported, the metal centres present identical coordination spheres. Independently of the reaction, one may reasonably anticipate that cooperating effects would be more apparent from homodinuclear species achieving electronically and sterically different environments at the metal centres, as expected and observed in heterodinuclear metal complexes [14]. In addition, while phosphite ligands have been intensively studied as auxiliaries for catalytic hydroformylation, only few reports are concerned with phosphonite auxiliaries [15]. For these reasons preliminary tests of our compounds in olefin hydroformylation were conducted.

The first rhodium mononuclear complex with phosphine-phosphonite ferrocenediyl ligands had shown a deceptively low activity in oct-1-ene hydroformylation (conversion 30%, ratio substrate/catalyst = 200),

although it has been observed that it exhibits a proclivity for producing unexpected aldehydes [1]. The catalytic results for **2** showed an activity mainly directed towards isomerisation (isomerisation 60%, hydroformylation 40%, ratio S/C = 250–800). It was then decided to explore the activity from pre-catalysts formed in situ with the ligand **1**. The pre-catalyst formed from **1** and the dinuclear [Rh(μ-S^{t}Bu)(CO)$_2$]$_2$ complex [16], led to complete conversion in nonanal and 2-methyl octanal with a selectivity linear: branched = 4. In non-optimised experiments, in comparison with the earlier reported results, the conversion was about nearly double (55% against 30%) for a ratio S/C *sixteen times higher* (S/C = 3200 against 200). An interesting point for the phosphine-menthylphosphonite ferrocenediyl **1** is that the activity found compares well with that of other reported catalytic systems. However, the actual dimeric or monomeric nature of the catalyst can not be deduced from these preliminary results. The somewhat low selectivity remains studies obtained with some bulky diphosphite ligands or the 1,1'-bis(diphenylphosphino)ferrocene (dppf) [15,17].

As underlined by Hor and Gan [18], the kind of "quasi-close bridging **A** frame" exhibited by **2** is rare. While several hundred dinuclear bridging rhodium complexes are known, to date, only one other of this type has been reported [17]. Moreover, this complex is significantly different since it bears the symmetric ligand dppf. Thus, the present study positively answer the question, whether this "**A** frame" chemistry could be developed [16,18]. Finally, another field of studies to explore using ligand **1**, and its coordination-complexes, might concern enantioelective catalytic reactions [19].

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[3] A simple empiric simulation taking into account the influence of the α, β, γ, δ environment of carbon atoms, allows to predict with a good correlation the chemical shift for these carbons, and to distinguish <u>b</u> from <u>e</u>, and <u>c</u> from <u>d</u>. For instance, between <u>e</u> and <u>b</u> a difference of 12 ppm is predicted, partly due to 4 aliphatic –C in γ for <u>b</u> (shielding), against 2 aliphatic –C in γ for <u>e</u>, a difference of 11 ppm is observed.

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