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New chiral zwitterionic iron hydride complexes with 'ephosium' and 'valphosium' ligands

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Abstract

New chiral cationic phosphinite ligands based on ephedrine or valinol skeletons, and corresponding zwitterionic hydridotricarbonylferrate complexes are described. IR data indicate an unusual *cis*-H–Fe–P arrangement in these complexes, and NMR studies show an unusual variation of $^2J_{PH}$ with temperature and solvent. The possibility that both these rare features are dictated by a stabilizing back folding of the $[NMeR_2]^+$ terminus onto the $[FeH]^-$ center is discussed. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Baird-type cationic phosphines [1], the counterparts of the well studied sulfonated, carboxylated and phosphonated anionic phosphines, have recently attracted a renewed interest for performing catalysis in aqueous medium [2,3]. In the search for asymmetric versions of hydrosoluble transition metal catalysts, chiral cationic phosphine ligands have received some attention [4]. This kind of ligands may also find applications in a recently disclosed possible strategy for controlling an asymmetric transformation through the use of a disymmetric ligand: P ~ E^+ chelating an anionic metal center by a P: → M^- dative bond on one side and by a weaker E^+...M^- interaction on the other [5]: although the latter interaction is schematized as an electrostatic attraction between formal atomic charges, it must be more generally regarded as a contact ion pairing which should be tightened by chelation (Fig. 1). The dative–

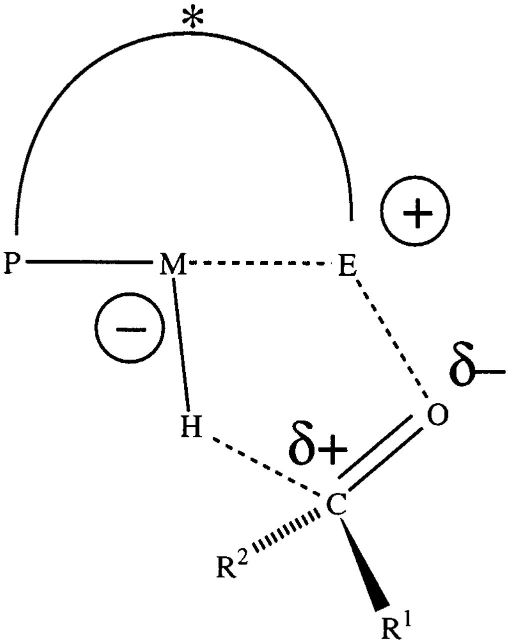

Fig. 1. Putative 'chiral zwitterionic control' strategy in asymmetric reduction by a transition metal hydride.

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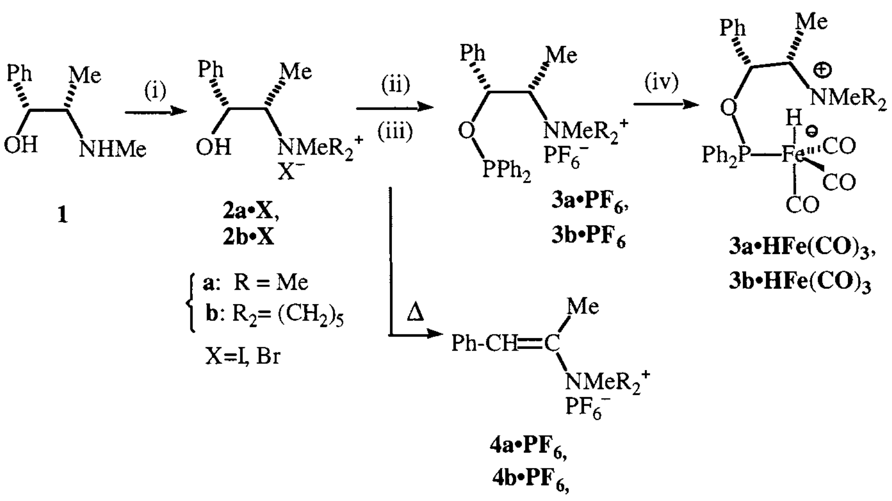


Scheme 1. Synthesis of diphenylephosium ligands and their hydridotricarbonylferrate complex: (i) RX = MeI or $Br(CH_2)_5Br$; (ii) KPF_6, H_2O; (iii) Ph_2PNEt_2,CH_3CN, reflux; (iv) $KHFe(CO)_4$, THF, r.t.

electrostatic chelation mode should exhibit peculiar properties to be compared with those of the classical dative–dative chelation mode of hemilabile ligands such as phosphine ethers and alcohols.

Few alkaloid-derived P^{III}-ammonium compounds are known [6], and within this prospect, cationic chiral phosphinites derived from ephedrine and named '*N*,*N*-dimethyl-R_2-ephosiums' R_2P–O–CHPh–CHMe–NMe_3^+ have been reported (R = Ph, NMe_2, $(NMeCH_2CH_2MeN)_{1/2}$, OH). Zwitterionic hydridotricarbonylferrate complexes of such ligands have been prepared [5], and we report here on preliminary reduction tests using these complexes and on complementary synthetic and analytic studies.

2. Reducing properties of *N*,*N*-dimethyldiphenylephosium hydridotricarbonylferrate

The complex **3a·HFe(CO)$_3$** was obtained from $KHFe(CO)_4$ and **3a·PF$_6$** as yellow crystals deposited from THF solution [5]. The solid is insoluble in water, methanol and isopropanol, and only slightly soluble in ethanol, THF, dichloromethane and acetonitrile [7]. Although reduction of electron-poor ketones by $KHFe(CO)_3L$ complexes (L = CO, $P(OMe)_3$) proceeds readily in methanol [8], preliminary attempts of asymmetric reduction were conducted in homogeneous DMSO solution. It was found that benzil was reduced to benzoin PhC(O)CH(OH)Ph (20°C, 24 h) in 66% yield and 100% selectivity, but with 0.4% e.e. only. Although the $[HFe(CO)_3P]^-$...$[NMe_4]^+$ contact interaction in THF is not readily removed by DMSO (as compared with the $[HFe(CO)_3P]^-$...Na^+ contact interaction: see last section and ref. [9](a)), the intramolecular ion pairing is likely to be perturbed by this highly dipolar solvent where the putative zwitterionic control strategy of Fig. 1 is more questionable. Nevertheless, **3a·HFe(CO)$_3$** can also be used in sursaturated THF solution, before triggering crystallization of freshly prepared complex: using this in situ method, trifluoroacetophenone has been reduced to $PhCH(OH)CF_3$ with 60% conversion and 60% yield (20°C, 24 h), but with no significant e.e. Under the basic conditions used, epimerization of configurationally fragile products cannot be ruled out, but before studying further the potential of the strategy, more lipophilic chiral zwitterionic complexes were needed. Two possibilities were envisioned: one is still based on the ephedrine skeleton quaternized by higher alkyl groups and the other on the more aliphatic valinol skeleton.

3. *N*,*N*-(1,5-pentylene)-diphenylephosium and its hydridotricarbonylferrate complex

Our first targets are ephosium ligands with a nitrogen atom quaternized by alkyl groups larger than the initial methyl groups. The flexibility of large alkyl substituents, however, is anticipated to dilute the eventual conformation controlling the reduction of a prochiral substrate: a substituted six-membered ring has a restricted freedom degree, and we tackled the synthesis of **3b·PF$_6$**, the piperidinium homologue of the ephosium **3a·PF$_6$** (Scheme 1).

N,*N*-(1,5-pentylene)-ephedrinium **2b*PF$_6$** was prepared in 81% yield from 1,5-dibromopentane and (−)-ephedrine **1**, followed by anion exchange of **2b·Br** with the hexafluorophosphate anion. The product reacted slowly with excess Ph_2PNEt_2 in refluxing acetonitrile for 4 days to afford the desired diphenylephosium hexafluorophosphate **3b·PF$_6$** in 90% yield. Attempts to reduce the reaction time by heating neat reactants

Table 1
Solvent dependence $|^2J_{PH}|$ at 20°C of zwitterionic diphenylephosium hydridotricarbonylferrates

NMR solvent	CD_3CN ($|^2J_{PH}|$ Hz)	$[D_8]THF$ ($|^2J_{PH}|$ Hz)
3a·HFe(CO)$_3$	25.8	34.9
3b·HFe(CO)$_3$	28.0	36.5

resulted in the formation of the ene–ammonium side-product **4b·PF$_6$** [10]. The phosphinite–ammonium salt **3b·PF$_6$** displaces both the potassium and one carbonyl ligand of $KHFe(CO)_4$ in THF to give the new zwitterionic diphenylephosium hydridotricarbonylferrate **3b·HFe(CO)$_3$**, which crystallizes from a sursaturated THF solution at −20°C (in mixture with 0.6 equivalents of KPF_6: 79% yield). NMR characteristics of **3a·HFe(CO)$_3$** and **3b·HFe(CO)$_3$** are similar. In particular, the IR spectra suggest that they both adopt a *cis*-H–Fe–P configuration (A'_1, A'_2 and A'' bands). The *cis*-geometry has been confirmed by single crystal X-ray analysis for **3a·HFe(CO)$_3$** [5]. Another unusual feature of these complexes is the dependence of the $|^2J_{PH}|$ coupling constants on the solvent: the magnitude of $|^2J_{PH}|$ is lowered by about 9 Hz while increasing the dielectric constant from 7 (THF) to 36 (acetonitrile) at room temperature (Table 1). The dielectric constant is known to vary as the reciprocal of the temperature [11], and, indeed, $|^2J_{PH}|$ also decreases with temperature in a given solvent (see last but one section): the possibility of a relationship between this phenomenon and the unusual *cis*-H–Fe–P geometry is discussed below.

Despite interesting structural features, the piperidinium derivative is still not very soluble and the use of a more lipophilic chiral backbone had to be explored.

4. *N,N,N*-trimethyl-diphenylvalphosium and its hydridotricarbonylferrate complex

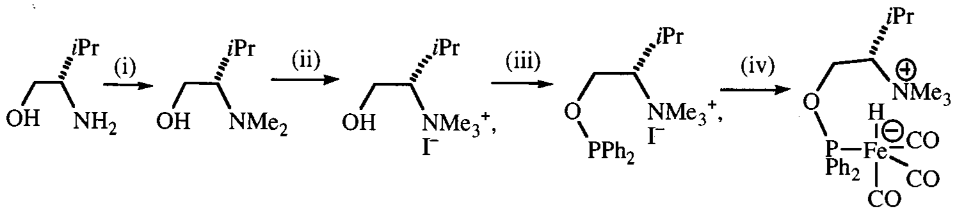
Natural amino acid-derived aminoalcohols have been widely used for the synthesis of chiral auxiliaries. Starting from valinol, a β-aminophosphine ('Valphos') [12], a secondary β-phosphinite–amine ('ValNHOP') and a β-(aminophosphine)–phosphinite ('ValNOP') have been reported [13]. A related quaternary β-phosphinite–ammonium is now described (Scheme 2).

Under Eschweiler-Clarke conditions, (−)-valinol leads to (−)-*N,N*-dimethyl valinol **5** in 74% yield [14]. Quaternization of **5** by methyl iodide occurs slowly in 71% yield. The primary alcohol function of *N,N,N*-trimethylvalinolium iodide **6·I** reacts with excess Ph_2PNEt_2 in acetonitrile to give '*N,N,N*-trimethyldiphenyl–valphosium' iodide **7·I** in 96% yield. This phosphinite–ammonium reacts with $KHFe(CO)_4$ in THF to give the zwitterionic complex, **7·HFe(CO)$_3$** in 97% yield (in a mixture with 0.2 equivalents of KI). Spectroscopic properties of **7·HFe(CO)$_3$** are similar to those of **3a·HFe(CO)$_3$** and **3b·HFe(CO)$_3$**, and similar structural features of these complexes are likely.

Surprisingly, the solid complex is still insoluble in most organic solvents. Nevertheless, **7·HFe(CO)$_3$** provides an example of a second structural kind of chiral zwitterionic complex, the characterization of which is compared below with that of the first structural kind based on the ephedrine backbone.

5. VTP-NMR study of the zwitterionic complexes

Although the $|^2J_{PH}|$ coupling constant of **7·HFe(CO)$_3$** in CD_3CN at 25°C (10.8 Hz) is half that of **3a·HFe(CO)$_3$**, both vary with temperature and moreover at the same rate, ca 0.15 Hz K^{-1} (Fig. 2). Such behaviour of $|^2J_{PH}|$ has been previously evidenced in non-zwitterionic phosphane–hydridotricarbonylferrate complexes having the classical *trans*-H–Fe–P geometry [15]: the occurrence of an equilibrium between several stereoisomers or of a tight intermolecular ion-pair interaction were ruled out, and this phenomenon was explained by a dielectric constant-induced variation of the H_{ax}–Fe–CO_{eq} angle while maintaining the overall C_{3v} symmetry. Nonetheless, ammonium cations were shown to give intermolecular contact ion-pairing interactions with $[HFe(CO)_3L]^-$ anions which can be detected by IR spectroscopy [9]: it is therefore reasonable to infer that intramolecular ammonium–



5 **6•I** **7•I** **7•HFe(CO)$_3$**,

Scheme 2. Synthesis of a diphenylvalphosium ligand and a zwitterionic complex. (i)CH_2O/HCO_2H, 100°C, 2 h, 74%. (ii) CH_3I, ether, 90 h, 71%. (iii) Ph_2PNEt_2, CH_3CN, 19 h, 96%. (iv) $KHFe(CO)_4$, THF, 25°C, 15 h, 97%.

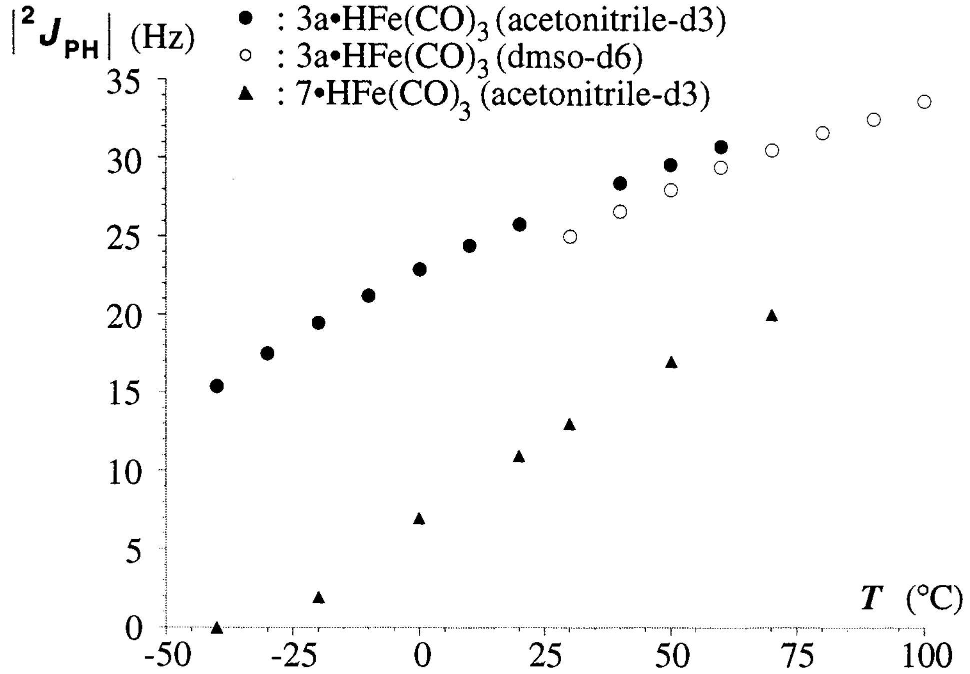


Fig. 2. $|^2J_{PH}|$ versus temperature between − 50 and + 100°C in CD_3CN or $[D_6]DMSO$ for the diphenylephosium complex **3a·HFe(CO)₃** and the diphenylvalphosium complex **7·HFe(CO)₃**. The average slope is 0.15 Hz K^{-1}.

$[HFe(CO)_3L]^-$ interactions could be enhanced enough to be detected by VTP-NMR spectroscopy. The dielectric constant effect can also be a priori invoked here for explaining the variation of $|^2J_{PH}|$ with temperature, but this phenomenon was claimed to occur specifically with *trans*-$[HFe(CO)_3L]^-$ anions and not with their *cis*-congeners [15]: indeed, the only known phosphanehydridotricarbonylferrate complex with a non-variable $|^2J_{PH}|$ is $[HFe(CO)_3\{P(OPh_3\}]^-$ which precisely exhibits an unusual *cis*-geometry [16]. The zwitterionic complexes **3a·HFe(CO)₃** and **7·HFe(CO)₃** are thus original phoshane–hydridotricarbonylferrates displaying both a *cis*-H–Fe–P geometry and a dependence of $|^2J_{PH}|$ with solvent and temperature.

The *cis*-geometry could be dictated by a stabilizing effect of an intramolecular interaction which could not take place in a *trans* isomer owing to a steric hindrance of the equatorial carbonyl ligands. Within this context, the variation of $|^2J_{PH}|$ would reveal a variation of the H–Fe–P angle with the temperature-dependent average opening of a seven-membered chelation ring with a hemilabile electrostatic edge $[HFe]^-\ldots{}^+[N]$ [17]. This average opening can be controlled not only by the temperature but also by the relative energy of competitive HFe^-...solvent (and/or N^+...solvent) interactions: the dependence of $|^2J_{PH}|$ with both the temperature and the solvent can therefore be explained by an effect of the solvent dielectric constant on the shift of the equilibrium:

$$\text{open-}[^+N \sim PFeH^- \ldots \text{solvent}] \leftrightarrows \text{closed-}[\sim N^+ \ldots {}^-HFeP \sim] + \text{solvent}.$$

This hypothesis also partially accounts for the observed shift and broadening of the hydride resonances at low temperature (in contrast with the sharp lines observed in the NMR spectra of non-zwitterionic $[HFe(CO)_3P]^-$ complexes at low temperature [15]), although no decoalescence could be obtained above − 50°C. More subtle effects of the $[FeH]^-$...solvent interaction in the open form may also superimpose, but their magnitude should be relatively weak according to previous results on the non-zwitterionic *cis*-phosphanehydridocarbonylferrate complex $[HFe(CO)_3\{P(OPh_3\}]^-$,$[PPN]^+$ [15,16]. Likewise, the presence of 0.2 equivalents of KI in the **7·HFe(CO)₃** sample should not influence the $^2J_{PH}$ values: in cat^+,$[HM(CO)_nP]^-$ salts, the cation has been recognized to exert a weak influence on $^2J_{PH}$: $|\Delta^2J_{PH}| < 2$ Hz for M = Fe [15,9](a)[18], Cr, W [19], when $cat^+ = K^+, Na^+, Et_4N^+, PPN^+, Li^+$). The nature of hydridocarbonylate–ammonium contact in solution cannot be detailed further [9](a)[20]. However, a multisite docking of Me_4N^+onto an external $[HFe(CO)_3P]^-$ anion has been proposed to occur in THF at both a [FeCO] level and the [Fe–H] level [15a]: an intramolecular contact of this type is found in the solid state structure of **3a·HFe(CO)₃** [5] and could be entropically favored in solution, even in polar solvents such as acetonitrile and dimethylsulfoxide.

6. Conclusion

Two kinds of chiral zwitterionic hydride complexes of iron with phophinite–ammonium ligands **3a**, **3b** and **7**, which are readily derived from commercially available optically pure ephedrine and valinol, have been compared. However, chiral phosphinites are sensitive to nucleophilic attack and protic cleavage. Akin cationic phosphines with three P–C bonds would require further preparation steps, but should be stable in alcoholic medium where asymmetric reduction has better chance to succeed. However, unlike phosphites [18] and phosphinites [21], phosphines require that they cannot be anchored directly to the hydridotricarbonylferrate moiety by CO-substitution from $KHFe(CO)_4$ [22], and a specific synthetic strategy is needed [23].

Beyond coordination chemistry and a possible use in asymmetric reduction of dipolar substrates, chiral cationic phosphanes could serve as ligands for the design of novel catalysts: whereas dative bonds are generally assumed to govern the stereoselectivity of transition metal catalysis, electrostatic interactions play a key role in stereoselective transformations occurring in enzyme pockets. Coordination chemistry of zwitterionic transition metallates with chiral ligands paves the way to the design of chiral reactants or catalysts based on a hybrid concept, where both dative and electrostatic interactions would take place.

7. Experimental

All experiments were carried out with standard vacuum line techniques under an argon atmosphere. THF and ether were distilled under argon and over Na/benzophenone, toluene over sodium and acetonitrile over P_2O_5 before use. Commercial synthesis grade pentane, dichloromethane, methanol and ethanol were degassed by bubbling argon before use. Elemental analyses were performed at the Service de Microanalyse du L.C.C. Optical rotations were measured in a 1 dm cell with a Perkin Elmer 241 polarimeter. IR spectra were recorded on a Perkin-Elmer 1725X FT-IR spectrometer using CaF_2 windows. NMR spectra were recorded on a Brucker AC 200 spectrometer: at 200 MHz for ^1H, 81 MHz for ^{31}P and 50 MHz for ^{13}C, in CD_3CN as solvent unless otherwise noted. 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. (–)-Ephedrine, (–)-valinol and chlorodiphenylphosphine were purchased from Aldrich. Ph_2PNEt_2 was prepared from Ph_2PCl and two equivalents of diethylamine in ether: $^{31}P\{^1H\}$-NMR: $\delta = 66.6$. ^1H-NMR: $\delta = 0.93$ (t, $^3J_{HH} = 7.1$ Hz; 6H), 3.07 (dq, $^3J_{PH} = 9.7$ Hz, $^3J_{HH} = 7.1$ Hz; 4H), 7.28–7.45 (10H). THF solutions of $KHFe(CO)_4$ were prepared from $Fe(CO)_5$ (Fluka) and KOH (technical 86%, Prolabo) according to literature procedures [18].

7.1. *N,N-(1,5-pentylene)ephedrinium hexafluorophosphate 2b · PF_6*

(–)-Ephedrine **1** (16.60 g, 100 mmol) and 1.5-dibromopentane (14.6 g, 63 mmol) were dissolved in 50 ml of refluxing toluene. After 15 h, a white solid had deposited and the reaction medium was cooled to r.t. and the solid mixture of **2b·Br** and **1·HBr** was filtered. A 50 ml sample of 5N aqueous NaOH was added to a slurry of the solid in 10 ml of water, which was then washed with ether (3 × 20 ml: one equivalent of base ephedrine was recovered from ether). The aqueous solution was then dropwise acidified to pH = 7 with concentrated HCl. A sample of 9.20 g KPF_6 (50 mmol) was added and a white solid filtered and dried (15.37 g, 81%). $C_{15}F_6H_{24}NOP$ (379.3): Calcd.: C, 47.50; H, 6.38; N, 3.69%; found: C, 47.48; H, 6.49; N, 3.64%. $^{31}P\{^1H\}$-NMR: $\delta = -139.1$ (hept, $^1J_{PF} = 705$ Hz). ^1H-NMR: $\delta = 1.14$ (d, $^3J_{HH} = 6.8$ Hz, 3H; $CC\underline{H}_3$); 1.71–1.85 (m, 6H; $C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 3.08 (s, 3H; $NC\underline{H}_3$); 3.34 (t, $^3J_{HH} = 5.7$ Hz, 2H; $NC\underline{H}_2$); 3.57 (t, $^3J_{HH} = 5.7$ Hz, 2H; $NC\underline{H}_2$); 3.64 (m, 1 H; $\underline{H}CCH_3$); 4.50 (1 H; $O\underline{H}$); 5.52 (d, $^3J_{HH} = 3.9$ Hz, 1 H; $\underline{H}CPh$); 7.32–7.38 (m, 5 H; Ph). $^{13}C\{^1H\}$-NMR: $\delta = 6.55$ ($C\underline{C}H_3$); 20.43, 20.82, 21.50 ($\underline{C}H_2\underline{C}H_2\underline{C}H_2$); 45.26 ($N\underline{C}H_3$); 60.62 ($N\underline{C}H_2$); 61.42 ($N\underline{C}H_2$); 69.39 ($\underline{C}HN$); 73.91 ($\underline{C}HO$); 126.67 ($C_{ortho}$); 128.81 ($C_{para}$); 129.40 ($C_{meta}$); 142.12 ($C_{ipso}$).

7.2. *N,N-(1,5-pentylene)-diphenylephosium hexafluorophosphate **3b · PF_6***

2b·PF_6 (1.65 g, 4.36 mmol) were dissolved in a refluxing solution of Ph_2PNEt_2 (3.36 g, 13.1 mmol) in 15 ml of acetonitrile. The reaction was monitored by ^1H and ^{31}P-NMR: after 100 h, the solution was cooled and evaporated. The yellow residue was washed with ether (2 × 50 ml, then 2 × 25 ml). 8 ml of a 7/1 THF/ether mixture are added: an orange oil deposited which was separated and dried (2.22 g; 90%). $C_{15}F_6H_{24}NOP$ (563.51): Calcd.: C, 57.55; H, 5.90; N, 2.49%; found: C, 57.82; H, 5.91; N, 2.48%. $^{31}P\{^1H\}$-NMR: $\delta = -139.1$ (hept, $^1J_{PF} = 705$ Hz, 1P; PF_6^-); 116.3 (s, 1P; Ph_2P). ^1H-NMR: $\delta = 1.41$ (d, $^3J_{HH} = 6.8$ Hz, 3H; $CC\underline{H}_3$); 1.51–1.75 (m, 6H; $C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 2.75 (s, 3H; $NC\underline{H}_3$); 3.12–3.25 (m, 5H; $C\underline{H}_2NC\underline{H}_2$, $\underline{H}CMe$); 5.61 (d, broad, $^3J_{PH} = 7.5$ Hz, 1H; $\underline{H}CPh$); 7.28–7.60 (m, 15 H; Ph). $^{13}C\{^1H\}$-NMR: $\delta = 7.27$ ($C\underline{C}H_3$); 20.17, 20.43, 21.14 ($\underline{C}H_2\underline{C}H_2\underline{C}H_2$); 44.43 ($N\underline{C}H_3$); 60.00 ($N\underline{C}H_2$); 61.17 ($N\underline{C}H_2$); 75.26 (d, $^3J_{PC} = 5.8$ Hz; $\underline{C}HN$); 77.12 (d, $^2J_{PC} = 22.4$ Hz; $\underline{C}HOP$); 127.5–141.0 (aromatic C with a complex degenerated spectrum of four singlets for $\underline{Ph}C$ + four pairs of diastereoisomeric doublets for $\underline{Ph_2}P$).

Heating of the neat reactants at 100–110°C under vacuum resulted in the formation of **3b·PF$_6$** in 50% yield, along with ca 20% of the ene–ammonium **4b·PF$_6$** which is purified as a white powder washed with ethyl acetate, and identified by NMR: ^{31}P{^{1}H}-NMR: $\delta = -139.1$ (hept, $^1J_{PF} = 705$ Hz). ^{1}H-NMR: $\delta = 1.79$–1.9 (m, 6H; $C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 2.06 (s, 3H; $=CC\underline{H}_3$); 3.15 (s, 3H; $NC\underline{H}_3$); 3.31 (dt; 2H axial or equatorial) and 3.92 (dt; 2H equatorial or axial) ($^2J_{HH} = 12.7$ Hz, 4H; $N(C\underline{H}_2)_2$); 7.04 (broad, 1H; $\underline{H}C=$); 7.3–7.6 (m, 5H; phenyl). ^{13}C{^{1}H}-NMR: $\delta = 12.71$ ($C\underline{C}H_3$); 20.78 ($\underline{C}H_2\underline{C}H_2\underline{C}H_2$); 53.54 ($N\underline{C}H_3$); 60.83 ($N(\underline{C}H_2)_2$) 106.93 ($=\underline{C}H$); 127–140 (aromatic C and $=\underline{C}N+$).

By comparison, the NMR data for **4a·PF$_6$** obtained as a side product of **3a·PF$_6$** under similar conditions are: ^{31}P{^{1}H}-NMR: $\delta = -139.1$ (hept, $^1J_{PF} = 705$ Hz). $\delta = 2.12$ (s, 3H; $=CC\underline{H}_3$); 3.29 (s, 9H; $N(C\underline{H}_3)_3$); 7.07 (broad, 1H; $\underline{H}C=$); 7.4–7.5 (m, 5H; phenyl).

7.3. *N,N-(1,5-pentylene)diphenylephosium hydridotricarbonylferrate **3b·HFe(CO)$_3$***

3b·PF$_6$ (0.84 g, 1.5 mmol) were dissolved in a solution of KHFe(CO)$_4$ (0.31 g, 1.5 mmol) in 10 ml of THF. The solution turned brown–yellow. After stirring for 4 h, KPF$_6$ was filtered. After 4 weeks at −20°C, a yellow powder deposited from the red supernatant liquid, which was filtered. After drying, 0.837 g of material was obtained. NMR spectra indicate the presence of residual THF (0.5 equivalents) and PF_6^- anion. For $C_{30}FeH_{34}NO_4P(C_4H_8O)_{0.5}(KPF_6)_{0.6}$ (705.54, 79%): Calcd.: C, 54.43; H, 5.43; N, 1.98%; found: C, 54.44; H, 5.40; N, 2.03%. Mp = 72–76°C (dec.). IR (THF): ν(CO) = 1946 (m; A_1' band), 1853 (s; A'' band), 1830 (m; A_2' band) cm^{-1}; ν(FeH) = 1888 (m) cm^{-1}. ^{31}P{^{1}H}-NMR: $\delta = 191.7$ (s). ^{1}H-NMR: $\delta = -9.21$ (d, $^2J_{PH} = 28.0$ Hz, 1H; FeH. In [D$_8$]THF, $^2J_{PH} = 36.5$ Hz); 1.54 (d, $^3J_{HH} = 6.8$ Hz, 3H; CCH$_3$); 1.6–1.9 (m, 6H; (CH$_2$)$_3$); 2.93 (s, 3H; NCH$_3$); 3.25 (m, 2H; $C\underline{H}_2N^+$); 3.51 (q, $^3J_{HH} = 6.8$ Hz, 1H; $\underline{H}$CMe); 3.70 (m, 2H; $C\underline{H}_2N^+$); 6.59 (d, broad, $^3J_{PH} = 9.0$ Hz, 1H; $\underline{H}$CPh); 7.0–8.0 (15H; aromatic C$\underline{H}$). ^{13}C{^{1}H}-NMR: $\delta = 7.77$ ($C\underline{C}H_3$); 20.28, 20.59, 21.32 ($\underline{C}H_2\underline{C}H_2\underline{C}H_2$); 44.51 (broad $^+N\underline{C}H_3$); 60.51, 61.03 ($^+N(\underline{C}H_2)_2$); 74.41 (d, $^2J_{PC} = 1.3$ Hz); 75.95 (s, broad, $^3J_{PC} < 2$ Hz; $C\underline{H}N^+$); 127.6–141.0 (aromatic C with a complex degenerated spectrum of four singlets for $\underline{Ph}$C + four pairs of diastereoisomeric doublets for $\underline{Ph_2}$P). 224.24 ($^2J_{PC} < 2$ Hz; $\underline{C}$O).

7.4. *N,N-dimethylvalinol **5***

A mixture of 96% (−)-valinol (4.91 g, 45.7 mmol), 37% aqueous formaldehyde (3.43 g, 114.3 mmol) and formic acid (8.41 g, 182.8 mmol) were heated at 100°C for 2 h. The solution was cooled to r.t. and 30 ml of 5 N aqueous NaOH was added. After extraction with ether (3 × 30 ml), the organic phase was washed with 20 ml of 5 N aqueous NaOH and then water (2 × 20 ml), dried over MgSO$_4$ and evaporated to dryness. A spectroscopically pure yellow oil **5** was obtained and used as such in the next step (4.46 g; 74%). $\alpha_D^{25} = -3.2°$ (neat). ^{1}H-NMR: $\delta = 0.80$ (d, $^3J_{HH} = 5.4$ Hz, 3H; $C\underline{H}_3$); 0.92 (d, $^3J_{HH} = 5.4$ Hz, 3H; $C\underline{H}_3$); 1.79 (sept. d, 1H; $C\underline{H}(CH_3)_2$); 2.10 (m, 1H; $C\underline{H}N$); 2.31 (s, 6H; $N(C\underline{H}_3)_2$); 3.05 (broad, 1H; $O\underline{H}$); 3.10–3.50 (m, $^3J_{HH} = 4.3$ Hz, $^3J_{HH} = 10.6$ Hz, $^3J_{HH} = 8.1$ Hz, 2H; $C\underline{H}_2OH$). ^{13}C{^{1}H}-NMR: $\delta = 19.98$ ($C\underline{C}H_3$); 22.15 ($\underline{C}H_3$); 28.30 ($\underline{C}HMe_2$); 41.47 ($N(\underline{C}H_3)_2$); 59.46 ($\underline{C}H_2OH$); 71.48 ($\underline{C}HNMe_2$).

7.5. *N,N,N-trimethylvalinolium iodide **6·I***

CH$_3$I (6.34 g, 45 mmol) was added into a solution of **5** (3.91 g, 29.8 mmol) in 20 ml of ether. The solution was stirred for 15 h, and a white solid was filtered and dried (2.76 g; 34%). Another 4 ml of CH$_3$I was added to the ether filtrate which was stirred for an additional 72 h. The solution was again filtered, the solid was dried (2.97 g; 37%) and combined with the first crop (5.74 g; 71%). $C_8H_{20}INO$ (273.16): Calcd.: C, 35.18; H, 7.38; N, 5.13%: found C, 35.31; H, 7.37; N, 5.12%. $[\alpha]_D^{25} = +10.2°$ ($c = 1.05$, CH$_3$CN). ^{1}H-NMR: $\delta = 0.98$ (d, $^3J_{HH} = 6.8$ Hz, 3H; $C\underline{H}_3$); 1.05 (d, $^3J_{HH} = 7.1$ Hz, 3H; $C\underline{H}_3$); 2.39 (m, 1H; $C\underline{H}(CH_3)_2$); 3.14 (s, 9H; $N(C\underline{H}_3)_3$); 3.32 (m, 1H; $C\underline{H}N$); 3.95 (broad, 3H; $O\underline{H}$ and $C\underline{H}_2OH$). ^{13}C{^{1}H}-NMR: $\delta = 17.75$ ($\underline{C}H_3$); 23.13 ($\underline{C}H_3$); 26.83 ($\underline{C}HMe_2$); 53.41 ($N(\underline{C}H_3)_3$); 56.21 ($\underline{C}H_2OH$); 80.13 ($\underline{C}HN$).

7.6. *N,N,N-trimethyl-diphenylvalphosium iodide **7·I***

6·I (1.40 g, 5.12 mmol) and Ph$_2$PNEt$_2$ (2.079 g, 8.20 mmol) were dissolved in 20 ml of refluxing acetonitrile. After 19 h, the solution was cooled to r.t. and evaporated to dryness. The pale yellow oil was stirred with ether (3 × 20 ml) for 15 h: the resulting white solid was filtered and dried (2.25 g; 96%). $C_{20}H_{29}INOP$ (457.34): Calcd.: C, 52.53; H, 6.39; N, 3.06%; found: C, 51.88; H, 6.23; N, 3.06%. $[\alpha]_D^{25} = -7.2°$ ($c = 1.05$, CH$_3$CN). ^{31}P{^{1}H}-NMR: $\delta = 123.4$ (s, $Ph_2\underline{P}$). ^{1}H-NMR: $\delta = 0.94$ (d, $^3J_{HH} = 6.7$ Hz, 3H; $C\underline{H}_3C$); 1.01 (d, $^3J_{HH} = 7.1$ Hz, 3H; $C\underline{H}_3C$); 2.40 (m, 1H; $C\underline{H}Me_2$); 3.10 (s, 9H; $N(C\underline{H}_3)_3$); 3.49 (m, 1H; $C\underline{H}N$); 4.02–4.30 (m, 2H; $C\underline{H}_2OP$). ^{13}C{^{1}H}-NMR: $\delta = 17.46$ ($\underline{C}H_3$); 22.70 ($\underline{C}H_3$); 26.76 ($\underline{C}HMe_2$); 53.31 ($N(\underline{C}H_3)_3$); 64.17 (d, $^2J_{PC} = 22.5$ Hz; $\underline{C}H_2OP$); 80.01 (d, $^3J_{PC} = 9.1$ Hz; $\underline{C}HN$); 129.16–131.10 (aromatic C: four pairs of diastereoisomeric doublets for $\underline{Ph_2}$P).

7.7. *N,N,N-trimethyl-diphenylvalphosium hydridotricarbonylferrate* $\mathbf{7 \cdot HFe(CO)_3}$

A solution of $KHFe(CO)_4$ (1.12 g, 5.4 mmol) in 2.5 ml of THF was added to a solution of **7·I** (2.11 g, 4.62 mmol) in 2.5 ml of THF. After stirring for 15 h, the brown solution was filtered. Ether (4 ml) was added and the solution was cooled to − 20°C: after 10 days, a solid had separated, which was dried (2.121 g; 97%). Elemental analysis consistent with $C_{23}H_{30}FeNO_4P(KI)_{0.2}$ (504.52): Calcd.: C, 54.50; H, 5.97; N, 2.76%; found: C, 54.53; H, 5.73; N, 2.65%. $[\alpha]^{25}_{578} = +7°$, $[\alpha]^{25}_{546} = +16°$ ($c = 0.2$; DMSO). IR (THF): $\nu(CO) = 1939$ (m), 1846 (s), 1830 (sh) cm^{-1}; $\nu(FeH) = 1883$ (m) cm^{-1}. $^{31}P\{^1H\}$-NMR: $\delta = 195.23$ ($Ph_2\underline{P}$). ^1H-NMR: $\delta = -8.84$ (d, $^2J_{HP} = 10.8$ Hz, 1H; FeH); 0.97 (d, $^3J_{HH} = 6.7$ Hz, 3H; $C\underline{H}_3$); 1.05 (d, $^3J_{HH} = 7.0$ Hz, 3H; $C\underline{H}_3$); 2.38 (m, 1H; $C\underline{H}Me_2$); 3.08 (s, 9H; $N(C\underline{H}_3)_3$); 3.46 (m, 1H; $C\underline{H}N$); 4.10–4.34 (2H; $C\underline{H}_2OP$); 7.30–7.75 (5H; $C_6\underline{H}_5$). $^{13}C\{^1H\}$-NMR: $\delta =$ 17.55 ($\underline{C}H_3C$); 23.05 ($\underline{C}H_3C$); 27.30 ($\underline{C}HMe_2$); 53.47 ($N^+(\underline{C}H_3)_3$); 59.63 (d, $^2J_{PC} = 6.6$ Hz; $\underline{C}H_2OP$); 80.64 (d, $^3J_{PC} = 9.2$ Hz; $\underline{C}HN$); 128.54–146.05 (aromatic C with a complex degenerated spectrum of four singlets for $\underline{Ph}C$ + four pairs of diastereoisomeric doublets for $\underline{Ph_2}P$); 223.12 (d, $^2J_{PC} = 11.2$ Hz; gated spectrum: dd, $^2J_{CH} = 12.6$ Hz; $\underline{C}O$).

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References

[1] (a) R.T. Smith, R.K. Ungar, L.J. Sanderson, M.C. Baird, Organometallics 2 (1983) 1138. (b) E. Renaud, R.B. Russel, S. Fortier, S.J. Brown, M.C. Baird, J. Orgonomet. Chem. 419 (1991) 403. (c) E. Renaud, M.C. Baird, J. Chem. Soc. Dalton Trans. (1992) 2905.

[2] See for example: (a) W.A. Herrmann, C.W. Kohlplainter, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524. (b) I.T. Horvath (Ed.), Catalysis in Water. J. Mol. Cat. A 116 (1997). (c) H. Gulyas, P. Arva, J. Bakos, J. Chem. Soc. Chem. Commun. (1997) 2385.

[3] For recent examples, see: (a) D.J. Brauer, J. Fisher, S. Kucken, K.P. Langhans, O. Stelzer, N. Weferling, Z. Naturforsch, B. Chem. Soc. 49 (1994) 1511. (b) I. Kovacs, M.C. Baird, J. Organomet. Chem. 502 (1995) 87. (c) B. Mohr, D.M. Lynn, R.H. Grubbs, Organometallics 15 (1996) 4317.

[4] (a) U. Nagel, E. Kinzel, Chem. Ber. 119 (1986) 1731. (b) I. Toth, B.E. Hanson, Tetrahedron Assym. 1 (1990) 895.

[5] J.-J. Brunet, R. Chauvin, G. Commenges, B. Donnadieu, P. Leglaye, Organometallics 15 (1996) 1752.

[6] For quinine derivatives, see: (a) K.N. Gavrilov, I.S. Mikhel, D.V. Lechkin, G.I. Timofeeva, Phosphorus, Sulfur, Silicon 108 (1996) 285. (b) E.E. Nifantyev, M.K. Gratchev, Tetrahedron Lett. 36 (1995) 1727.

[7] The previous unreported optical rotation has been measured: $[\alpha]^{25}D = -7.2°$ ($c = 0.19$, CH_3CN).

[8] J.-J. Brunet, R. Chauvin, F.B. Kindela, D. Neibecker, Tetrahedron Lett. 47 (1994) 8801.

[9] (a) C.E. Ash, T. Delord, D. Simmon, M.Y. Darensbourg, Organometallics 5 (1986) 17. (b) M. Darensbourg, H. Barros, C. Borman, J. Am. Chem. Soc. 88 (1977) 1647.

[10] On the synthesis of ene–ammoniums, see for example: E. Elkik, Bull. Soc. Chim. Fr. (1969) 903.

[11] J. Wymann Jr., J. Am. Chem. Soc. 58 (1936) 1482.

[12] T. Hayashi, M. Konishi, M. Fukushima, K. Kanahira, T. Hioki, M. Kumada, J. Org. Chem. 48 (1983) 2195.

[13] A. Mortreux, F. Petit, G. Buono, G. Pfeiffer, Bull. Soc. Chim. Fr. (1987) 631.

[14] Although the obtained dimethylvalinol is optically active ($\alpha^{25}_D = -3.2°$ (neat)), the possibility of a partial epimerization through an internal iminium intermediate could be a priori considered:

$$H_2C{=}^+NMeC^*H(i\text{-}Pr)CH_2OH \leftrightarrows Me_2N^+{=}C(i\text{-}Pr)CH_2OH$$

Dimethylation of (*S*)-valine by $H_2CO/H_2/Pt–C$ followed by $LiAlH_4$ reduction of the acid led to (−)-valinol with $\alpha^{25}_D = -3.68°$ (neat), but no precision on the e.e. was given [11]. Previous studies, however, indicated that substitution at asymmetric α-carbons of primary amines is not sufficient to bring about a significant isomerization unless this carbon is benzylic (methylation of optically pure 1-phenylethylamine occurs with 61% e.e.: (a) A.C. Cope, E. Ciganeck, L.J. Fleckenstein, M.A.P. Meisinger, J. Am. Chem. Soc. 82 (1960). Eschweiler-Clarke conditions have also been used for dimethylation of D-penicillamine which is structurally closely related to valinol: the e.e. is 82% and the authors 'suspect that partial racemization occurs, although this has neither been proved nor have exhaustive attempts been made to avoid racemization'. (b) J.H. Griffin, R.M. Kellogg, J. Org. Chem. 50 (1985) 3261. A similar e.e. for **5** is likely.

[15] C.E. Ash, M.Y. Darensbourg, M.B. Hall, J. Am. Chem. Soc. 109 (1987) 4173.

[16] C.E. Ash, C.M. Kim, M.Y. Darensbourg, A.L. Rheingold, Inorg. Chem. 26 (1987) 1357.

[17] In $\mathbf{3a \cdot HFe(CO)_3}$, the electrostatic pairing in solution has been indicated by a measure of a large ^1H-NOE (36%) from $[N(CH_3)_3]^+$ onto $[FeH]^-$ [5].

[18] J.-J. Brunet, G. Commenges, F.B. Kindela, D. Neibecker, Organometallics 11 (1992) 3023.

[19] S.C. Kao, M.Y. Darensbourg, W. Schenk, Organometallics 3 (1984) 871.

[20] M.Y. Darensbourg, J.M. Hanckel, Organometallics 1 (1982) 82.

[21] J.-J. Brunet, R. Chauvin, B. Donnadieu, P. Leglaye, D. Neibecker, submitted for publication in this journal (1998).

[22] J.-J. Brunet, G. Commenges, F.B. Kindela, D. Neibecker, Organometallics 11 (1992) 1343.

[23] J. Chiffre, S. Huguet, P. Leglaye, R. Chauvin, unpublished results.