FULL PAPER

Dalton
www.rsc.org/dalton

Synthesis, structure and dynamics of methoxynaphthalene-substituted phospha-ruthenocenes and -ferrocenes

Duncan Carmichael,*[a] Louis Ricard,[a] Nicolas Seeboth,[a] John M. Brown,[b] Timothy D. W. Claridge[b] and Barbara Odell*[b]

[a] *CNRS UMR 7653, DCPH Ecole Polytechnique, 91128, Palaiseau cedex, France. E-mail: Duncan.Carmichael@polytechnique.fr.; Fax: Intl + 33 1 69333990; Tel: Intl + 33 1 69334571*

[b] *Chemistry Research Laboratory, University of Oxford, Mansfield Road, UK OX1 3TA. E-mail: Barbara.Odell@chem.ox.ac.uk.; Fax: Intl + 44 1865 285002; Tel: Intl + 44 1865 275620*

Received 17th December 2004, Accepted 20th April 2005
First published as an Advance Article on the web 18th May 2005

The syntheses of potassium 2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholide **4** and η^5-pentamethylcyclopentadienyl{η^5-2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholyl}-ruthenium(II) **5** and -iron(II) **6** are described. The barrier to rotation of the naphthyl group (79 kJ mol^{-1} and 72 kJ mol^{-1} in CD_2Cl_2 respectively) characterises **5** and **6** as potential '*tropos*' type ligands. Coordination of **5** to [$PtCl_2(PEt_3)$] gives two *cis* and two *trans* complexes [$PtCl_2(PEt_3)$**5**] wherein rotation about the phospholyl–naphthyl vector is slow.

Introduction

The area of naphthalene-derived ligands is one of the most vibrant in homogeneous catalysis because of the excellent organisation of space provided by the 2,2′-substituted binaphthyl skeleton. In addition to symmetrically substituted O,[1] N,[2] P[3] *etc* donor pairs, this framework has provided a very easily accessible[4] and useful second generation of C_1-symmetrical ligands exemplified by MOP,[5–7] MAP,[8–11] NOBINs,[12–14] quinap,[15,16] *etc.* (see Fig. 1).[17,18] Ferrocene–phosphine based MOPF ligands bearing simple non-functionalised naphthalene groups have also been shown to possess useful properties, particularly in fast Pd-catalysed hydrosilylation reactions.[19,20] We were therefore interested in developing one of the few classes of ligands which has not so far been elaborated with a naphthalene-derived skeleton: the phosphametallocenes,[21] which themselves have been shown to be quite versatile ligand platforms, notably in enantioselective Cu-catalysed [3 + 2] cycloadditions,[22] Kinugasa reactions,[23] and 1,4 additions to enones[24] as well as Rh-based allylic alcohol isomerisations,[25,26] and hydrogenations[27] and Pd-catalysed allylic alkylations.[28,29] They have also proved efficient in racemic Suzuki[30] and Miyaura[31] cross-coupling chemistry and epoxide ring openings.[32,33] For an initial study in this area we intended to prepare and evaluate the configurational stability and coordination chemistry of one of the simpler classes, the methoxynaphthylphosphametallocenes.

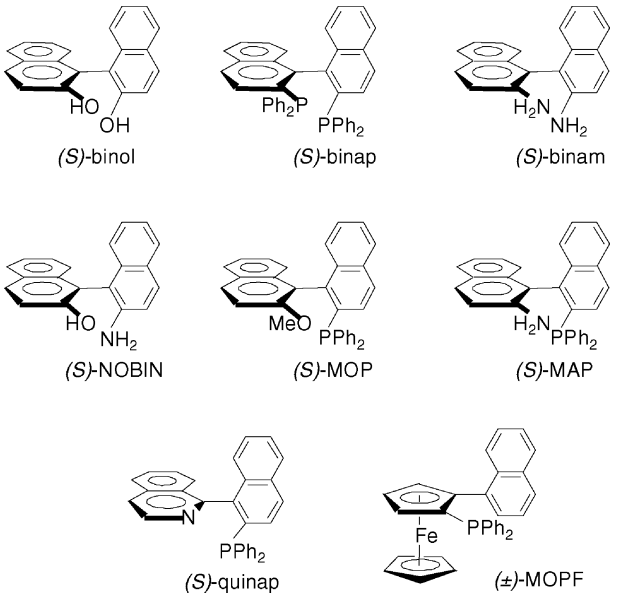


Fig. 1 Some naphthalene-derived ligands.

At present, the use of phosphametallocenes as ligands in catalysis has been restricted almost exclusively to the phosphaferrocenes. It has been noted previously[34] that variation of the phosphametallocene metal centre is desirable in allowing a nuancing of properties which might be advantageous in terms of catalyst lifetime, sensitivity, enantioselection, *etc*, but late transition metal phosphametallocenes where M ≠ Fe can only be prepared easily and in acceptable yields[35] in cases where the phospholide ring bears an electron-withdrawing group[34] or is hindered about phosphorus.[36–39] The 2-methoxynaphth-1-yl substituent seemed likely to provide sufficient bulk to allow the synthesis of both phospharuthenocene and phosphaferrocene relatives of MOP.[5–7] This paper describes the preparation and properties of such complexes, and presents the dynamics and some preliminary coordination chemistry of a 2-(2′-methoxynaphth-1′-yl)-phospharuthenocene.

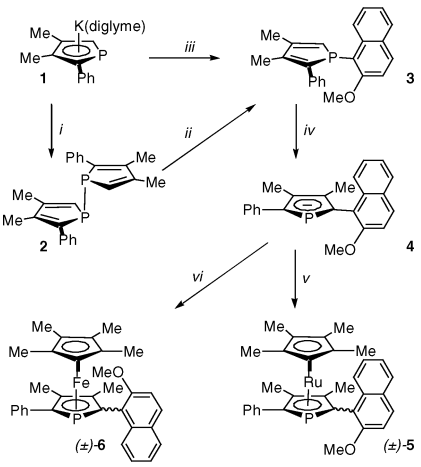
Results and discussion

Synthetic aspects

The best route to the desired naphthalene-substituted phospholyl ligand seemed to involve the preparation of the unknown 1-(2′-methoxynaphth-1′-yl)phosphole **3**, whereupon a thermally driven [1,5] sigmatropic shift-step coupled to a deprotonation[40,41] would lead to the new phospholide anion **4**. This technology is straightforward in practical terms and is easily scaled up.

Two routes to the requisite 1-(2′-methoxynaphth-1′-yl)phosphole derivative **3** were evaluated. Both start from the 2-phenyl-3,4-dimethylphospholide anion **1**,[41] which was preferred over the ubiquitous 3,4-dimethylphospholide[21] in this preliminary study because of its easier large-scale preparation and slightly increased bulk. In the first method (steps *i* and *ii* of Scheme 1), the 2-phenyl-3,4-dimethylphospholide was initially oxidised cleanly

DOI: 10.1039/b418926d



Scheme 1 *Reagents and conditions*: *i*: I_2 (0.5 eq.) THF, 0 °C, 30 min; *ii*: I_2 (1 eq.) THF, 0 °C, 30 min, then 2-methoxynaphth-1-yl magnesium bromide, −40 °C, 2 h; *iii*: 1-iodo-2-methoxynaphthalene (1.5 eq.), KO*t*-Bu (1.2 eq.) diglyme, 110 °C, 1.5h; *iv*: KO*t*-Bu (1 eq.) diglyme, 140 °C, 12 h; *v*: $[RuCp^*Cl]_4$ (0.25 eq.), THF, 30 min; *vi*: [FeCp*Cl] (1 eq.), THF, 30 min.

to the diastereomeric 1,1′-biphosphole **2**† using iodine. After isolation, a second (rather experimentally taxing) oxidation using a further equivalent of iodine gave the corresponding 1-iodophosphole, which was allowed to react without isolation with the appropriate 2-methoxynaphth-1-yl Grignard or lithium reagent. The attack of the carbon nucleophile was complicated by redox reactions and the 1-(2′-methoxynaphth-1′-yl)phosphole **3** was obtained in only moderate yield, contaminated with **2** and 1-iodo-2-methoxynaphthalene. Attempts to prevent the formation of the redox-controlled biphosphole byproduct **2** through transmetallation of the Grignard reagent with $ZnCl_2$ proved tedious and this methodology was abandoned. A second approach, based upon the formal S_N2Ar attack of the phospholide anion upon either 1-bromo- or 1-iodo-2-methoxynaphthalene in the presence of potassium *tert*-butoxide (step *iii* of Scheme 1), proved much more satisfactory and, after chromatography on silica, samples of the bright yellow relatively air-stable phosphole **3** could be obtained on a *ca*. 25 g scale. The synthesis was completed by a 12h thermolysis of **3** with KO*t*-Bu in diglyme at 140 °C which gave crude yields of **4** in the region of 90% according to ^{31}P NMR. Excessive reaction times led to demethylation of the anisyl group[42,43] and formation of the corresponding phospholide–naphtholate (*vide infra*). Once obtained, the product phospholide was generally complexed to $[RuCp^*Cl]_4$ or '[FeCp*Cl]' *in situ* with careful control of stoichiometry to avoid the formation of coordination complexes through reaction of the desired phosphametallocenes with excess [MCp*Cl]. This appeared to be a particular problem in the ruthenium case, where the undesired complexes could be identified by their chemical shifts between +35 and +50 ppm in the ^{31}P NMR spectrum. To ensure completion, a slight excess of phospholide and gentle warming were employed.

Structural studies of naphthyl-substituted phosphametallocenes (M = Ru, Fe)

A structural study of the phospharuthenocene **5** was made. Crystallisation of the mixture obtained from reaction of **4** with $[RuCp^*Cl]_4$ was effected from CH_2Cl_2–EtOH and visual inspection of the yellow air-stable product indicated the presence of only one form in the bulk. A suitable monocrystal was investigated by low-temperature X-ray diffraction (Fig. 2). The phenyl ring lies nearly coplanar with the phospholyl but the methoxynaphthyl component is oriented almost perpendicularly to the phospholyl plane {P1–C(4)–C(13)–C(14) −72.9°} with the methoxyl group lying *exo* to the 'sandwich' defined by the complex. The unsubstituted arene ring of the naphthyl group intercalates cleanly between two methyl groups of the Cp* ligand, suggesting a degree of hindrance within the structure. Steric strain within the phospharuthenocene is also apparent in a tilting of the phospholyl ligand which causes the Ru–C(4) distance of 2.295(2) Å to be much longer than Ru–C(1) {2.196(2) Å}, to a degree which is comparable with that in the triisopropylsilyl analogue **7**.[38] Simple rotation about the C(4)–C(13) bond to make the naphthyl ligand coplanar with the phospholyl ring whilst holding all other bond lengths and angles constant brings C(15) to within 2.01 Å or O(1) to within 1.64 Å of the methyl carbon attached to C(3).

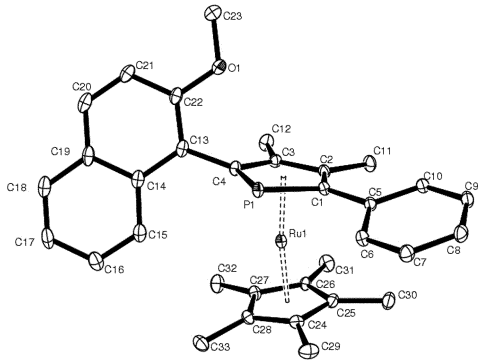
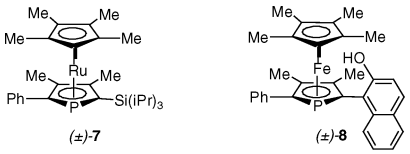


Fig. 2 X-Ray crystal structure of **5** showing 30% probability ellipsoids. Selected bond lengths: Ru(1)–P(1), 2.422(1); Ru(1)–C(1), 2.196(2); Ru(1)–C(2), 2.175(2); Ru(1)–C(3), 2.225(2); Ru(1)–C(4), 2.295(2); Ru(1)–C(25), 2.176(2); Ru(1)–C(24), 2.189(2); Ru(1)–C(26), 2.204(2); Ru(1)–C(27), 2.212(2); Ru(1)–C(28), 2.224(2); P(1)–C(1), 1.796(2); P(1)–C(4), 1.778(2); C(1)–C(2), 1.434(3); C(2)–C(3), 1.435(3); C(3)–C(4), 1.427(3); C(1)–C(5), 1.480(3) Å. Torsion angles: P1–C(4)–C(13)–C(14), −72.9; P1–C(4)–C(13)–C(22), +99.9; P1–C(1)–C(5)–C(6), +22.0; P1–C(1)–C(5)–C(10), −154.2°.

In an early study aimed at recording the crystal structure of **6**, a crude sample of phospholide solution was prepared by prolonged basic thermolysis of **3** using a non-optimised protocol and reacted with [FeCp*(acac)]. Instead of the anticipated **6**, crystallisation from dichloromethane–methanol gave a poor yield of orange crystals which were shown to be the phosphaferrocene–naphthol **8**.



The structure shows the anticipated[39] *ca*. 5% shortening in M–ligand bond lengths upon passing from ruthenium to iron. In this case, the naphthyl group again lies almost perpendicular to the phospholyl plane, but shows a P1–C(4)–C(5)–C(6) torsion angle of −101.5°, which brings the oxygen atom quite close to the Fe centre (3.47 Å). The hydroxyl hydrogen atom was located in the final difference map and is oriented away from the iron atom, so the naphthyl orientation does not result from an O–H···Fe interaction.[44,45] Rotating the C–C bond to allow maximum coplanarity between the phospholyl and naphthyl groups gives minimum distances from the C(3) methyl group of 1.66 Å to C(13) and 1.84 Å to O(1).

NMR studies

A priori, the crystallographic results show that the naphthyl groups in **5** and **8** adopt orientations which might be favourable

† The two diastereomers could not be separated because of rapid interconversion. 300 MHz ^1H EXSY experiments give an estimated energy barrier for this process of 66 kJ mole^{-1} at 294 K in deuterodichloromethane. This barrier lies close to values previously observed for pyramidal inversion in other phospholes.[73,87–89]

for use in enantioselection.[46–48] However, whilst dissolution of crystalline **5** in dichloromethane at −78 °C and measurement at the same temperature gave a single ^{31}P NMR peak at −25.8 ppm characteristic of **5a**,[49] warming to room temperature provoked the appearance of rotamer **5b** (−20.8 ppm). Consistently, addition of deuterobenzene to the bulk solid employed for the crystal structure analysis of **5** at room temperature gave a solution containing two compounds, with repeated crystallisation of the sample producing no effect on the ratio of 3.58 (**5a**) : 1 (**5b**) in C_6D_6 at 298 K. Thus, conformers **5a** and **5b** clearly equilibrate in solution (see Fig. 3). Analogous results were obtained with **6**, but the ratio was found to be 1 (**6a**) : 2.31 (**6b**), so that the favoured solution conformer resembles the crystallographically determined structure **8** (see Fig. 4).

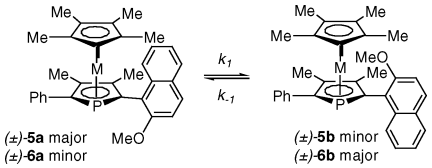


Fig. 3 Equilibration of **5a** and **5b** and **6a** and **6b** through rotation about the phospholyl–naphthyl bond.

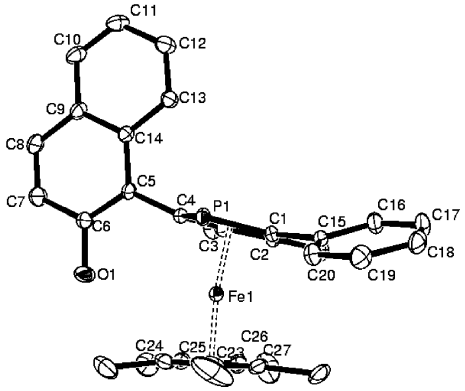


Fig. 4 X Ray crystal structure of **8** showing 20% ellipsoids. Selected bond lengths: Fe(1)–P(1), 2.2959(6); Fe(1)–C(1), 2.109(2); Fe(1)–C(2), 2.080(2); Fe(1)–C(3), 2.093(2); Fe(1)–C(4), 2.145(2); Fe(1)–C(23), 2.068(3); Fe(1)–C(24), 2.093(2); Fe(1)–C(25), 2.102(2); Fe(1)–C(26), 2.076(3); Fe(1)–C(27), 2.057(3); P(1)–C(1), 1.793(2); P(1)–C(4), 1.771(2); C(1)–C(2), 1.426(3); C(2)–C(3), 1.429(3); C(3)–C(4), 1.423(3); C(4)–C(5), 1.494(3) Å. Torsion angles: P1–C(4)–C(5)–C(6), −101.5; P1–C(4)–C(5)–C(14) +57.1; P1–C(1)–C(15)–C(20), +27.7; P1–C(1)–C(15)–C(16), −146.4°.

The spectra of **5a** and **5b** were assigned through a combination of COSY, HMQC and HMBC experiments. Large NOE (nuclear Overhauser effects) were observed in 1D selective NOESY experiments[50] from the Cp* methyl protons to the methoxyl group in the minor isomer **5b** and from the Cp* methyls to the characteristically[19] high frequency shifted naphthyl 8-proton in the major isomer **5a**. These further confirm that the crystallographically observed form resembles the preferred structure in solution. The conformations of the corresponding phosphaferrocene isomers were deduced from the chemical shifts of the 8-naphthyl protons, which were very similar to those of the phospharuthenocenes (Fig. 6, upper). The equilibrium relating both sets of complexes was probed by 2D and 1D exchange experiments. In principle, a single 2D exchange spectroscopy (EXSY) experiment using an optimised mixing time suffices to establish the rotation barrier about the phospholyl–naphthyl bond,[51,52] but a more complete approach was chosen, wherein methods evaluating the rotation barrier through both ^{1}H and ^{31}P EXSY measurements‡ were compared for **5**. A series of two-dimensional ^{1}H EXSY experiments alone was used for **6** due to lower quality ^{31}P 2D EXSY data.

‡ In principle, the ^{1}H EXSY experiment may suffer from interference from NOESY effects. The very similar values obtained here through the two measurements imply that the NOE influence is negligible.

^{31}P 2D EXSY measurements. These were performed in CD_2Cl_2 to maximise the solute concentration. A series of two-dimensional spectra were collected (Fig. 5) with the exchange mixing times varied from 0.1 to 1.2 s. Data were analysed according to the procedure described in detail in refs. 53 and 54 and further exemplified by Willem *et al.*[55] for the extraction of exchange rate constants. For the short mixing times (t_m) used the initial rate approach is valid and the simple two-spin system rate constant tends to the differential of B_{ij} with respect to time, where B_{ij} is the so-called normalised cross-peak volume, that is, the ratio of the cross- to diagonal-peak volumes (V_{ij} and V_{jj} respectively):[54]

$$B_{ij}(t_m) = \frac{V_{ij}(t_m)}{V_{jj}(t_m)} \xrightarrow{t_m \to 0} k_{ij} t_m \qquad (1)$$

The forward and back isomerisation rate constants (k_{ij}) were obtained upon plotting the build-up of cross-peak relative to diagonal-peak volumes against incremented mixing times over a sequence of 13 experiments. The rate constants are then represented as the slopes in the linear build-up regime (Fig. 7). The first order i to j exchange half-life ($t_{1/2}$) calculated from eqn. (2):

$$t_{1/2ij} = \ln 2 / k_{ij} \qquad (2)$$

and rotational barriers $\Delta G^{\ddagger}$ obtained from a simplified Eyring equation neglecting correlation time effects (eqn. (3)):

$$\Delta G^{\ddagger}_{ij} = RT\ln[(k_B T)/(k_{ij} h)] \qquad (3)$$

(k_B being Boltzmann's constant) are given in Table 1. The calculated equilibrium constant K_{calc} of 0.25 obtained from the right hand side of eqn. (4)

$$\frac{[\mathbf{5b}]}{[\mathbf{5a}]} = K = \frac{k_1}{k_{-1}} \qquad (4)$$

compares well with the experimental value K_{exp} of 0.23 obtained from the same sample by integration of the peaks for **5a** and **5b**.

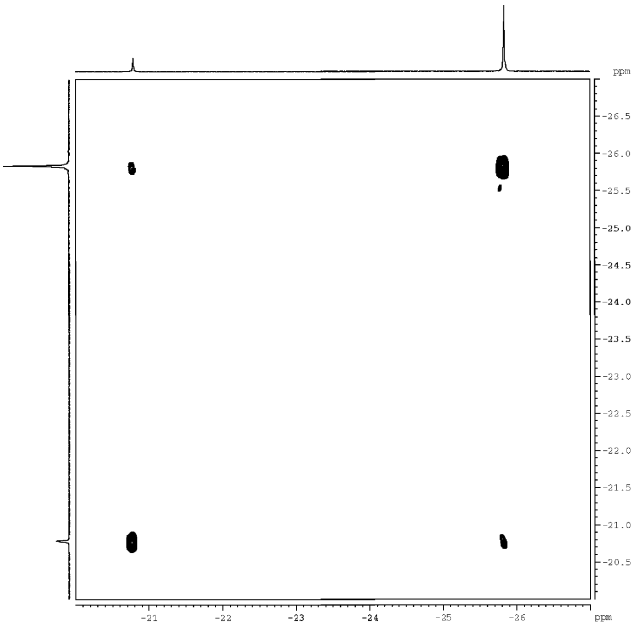


Fig. 5 A typical example of a 2D ^{31}P EXSY spectrum of **5** in CD_2Cl_2. Technical data: Bruker AMX 500, SF = 202.395 MHz, NS = 8, NE = 64, mixing time = 1.2 s, total recycling time 1 s, total acquisition time for each entire 2D spectrum *ca.* 2 h.

Table 1 ^{31}P 2D EXSY-derived rate constants and energy barriers for rotation about the phospholyl–naphthalene bond in **5** (at 298 K, in CD_2Cl_2)

	$10^2k/s^{-1}$	$\Delta G^{\ddagger}$/kJ mol^{-1}
k_1: **5a** → **5b**	4.5 ± 0.6	80.7 ± 0.4
k_{-1}: **5b** → **5a**	18 ± 2	77.2 ± 0.4

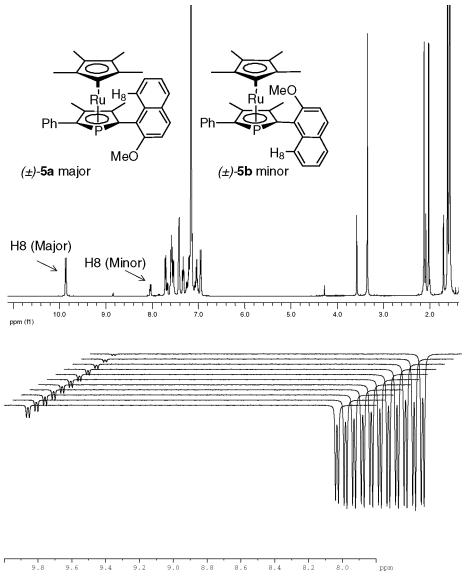


Fig. 6 Upper: ^{1}H spectrum showing the two conformers of phospharuthenocene **5** in C_6D_6. Lower: stacked plots showing magnetisation transfer upon selective inversion at 8.1 ppm of the naphthyl 8-proton of the minor conformer **5b**. Mixing times increase from 100 ms to 1.2 s in 100 ms increments (except for the last, at 200 ms) from back to front.

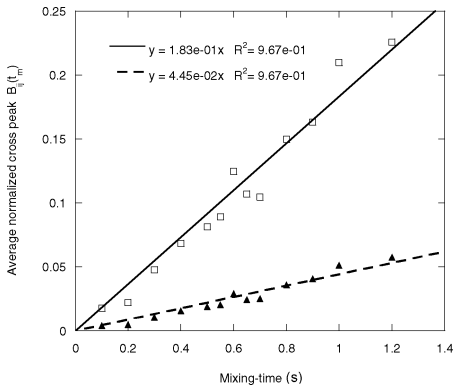


Fig. 7 Normalised cross-peak build-up curves obtained from the 2D ^{31}P EXSY experiments on a deuterodichloromethane solution of **5**. □: site exchange from **5b**, ▲: site exchange from **5a**.

^{1}H measurements. The ^{31}P determinations for **5** were complemented by twenty-two 1-dimensional ^{1}H EXSY spectra for **5** and seven 2-dimensional ^{1}H EXSY spectra for **6**. C_6D_6 was chosen as the solvent in both cases to maximise the ^{1}H NMR chemical shift dispersion. It provided a particularly marked separation of the naphthyl 8-proton resonances in the two rotamers (Fig. 6).

For the 1-dimensional EXSY experiments on **5**, 1D double pulsed field gradient spin-echo techniques[50,56] were employed to invert the naphthyl 8-protons which were used as the source for the magnetisation transfer process. Two separate sets of 11 spectra with mixing times from 0.1 to 1.2 seconds were recorded with selective inversion of the naphthyl 8-proton in both the major and minor conformers. Data were analysed using the initial rate method referenced above with the normalised exchange peak area calculated as the area ratio between the exchange peak itself and the selectively inverted peak (Fig. 8).

Table 2 ^{1}H 1D EXSY derived rate constants and energy barriers for rotation about the phospholyl–naphthalene bonds in **5** and **6**

T/K	k (C_6D_6)	$10^2k/s^{-1}$	$\Delta G^{\ddagger}$/kJ mol^{-1}
298	k_1: **5a** → **5b**	2.6 ± 0.1	82.0 ± 0.1
298	k_{-1}: **5b** → **5a**	9.8 ± 0.2	78.7 ± 0.05
295	k_1: **6a** → **6b**	119 ± 1	71.8 ± 0.1
295	k_{-1}: **6b** → **6a**	48 ± 3	74.0 ± 0.1

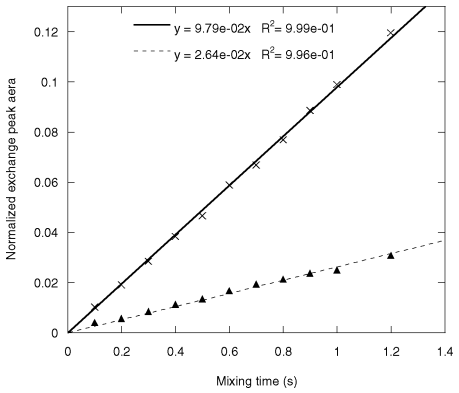


Fig. 8 Magnetisation transfer observed by 1D ^{1}H EXSY upon inversion of the naphthyl 8-proton in phospharuthenocenes **5** (×: inversion of **5b**, ▲: inversion of **5a**).

The calculated rate constants and rotational barriers (Table 2; derived as above), are comparable with those obtained in the first experiment, although the rate constants differ by a factor of *ca.* 2. This may be attributed to the different solvents employed for the ^{31}P (CD_2Cl_2) and ^{1}H (C_6D_6) experiments, as described above. The $K_{calc} = 0.27$ and the $K_{exp} = 0.28$ equilibrium constants again show good agreement. For **6**, exchange between the methoxy signals gave a slightly poorer quality 2D EXSY data set from which somewhat lower rotation barriers could be demonstrated (Table 2).

The barriers in **5** and **6** of *ca.* 80 and 72 kJ mol^{-1} respectively (equating to a rotational half life of approximately 12 s (for **5**) and 1 s (for **6**) at 298 K) are significantly below the value for the configurationally labile biphep (*ca.* 92 kJ mol^{-1} at 398 K)[57] and much smaller than in genuine atropomeric ligands such as *e.g.* 1,1′-binaphthyl (100 kJ mol^{-1} at 373 K)[58,59] and BINOL (*ca.* 156 kJ mol^{-1} at 398 K).[60]

Coordination chemistry at [$PtCl_2(PEt_3)$] centres

Ligands having rapidly interconverting structures in the free state, such as biphep,[57] nuphos[61] *etc.* are increasingly recognised as offering useful and highly stable ligand geometries after coordination-resolution at a metal centre.[62,63] Platinum is frequently employed because, in addition to binding strongly to phosphorus donors, resolved Pt(II) complexes of such '*tropos*' ligands have been shown to be efficient catalysts for enantioselective cycloadditions.[61,64,65] It therefore seemed useful to evaluate the configurational stability of a coordinated phospharuthenocene–naphthalene ligand and reaction at a Pt(II) centre was effected. The system resulting from the addition of **5** to $[PtCl_2(PEt_3)]_2$ (see Fig. 9), was chosen to facilitate analysis of the product mixture by NMR measurements.§ Upon reaction in C_6D_6, two products were formed instantaneously in a 1 : 0.58 ratio. These were identifiable as *trans*-configured complexes on the basis of their large $^2J_{PP}$ and relatively small $^1J_{PtP}$ values,[66] with the predominant product being structure **10** as shown by the

§ Complexation to the more conventional $[PtCl_2(PhCN)_2]$ gave much more complex spectra which presumably result from the presence of multiple diastereomers. This system was not investigated in detail.

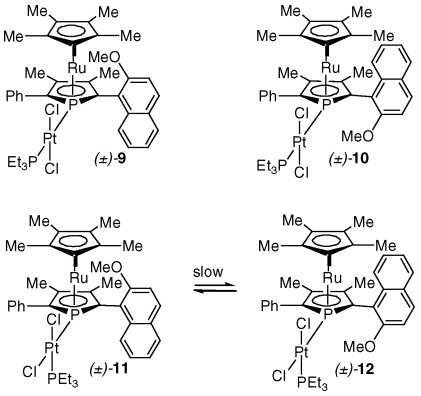


Fig. 9 Phospharuthenocene complexes formed through upon interaction of **5** with $[PtCl_2(PEt_3)]_2$.

characteristic[19] high frequency shift of the naphthyl 8-proton. The mixture evolved in $CDCl_3$ in the absence of further ligand and, after standing for two weeks, *ca.* 80% of the spectrum integral comprised resonances attributable to the *cis*-complexes **11** and **12**. No EXSY evidence for exchange between any of the possible pairs of complexes **9** to **12** was obtained and it is clear that interconversion between the various complexes is slow. ^{1}H NMR data indicate that the major *cis*-diastereomer in solution after long standing is **12** and crystallisation of the mixture by diffusion of ethanol into the chloroform solution gave a clean sample of this complex. Upon redissolution of the crystals, the spectrum showed clean **12**, with a return to the previously observed equilibrium mixture of **11** and **12** occurring only over a week.

To probe the loss of rotational freedom about the phospholyl–naphthalene vector associated with the coordination to Pt, a structural determination of **12** was undertaken (see Fig. 10). The complex shows an expectedly short Pt(1)–P(1) bond 2.210(2)Å, which results from the high s-character in the phosphametallocene donor hybrid, and a short Pt(1)–Cl(2) separation of 2.344(2)Å as a consequence of its correspondingly weak *trans* influence.[67–69] As anticipated, the methoxyl group lies *exo* to the phosphametallocene sandwich but is oriented away from platinum centre by a P1–C(1)–C(5)–C(14) torsion angle of −118.9°. Thus, as in structures containing the MOP ligand,[70–72] no interaction between the MeO group and the empty metal d_{z^2} orbital is observed (Pt–O = 5.27 Å) and it seems likely that the rigidity of **12** results purely from increased hindrance within the ensemble.

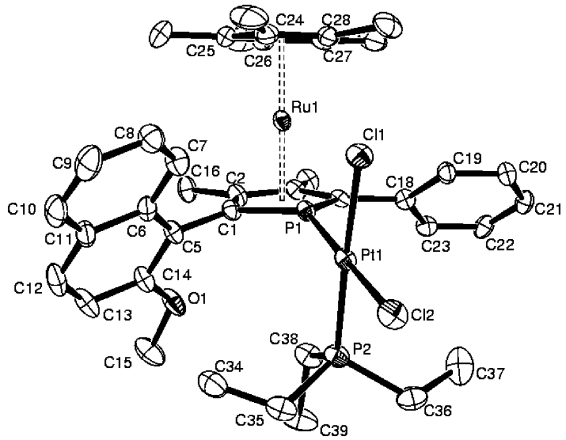


Fig. 10 X Ray crystal structure of **12** showing 20% probability ellipsoids. Selected bond lengths: Pt(1)–P(1), 2.210(2); Pt(1)–P(2), 2.242(3); Pt(1)–Cl(1), 2.374(2); Pt(1)–Cl(2), 2.344(2); Ru(1)–P(1), 2.313(2); Ru(1)–C(1), 2.300(8); Ru(1)–C(2), 2.215(8); Ru(1)–C(3), 2.192(8); Ru(1)–C(4), 2.228(8); Ru(1)–C(24), 2.21(1); Ru(1)–C(25), 2.24(1); Ru(1)–C(26), 2.21(1); Ru(1)–C(27), 2.185(8); Ru(1)–C(28), 2.18(1); P(1)–C(1), 1.782(8); P(1)–C(4), 1.775(8); C(1)–C(2), 1.41(1); C(2)–C(3), 1.44(1); C(3)–C(4), 1.42(1); C(1)–C(5), 1.48(1) Å. Torsion angles: P1–C(1)–C(5)–C(6), +57.1; P1–C(1)–C(5)–C(14), −118.9; P1–C(4)–C(18)–C(23), +137.9; P1–C(4)–C(18)–C(19), −40.8°.

Conclusions

The preparation of 2-naphthyl-substituted phospholide anions is straightforward and these precursors are bulky enough to allow the synthesis of transition metal phosphametallocenes other than those containing iron. As anticipated, the phospharuthenocene complex **5** proved easier to handle than its phosphaferrocene analogues **6** and **8**. The 2-(2-methoxynaphth-1-yl) substituent is unusual because, with the exception of Hayashi and Ogasawara's elegant but difficultly-accessible[73] menthyl-substituted system,[74] the phospholides which have been used to prepare phospharuthenocenes to date have either required further elaboration (from esters,[34] silanes[38]) to provide ligands having useful functionality or are essentially impossible to modify further (bearing *tert*-butyl,[75] cyclohexyl[39] groups, *etc.*). The simple 2-methoxynaphth-1-yl substituent employed here is not sufficiently bulky to allow the resolution of atropomers of either the phospharuthenocene or -ferrocene complexes but the relatively high rotation barriers mean that a further small increase in hindrance will probably suffice to block rotation about the phospholyl–naphthalene bond. That the rotation barrier is higher for **5** than **6** implies that the latter's more tightly packed coordination sphere does not have a significant impact upon the rotation of the naphthyl ring, probably because of the rather soft potential surface for ring bending in metallocenes.[76,77] Thus any hindrance introduced to block a configuration will probably function better when located at an appropriate site within the naphthylphospholyl ligand than when incorporated into the Cp*.

The configurational stability of the coordinated phosphametallocene–naphthalene ligand is quite high when bound to the reasonably inert transition metal centre **12**. The data available at this stage do not preclude an 'on-metal' equilibration mechanism for the interconversion of **11** and **12**,[78,79] but the relative weakness of the Pt–phosphametallocene bond[80] leads us to speculate that a dissociation–rotation–recombination mechanism may be more likely. Such a pathway should be inhibited should a coordinating group replace the OMe substituent. Methods for preparing enantiopure derivatives of **5** and related ligands are under investigation.

Experimental

All operations were performed either using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun Labmaster 130 drybox under dry purified argon. Column chromatography was performed on 63–200 μm silica or 50–160 μm neutral alumina as appropriate. $[RuCp^*Cl]_4$,[81] '$[FeCp^*Cl]$',[24,82,83] $[PtCl_2(PEt_3)]_2$,[84] 1-phenyl-3,4-dimethylphosphole[85] and $[K(PC_4PhMe_2H)\cdot diglyme]$ **1**[86] were prepared as described previously. Tetrahydrofuran was distilled from sodium–benzophenone ketyl and pentane from sodium–benzophenone ketyl–tetraglyme under an atmosphere of dry nitrogen and stored for short periods over 4 Å molecular sieves. Diglyme was distilled under reduced pressure from CaH_2. Dichloromethane was distilled from P_4O_{10} under nitrogen. Deuterobenzene was used as received, and deuterochloroform was deacidified through alumina prior to use. NMR measurements were made on Bruker AM 200, Avance 300, AMX500 and DRX500 spectrometers and are referenced to residual proton signals (C_6D_5H or $CHCl_3$) in the deuterated solvents or external H_3PO_4 as appropriate. Mass spectra were obtained under 70 eV electron impact using direct inlet methods on a Hewlett Packard 5989B spectrometer. Combustion analyses were performed by the 'Service de microanalyse du CNRS', Gif sur Yvette, France.

2,2′-Diphenyl-3,3′,4,4′-tetramethyl-1,1′-biphospholes 2

Method 1. A THF (45 mL) solution of I_2 (1.77 g, 6.95 mmol) was added dropwise at −78 °C to a THF (10 mL) solution of potassium 2-phenyl-3,4-dimethylphospholide–diglyme (5.0 g, 13.9 mmol). A color change from pale to intense yellow was observed and a white precipitate was formed. The mixture was evaporated to dryness under reduced pressure and purified by flash chromatography on degassed silica (pentane–toluene 85 : 15). The mixture of equilibrating 1,1′-biphospholes **2** was obtained as a yellow solid (571 mg, 22%).

Method 2. Solid $PbCl_2$ (2.78 g, 10 mmol) was added to a THF (10 mL) solution of potassium 2-phenyl-3,4-dimethylphospholide–diglyme (7.15 g, 19.9 mmol) causing an immediate colour change from light yellow to intense red. The solution was then heated for 30 min at 45 °C. A dense grey precipitate was separated from the yellow solution and the solvent was removed. Flash chromatography on degassed silica (pentane–toluene 85 : 15) afforded the 1,1′-biphospholes **2** as a yellow solid (1.61 g, 22%). Major diastereoisomer (203 K). ^{31}P NMR (CD_2Cl_2, 203 K): δ −20.0. ^{1}H NMR (CD_2Cl_2, 203 K): δ 7.35 (pseudo-t, J = 7.2 Hz, 4H, *m*-Ph), 7.24 (pseudo-t, J = 7.2 Hz, 2H, *p*-Ph), 6.98 (d, J = 7.1 Hz, 4H, *o*-Ph), 6.06 (pseudo-t, J = 20.7 Hz, 2H, PCH), 1.96 (s, 6H, MeCCH), 1.74 (s, 6H, MeCCPh). ^{13}C (CD_2Cl_2, 203 K): δ 151.4 (br, PC*C*), 142.9 (br, P*C*CPh), 141.9 (pseudo-t, J = 5.3 Hz, PC*C*), 137.1 (pseudo-t, J = 8.8 Hz, *ipso*-Ph), 129.2 (pseudo-t, J = 4.3 Hz, *o*-Ph), 127.8 (*m*-Ph), 126.0 (*p*-Ph), 124.6 (pseudo-t, J = 3.4 Hz, P*C*H), 18.5 (*Me*CCH), 14.4 (*Me*CCPh). Minor diastereoisomer (203 K). ^{31}P NMR (CD_2Cl_2, 203 K): δ −28.7. ^{1}H NMR (CD_2Cl_2, 203 K): δ 7.27 (pseudo-t, J = 7.3 Hz, 4H, *m*-Ph), 7.14 (t, J = 7.3 Hz, 2H, *p*-Ph2), 6.99 (d, J = 7.2 Hz, 4H, *o*-Ph), 5.91 (pseudo-t, J = 20.7 Hz, 2H, PCH), 1.81 (s, 6H, MeCCPh), 1.35 (s, 6H, MeCCH). ^{13}C (CD_2Cl_2, 203 K): δ 151.4 (br, PC*C*), 144.3 (pseudo-t, J = 7.4 Hz, P*C*CPh), 140.4 (pseudo-t, J = 3.1 Hz, PC*C*), 137.0 (pseudo-t, J = 8.8 Hz, *ipso*-Ph), 128.9 (pseudo-t, J = 4.8 Hz, *o*-Ph), 127.5 (*m*-Ph), 125.7 (*p*-Ph), 121.3 (br, P*C*H), 18.2 (*C*H_3CCH), 13.9(*C*H_3CCPh). EI-MS (*m*/*z*,%) 374 ([M]$^+$, 100%).

1-(2′-Methoxynaphth-1′-yl)-2-phenyl-3,4-dimethylphosphole 3

Method 1. A THF (20 mL) solution of iodine (1.77 g, 6.95 mmol) was added dropwise over 30 min at 0 °C to a THF (25 mL) solution of **2** (5.2 g, 13.9 mmol). The mixture was stirred for 15 min and subsequently treated dropwise at −40 °C with 2-methoxynaphthylmagnesium bromide (17.0 mmol) in THF (60 mL) of over a period of 1 hour. After evaporation to dryness *in vacuo*, the residue was purified by chromatography on silica using a solvent gradient rising from pentane : toluene 3 : 2 to pure toluene. After, the sequential addition of 2,2′-diphenyl-3,3′,4,4′-tetramethyl-1,1′-biphospholes **2** and 1-iodo-2-methoxynaphthalene, the product was recovered as a bright yellow solid. Yield 2.01 g, (21%).

Method 2. A diglyme (20 mL) solution of potassium 2-phenyl-3,4-dimethylphospholide–diglyme **1** (5.0 g, 13.9 mmol), 1-iodo-2-methoxynaphthalene (4.74 g, 16.7 mmol) and potassium *tert*-butoxide (1.87 g, 16.7 mmol) was heated to 110 °C for 90 min. After cooling, evaporation to dryness under reduced pressure and extraction with toluene (40 mL), purification by flash chromatography on silica gel (pentane–toluene 4 : 1) gave yellow crystalline phosphole **3**. Yield 2.33 g (41%). Found C, 80.20; H, 6.09; P, 8.88. Calc. for $C_{23}H_{21}OP$ C, 80.21; H, 6.15; P, 8.99%. ^{31}P NMR (C_6D_6): δ −12.9. ^{1}H NMR (C_6D_6): δ 7.98 (d, J_{HH} = 8.6 Hz, 1H, 8-Np), 7.53 (ddd, J_{HH} = 8.3 Hz, J_{HH} = 1.2 Hz, J_{PH} = 2.2 Hz, 2H, *o*-Ph), 7.42 (d, J_{HH} = 8.1 Hz, 1H, 5-Np), 7.38 (d, J_{HH} = 9.0 Hz, 1H, 4-Np), 7.30 (ddd, J_{HH} = 8.4 Hz, J_{HH} = 6.8 Hz, J_{HH} = 1.3 Hz, 1H, 7-Np), 7.06 (ddd, J_{HH} = 8.0 Hz, J_{HH} = 6.9 Hz, J_{HH} = 1.1 Hz, 1H, 6-Np), 7.00 (pseudo-t, J_{HH} = 7.9 Hz, 2H, *m*-Ph), 6.81 (tt, J_{HH} = 7.4 Hz, J_{HH} = 1.2 Hz, 1H, *p*-Ph), 6.67 (d, J_{PH} = 38.2 Hz, 1H, PC*H*), 6.64 (dd, J_{HH} = 9.0 Hz, J_{PH} = 4.6 Hz, 1H, 3-Np), 3.36 (s, 3H, MeO), 2.07 (d, J_{PH} = 4.8 Hz, 3H, *Me*CCH), 2.01 (dd, J_{HH} = 1.1 Hz, J_{PH} = 5.0 Hz, 3H, *Me*CCPh). ^{13}C (C_6D_6): δ 163.5 (d, J = 14.9 Hz, 2-napthyl), 149.2 (P*C*Ph), 147.5 (d, J = 12.7 Hz, PC*C*); 140.5 (d, J = 19.5 Hz, PC*C*), 139.7 (d, J = 2.2 Hz, 8a-Np), 139.2 (d, J = 17.5 Hz, *ipso*-Ph), 134.0 (4-Np), 130.2 (d, J = 2.1 Hz, 4a-Np), 129.9 (d, J = 9.0 Hz, *o*-Ph), 129.1 (5-Np), 128.9 (*m*-Ph),128.5 (P*C*H), 127.8 (7-Np), 126.8 (d, J = 10.3 Hz, 8-Np), 126.7 (*p*-Ph), 124.5 (6-Np), 114.5 (d, J = 3.8 Hz, 3-Np), 112.2 (d, J = 15.7 Hz, 1-Np), 57.3 (*C*H_3O), 19.2 (d, J = 3.2 Hz, *C*H_3CCH), 15.4 (d, J = 1.7 Hz, *C*H_3CCPh). MS (CI{NH_3} *m*/*z*, %) 344 ([M]$^+$, 100%).

Potassium 2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholide–diglyme 4

A mixture of 1-(2′-methoxynaphth-1′-yl)-2-phenyl-3,4-dimethylphosphole **3** (2.00 g, 5.8 mmol) and potassium *tert*-butoxide (620 mg, 5.5 mmol) in diglyme (45 mL) was heated at 140 °C for 12 hours. After checking complete conversion to the phospholide by ^{31}P NMR, the diglyme solvent was evaporated under reduced pressure. The residue was redissolved in a minimum of toluene (*ca.* 10 mL) and precipitated with pentane to afford solid yellow **4** which was washed several times with pentane. ^{31}P NMR (THF-d^8): δ 86.7. ^{1}H NMR (THF-d^8): δ 8.23–8.20 (m, 1H, 8-Np), 7.67–7.64 (m, 1H, 5-Np), 7.64 (d, J_{HH} = 9.0 Hz, 1H, 3-Np), 7.52 (pseudo-d, J_{HH} = 8.2 Hz, 2H, *o*-Ph), 7.28 (d, J_{HH} = 9.0 Hz, 1H, 4-Np), 7.22–7.08 (m, 2H, 6 and 7-Np), 7.14 (pseudo-t, J_{HH} = 7.8 Hz, 2H, *m*-Ph), 6.90 (pseudo-t, J_{HH} = 7.9 Hz, 1H, *p*-Ph), 3.77 (s, 3H, MeO), 3.49 (m, 4H, diglyme), 3.41 (m, 4H, diglyme), 3.24 (s, 6H, diglyme), 2.34 (s, 3H, PCPhC*Me*), 1.80 (s, 3H, PCC*Me*). ^{13}C (C_6D_6): δ 154.3 (d, J = 4.0 Hz, 2-Np), 148.3 (d, J = 39.0 Hz, P*C*Ph), 146.5 (d, J = 22.1 Hz, *ipso*-Ph), 139.9 (d, J = 36.7 Hz, P*C*Np), 137.2 (d, J = 2.5 Hz, 8a-Np), 130.7 (4a-Np), 130.6 (d, J = 19.5 Hz, 1-Np), 129.8 (8-Np), 129.6 (d, J = 10.0 Hz, *o*-Ph), 128.7 (d, J = 11.1 Hz, PCPhC*M*e), 128.0 (*m*-Ph), 127.5 (5-Np), 126.5 (4-Np), 125.1 (7-Np), 123.7 (6-Np), 123.7 (d, J = 5.5 Hz, PCNpC*M*e), 122.8 (*p*-Ph), 113.8 (3-Np), 72.9 (*C*H_2, diglyme), 71.3 (*C*H_2, diglyme), 59.13 (*C*H_3, diglyme), 57.0 (*C*H_3O), 16.1(*C*H_3CCPh), 15.4 (*C*H_3CCNp).

η^5-Pentamethylcyclopentadienyl{η^5-2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholyl}ruthenium(II) 5

A room temperature THF (100 mL) solution of $[RuCp^*Cl]_4$ (1.20 mg, 1.10 mmol) was added to a THF (100 mL) solution of **4** (4.40 mmol) and the orange mixture was stirred for 30 min. After refluxing for a further 30 min, the mixture was evaporated to dryness *in vacuo* and purified by flash chromatography in pure toluene on silica. Crystallisation of the crude from dichloromethane–ethanol gave pale yellow essentially air-stable crystals of the product **5** (2.20 g, 86%). Ratio: 0.31 (**5b**) : 1 (**5a**) in C_6D_6 at 298 K. Major (**5a**): ^{31}P NMR ($CDCl_3$): δ −24.8. ^{1}H NMR (C_6D_6): δ 9.86 (d, J_{HH} = 8.5 Hz, 1H, 8-Np), 7.71 (d, J_{HH} = 8.1 Hz, 1H, 5-Np), 7.59 (ddd, J_{HH} = 8.3 Hz, J_{HH} = 6.8 Hz, J_{HH} = 1.3 Hz, 1H, 7-Np), 7.57 (d, J_{HH} = 9.1 Hz, 1H, 4-Np), 7.42 (pseudo-d, J_{HH} = 7.3 Hz, 2H, *o*-Ph), 7.33 (ddd, J_{HH} = 7.9 Hz, J_{HH} = 6.9 Hz, J_{PH} = 1.0 Hz, 1H, 6-Np), 7.15 (pseudo-t, J_{HH} = 7.9 Hz, 2H, *m*-Ph), 7.03 (tt, J_{HH} = 7.3 Hz, J_{HH} = 1.1 Hz, 1H, *p*-Ph), 6.95 (d, J_{HH} = 9.1 Hz, 1H,3-Np), 3.35 (s, 3H, MeO), 2.12 (s, 3H, *Me*CCPh), 2.02 (s, 3H, *Me*CCNp), 1.57 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): 155.5 (d, J = 2.5 Hz, 2-Np), 140.5 (d, J = 17.5 Hz, *ipso*-Ph), 133.1 (8a-Np), 130.5 (4a-Np), 130.1 (d, J = 7.6 Hz, *o*-Ph), 128.9–127.8 (m-Ph, 4,5 and 8-Np), 126.0 (*p*-Ph), 125.5 (7-Np), 124.2 (6-Np), 122.2 (d, J = 14.0 Hz, 1-Np), 115.2 (3-Np), 102.6 (d, J = 59.2 Hz, P*C*Ph), 98.3 (d, J = 60.6 Hz, P*C*Np), 96.5 (d, J = 3.5 Hz, PC*CMe*), 90.8 (d, J = 3.7 Hz, PC*CMe*), 88.9 (Cp*), 56.4 (MeO), 15.1 (MeCCNp), 14.4 (*Me*CCPh), 11.0 (*Me*Cp*). Minor (**5b**): ^{31}P NMR ($CDCl_3$): δ −19.7. ^{1}H NMR (C_6D_6): δ 8.0 (d, J_{HH} = 8.5 Hz, 1H, 8-Np), 7.66 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.3 Hz, 1H, 5-Np), 7.54

(d, J_{HH} = 8.9 Hz, 1H, 4-Np), 7.54 (pseudo-d, J_{HH} = 8.3 Hz, 2H, *o*-Ph), 7.25 (ddd, J_{HH} = 8.3 Hz, J_{HH} = 6.8 Hz, J_{HH} = 1.5 Hz, 1H, 7-Np), 7.201 (ddd, J_{HH} = 8.1 Hz, J_{HH} = 6.7 Hz, J_{PH} = 1.4 Hz, 1H, 6-Np), 7.195 (pseudo-t, J_{HH} = 8.1 Hz, 2H, *m*-Ph), 7.0 (tt, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz, 1H, *p*-Ph), 6.94 (d, J_{HH} = 8.9 Hz, 1H, 3-Np), 3.58 (s, 3H, MeO), 2.08 (s, 3H, PCPhC*Me*), 1.70 (s, 3H, PCNpC*Me*), 1.62 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): δ 154.6 (2-Np), 140.7 (d, J = 17.8 Hz, *ipso*-Ph), 134.7 (8a-Np), 130.4 (4a-Np), 130.3 (d, J = 7.7 Hz, *o*-Ph), 128.9–127.8 (*m*-Ph, 4,5 and 8 Np), 126.0 (*p*-Ph), 126.0 (7-Np), 124.0 (6-Np), 123.4 (d, J = 12.8 Hz, 1-Np), 116.3 (3-Np), 102.4 (d, J = 59.5 Hz, P*C*Ph), 97.9 (d, J = 61.5 Hz, P*C*Np), 93.5 (d, J = 3.9 Hz, PC*CMe*), 90.5 (d, J = 2.7 Hz, PC*CMe*), 88.6 (Cp*), 58.5 (MeO), 16.8 (MeCCNp), 14.1 (*Me*CCPh), 10.9 (*Me*Cp*). MS (CI{NH_3} *m*/*z*, %) 580 ([M]$^+$, 45%), 190 (100%).

η^5-Pentamethylcyclopentadienyl{η^5-2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholyl}iron(II) 6

A THF (50 mL) solution of **4** (4.7 mmol) was added to a THF (40 mL) solution of freshly prepared '[Cp*FeCl]$_n$' (4.7 mmol), causing a colour change from bright green to orange. After checking completion of the reaction by ^{31}P NMR, the solvent was evaporated *in vacuo* and the residue was taken up in toluene (100 mL). After filtration through a pad of Celite, the orange solution was concentrated to *ca*. 20 mL and layered with degassed methanol (50 mL) to give an orange solution. Orange crystalline **6** was obtained upon standing (1.5 g, 60%). Solution rotamer ratio: 1 (**6b**) : 0.42 (**6a**) in C_6D_6 at 298 K. Major (**6b**): ^{31}P (C_6D_6): δ −36.4. ^{1}H NMR (C_6D_6): δ 7.71 (m, 1H, 8-Np), 7.70 (pseudo-d, J_{HH} = 7.7 Hz, 1H, 5-Np), 7.65 (pseudo-t, J_{HH} = 7.7 Hz, 1H, 7-Np), 7.64 (pseudo-d, J_{HH} = 7.1 Hz, 2H, *o*-Ph), 7.57 (d, J_{HH} = 9.0 Hz, 1H, 4-Np), 7.36 (ddd, J_{HH} = 7.9 Hz, J_{HH} = 6.9 Hz, J_{PH} = 1.1 Hz, 1H, 6-Np), 7.16 (pseudo-t, J_{HH} = 7.1 Hz, 2H, *m*-Ph), 7.06 (pseudo-t, J_{HH} = 7.1 Hz, 1H, *p*-Ph), 6.93 (d, J_{HH} = 9.0 Hz, 1H, 3-Np), 3.62 (s, 3H, MeO), 2.30 (s, 3H, *Me*CCP), 1.86 (s, 3H, *Me*CCP), 1.57 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): δ 154.2 (2-Np), 141.6 (d, J = 16.9 Hz, *ipso*-Ph), 135.2 (d, J = 3.4 Hz, 8a-Np), 130.5 (4a-Np), 130.3 (d, J = 11.4 Hz, *o*-Ph), 128.9–128.0 (*m*-Ph, 4-, 5- and 8-Np), 125.9 (*p*-Ph), 125.8 (7-Np), 123.9 (6-Np), 123.4 (d, J = 13.6 Hz, 1-Np), 115.7 (3-Np), 98.8 (d, J = 56.9 Hz, P*C*Ph), 96.2 (d, J = 58.7 Hz, P*C*Np), 93.5 (d, J = 4.9 Hz, PC*C*Me), 89.3 (d, J = 4.2 Hz, PC*C*Me), 83.3 (Cp*), 57.8 (MeO), 17.5 (MeCCP), 14.9 (*Me*CCP), 10.8 (*Me*Cp*). Minor (**6a**): ^{31}P (C_6D_6): δ −42.8. ^{1}H NMR (C_6D_6): δ 10.1 (d, J_{HH} = 8.5 Hz, 1H, 8-Np), 7.74 (pseudo-d, J_{HH} = 7.5 Hz, 2H, *o*-Ph), 7.73 (m, 1H, 5-Np), 7.70 (m, 1H, 8-Np), 7.67 (m, 1H, 7-Np), 7.55 (d, J_{HH} = 8.8 Hz, 1H, 4-Np), 7.21 (pseudo-t, J_{HH} = 7.5 Hz, 2H, *m*-Ph), 7.16 (m, 1H, 6-Np), 7.10 (pseudo-t, J_{HH} = 7.5 Hz, 1H, *p*-Ph), 6.95 (d, J_{HH} = 8.8 Hz, 1H, 3-Np), 3.21 (s, 3H, MeO), 2.35 (s, 3H, *Me*CCP), 2.17 (s, 3H, *Me*CCP), 1.51 (s, 15H, Cp*). ^{13}C NMR (C_6D_6): δ 156.3 (d, J = 2.5 Hz, 2-Np), 141.2 (d, J = 17.2 Hz, *ipso*-Ph), 132.8 (8a-Np), 130.4 (4a-Np), 130.1 (d, J = 11.6 Hz, *o*-Ph), 128.9–128.0 (*m*-Ph, 4-, 5- and 8-Np), 125.8 (*p*-Ph), 125.1 (7-Np), 124.3 (6-Np), 123.4 (d, J = 13.6 Hz, 1-Np), 117.7 (3-Np), 98.6 (d, J = 56.1 Hz, P*CPh*), 96.1 (d, J = 4.5 Hz, PC*C*Me), 95.9 (d, J = 57.2 Hz, P*C*Np), 89.7 (d, J = 3.6 Hz, PC*C*Me), 83.9 (Cp*), 56.5 (MeO), 15.8 (MeCCNp), 15.2 (*Me*CCPh), 11.0 (*Me*Cp*). EI-MS (*m*/*z*, %) 534 ([M]$^+$, 100%).

η^5-Pentamethylcyclopentadienyl[η^5-2-(2′-hydroxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholyl}iron(II) 8

A THF (5 mL) solution containing **4** and dipotassium{2-(2′-oxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholide (δ^{31}P (THF): 76 ppm) (0.5 mmol) was added to a THF (5 mL) solution of freshly prepared [FeCp*(acac)] (0.5 mmol). The solvents were evaporated *in vacuo* and the residue was extracted into toluene and passed through a pad of silica. The orange filtrate was evaporated to dryness under reduced pressure and recrystallised from dichloromethane/methanol. The title compound was obtained as deep orange crystals (50 mg, 19%). Only one rotamer was visible in solution. ^{31}P (C_6D_6): δ −53.3. ^{1}H ($CDCl_3$): δ 8.36 (d, J_{PH} = 2.7 Hz, 1H), 7.68 (pseudo-t, J_{HH} = 8.1 Hz, 2H), 7.56 (pseudo-d, J_{HH} = 8.1, 2H), 7.27–7.17 (m, 7H), 2.53 (s, 3H), 1.76 (s, 3H), 1.66 (s, 15H). ^{13}C ($CDCl_3$): δ 149.8 (d, J = 1.6 Hz, 2-Np), 139.9 (d, J = 17 Hz, *ipso*-Ph), 133.9 (8a-Np), 129.2 (d, J = 11.6 Hz, *o*-Ph), 129.0 (*C*H), 128.8 (*C*H), 128.4 (*C*H), 128.0 (*m*-Ph), 126.1 (*C*H), 125.8 (*C*H), 125.3 (*C*H), 122.7 (*C*H), 117.0 (*C*H), 114.2 (d, J = 13.1 Hz, 1-Np), 98.5 (d, J = 56.8 Hz, P*C*), 96.5 (d, J = 3.9 Hz, PC*C*), 91.4 (d, J = 55.6 Hz, P*C*), 91.1 (d, J = 3.7 Hz, PC*C*), 83.7 (Cp*), 14.9 (*Me*CCP); 14.2 (*Me*CCP), 10.1 (Me from Cp*). EI-MS (*m*/*z*, %) 521 ([M]$^+$, 100%)

trans-Dichloro(triethylphosphine)[η^5-pentamethylcyclopentadienyl{η^5-2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholyl}ruthenium(II)]platinum(II) 9 and 10

Finely divided $[PtCl_2(PEt_3)]_2$ (6.6 mg, 8.6 μmol) was added to a C_6D_6 (0.4 mL) solution of **5** (10 mg, 0,017 mmol) at room temperature. The sample was shaken vigorously and the composition of the yellow solution was investigated *in situ* by NMR spectroscopy. A ratio of 0.58 (**9**) : 1 (**10**) was observed in C_6D_6 at 298 K. **10** (Major): ^{31}P NMR ($CDCl_3$): δ 20.52 ($J_{P\text{-}Pt}$ = 2637 Hz, $J_{P\text{-}P}$ = 562 Hz); 14.49 ($J_{P\text{-}Pt}$ = 2955 Hz, $J_{P\text{-}P}$ = 562 Hz). ^{1}H NMR (C_6D_6): δ 9.96 (d, J_{HH} = 8.5 Hz, 1H, 8-Np), 7.85 (ddd, J_{HH} = 8.2 Hz, J_{HH} = 6.8 Hz, J_{HH} = 1.3 Hz, 1H, 7-Np), 7.73 (d, J_{HH} = 8.3 Hz, 1H, 5-Np), 7.72 (pseudo-d, J_{HH} = 7.9 Hz, 2H, *o*-Ph), 7.60 (d, J_{HH} = 9.0 Hz, 1H, 4-Np), 7.40 (ddd, J_{HH} = 7.4 Hz, J_{HH} = 6.9 Hz, J_{PH} = 1.0 Hz, 1H, 6-Np), 7.22 (pseudo-t, J_{HH} = 7.9 Hz, 2H, *m*-Ph), 7.04 (pseudo-t, J_{HH} = 7.9 Hz, 1H, *p*-Ph), 7.02 (d, J_{HH} = 9.0 Hz, 1H, 3-Np), 3.65 (s, 3H, MeO), 2.05 (s, 3H, *Me*CCP), 2.04 (s, 3H, *Me*CCP), 1.71 (s, 15H, Cp*), 1.43 (m, 6H, CH_2), 0.7 (m, 9H, CH_3). **9** (Minor): ^{31}P NMR ($CDCl_3$): δ 25.9 ($J_{P\text{-}Pt}$ = 2689 Hz, $J_{P\text{-}P}$ = 572 Hz), 13.24 ($J_{P\text{-}Pt}$ = 2931 Hz, $J_{P\text{-}P}$ = 572 Hz). ^{1}H NMR (C_6D_6): δ 8.14 (d, J_{HH} = 7.3 Hz, 1H, 8-Np), 8.10 (pseudo-d, J_{HH} = 8.0 Hz, 2H, *o*-Ph), 7.60 (d, J_{HH} = 8.0 Hz, 1H, 5-Np), 7.54 (d, J_{HH} = 8.9 Hz, 1H, 4-Np), 7.32 (pseudo-t, J_{HH} = 7.9 Hz, 2H, *m*-Ph), 7.29 (pseudo-t, J_{HH} = 7.5 Hz, 1H, 7-Np), 7.16 (pseudo-t, J_{HH} = 8 Hz, 1H, 6-Np), 7.14 (pseudo-t, J_{HH} = 7.9 Hz, 1H, *p*-Ph), 7.05 (d, J_{HH} = 8.9 Hz, 1H, 3-Np), 4.26 (s, 3H, MeO), 2.04 (s, 3H, *Me*CCP), 1.91 (s, 3H, *Me*CCP), 1.74 (s, 15H, Cp*), 1.25 (m, 6H, CH_2), 0.6 (m, 9H, CH_3).

cis-Dichloro(triethylphosphine)-η^5-[pentamethylcyclopentadienyl-η^5-{2-(2′-methoxynaphth-1′-yl)-3,4-dimethyl-5-phenylphospholyl}ruthenium(II)]platinum(II) 11 and 12

Finely divided $[PtCl_2(PEt_3)]_2$ (6.6 mg, 8.6 μmol) was added to a $CDCl_3$ (0.4 mL) solution of **5** (10 mg, 0,017 mmol) and the initially formed mixture of **9** and **10** was allowed to stand at room temperature for 15 days, whereupon the combined conversion into the *cis* isomers **11** and **12** had reached 78%. Diffusion of methanol into the solution afforded pure colourless crystals of **12** suitable for X-ray analysis. Redissolution of the crystals gave only one *cis*-isomer whose spectrum was identical to the major isomer originally present in the mixture. **12**: ^{31}P NMR($CDCl_3$): δ 21.82 ($J_{P\text{-}Pt}$ = 4552 Hz, $J_{P\text{-}P}$ = 24.5 Hz), 12.99 ($J_{P\text{-}Pt}$ = 3184 Hz, $J_{P\text{-}P}$ = 24.5 Hz). ^{1}H NMR ($CDCl_3$): δ 9.49 (d, J_{HH} = 8.5 Hz, 1H, 8-Np), 7.79 (d, J_{HH} = 8.8 Hz, 1H, 4-Np), 7.76 (ddd, J_{HH} = 7.7 Hz, J_{HH} = 7.7 Hz, J_{HH} = 1.3 Hz, 1H, 7-Np), 7.70 (d, J_{HH} = 7.5 Hz, 1H, 5-Np), 7.59 (d, J_{HH} = 7.5 Hz, 1H, *o*-Ph), 7.38 (ddd, J_{HH} = 7.7 Hz, J_{HH} = 7.7 Hz, J_{HH} = 1.1 Hz, 1H, 6-Np), 7.30 (pseudo-t, J_{HH} = 7.6 Hz, 2H, *m*-Ph), 7.17 (d, J_{HH} = 8.5 Hz, 1H, 3-Np), 7.15 (pseudo-t, J_{HH} = 7.6 Hz, 1H, *p*-Ph), 3.93 (s, 3H, MeO), 2.26 (s, 3H, *Me*CCP), 1.97 (s, 3H, *Me*CCP), 1.82 (s, 15H, *Me*-Cp*), 1.55 (m, 6H, C*H*2), 0.19 (m, 9H, C*H*$_3$). **11**: ^{31}P NMR ($CDCl_3$): δ 26.0 ($J_{P\text{-}Pt}$ = 4665 Hz, $J_{P\text{-}P}$ = 22.4 Hz), 13.1 ($J_{P\text{-}Pt}$ = 3199 Hz, $J_{P\text{-}P}$ = 22.4 Hz).

Crystallography

All structures measured using graphite monochromated X-ray Mo-K_α radiation, $\lambda = 0.71069$ Å, on a Kappa CCD diffractometer and refined using direct methods in Shelxl. R given for $I > 2\sigma(I)$.

Crystal data for 5. $C_{33}H_{35}OPRu$, $M = 579.65$, triclinic, space group $P\bar{1}$, $a = 9.992(5)$, $b = 11.740(5)$, $c = 12.042(5)$ Å, $\alpha = 79.530(5)$, $\beta = 71.170(5)$, $\gamma = 89.490(5)°$, $U = 1312.9(10)$ Å^3. $Z = 2$, $D_c = 1.466$ g cm^{-3}, $F(000) = 600$. $\mu = 0.$ 0.683 cm^{-1}, $T = 150.0(10)$ K. Of 7645 independent reflections out of a total of 11067 from a pale yellow cube of dimensions 0.20 × 0.20 × 0.20 mm over $h = -13$ to 14, $k = -16$ to 16, $l = -16$ to 16° at 150(10)K, 6403 having $I > 2\sigma(I)$ were refined on F^2. $wR_2 = 0.0824$, $R_1 = 0.0366$, GoF = 1.057.

Crystal data for 8. $C_{32}H_{33}FeOP$, $M = 520.40$, monoclinic, space group $P21/c$, $a = 10.492(1)$, $b = 8.013(1)$, $c = 31.164(1)$ Å. $\beta = 93.320(1)°$, $U = 2615(6)$ Å^3. $Z = 4$, $D_c = 1.322$ g cm^{-3}, $F(000) = 1096$. $\mu = 0.661$ cm^{-1}, $T = 298(5)$ K. Of 5924 independent reflections from a total of 10129 collected as above using an orange needle of dimensions 0.20 × 0.08 × 0.08 mm over $h = -13$ to 13, $k = -9$ to 10, $l = -40$ to 40°, 4619 having $I > 2\sigma(I)$ were refined on F^2. $wR_2 = 0.1180$, $R_1 = 0.0426$, GoF = 1.079.

Crystal data for 12. $C_{41}H_{52}Cl_8OP_2PtRu$, $M = 1202.53$, monoclinic, space group $P21/n$, $a = 9.809(5)$, $b = 24.651(5)$, $c = 19.909(5)$ Å, $\beta = 91.420(5)°$, $U = 4813(3)$ Å^3. $Z = 4$, $D_c = 1.660$ g cm^{-3}, $F(000) = 2376$. $\mu = 3.759$ cm^{-1}, $T = 150.0(10)$ K. Of 7527 independent reflections out of a total of 12590 collected as above from a yellow needle of dimensions 0.60 × 0.20 × 0.10 mm over $h = -11$ to 11, $k = -28$ to 26, $l = -23$ to 23° at 298(10) K, 5943 having $I > 2\sigma(I)$ were refined on F^2. $wR_2 = 0.1573$, $R_1 = 0.0584$, GoF = 1.019.

CCDC reference numbers 258042–258044.

See http://www.rsc.org/suppdata/dt/b4/b418926d/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Financial support for this work from CNRS, Ecole polytechnique (Gaspard Monge grant to NS) and the European Commission (through Marie Curie grant HPMT-CT-2001-00317 to NS and FP5 network funding through HPRN CT-2001-00172 to DC and JMB) is gratefully acknowledged.

We also wish to thank a referee for suggesting the NMR experiment involving dissolution of **5** at low temperature which was used to confirm the exclusive presence of **5a** in the crystalline sample.

References

1 J. Jacques and C. Fouquey, *Tetrahedron Lett.*, 1971, 4617.
2 S. Miyano, M. Nawa, A. Mori and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2171.
3 A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi and R. Noyori, *J. Am. Chem. Soc.*, 1980, **102**, 7932.
4 L. Kurz, G. Lee, D. Morgans, M. J. Waldyke and T. Ward, *Tetrahedron Lett.*, 1990, **31**, 6321.
5 T. Hayashi, *Acta Chem. Scand.*, 1996, **50**, 259.
6 T. Hayashi, *Acc. Chem. Res.*, 2000, **33**, 354.
7 Y. F. Luo, F. Wang, G. G. Zhu and Z. G. Zhang, *Tetrahedron: Asymmetry*, 2004, **15**, 17.
8 S. Vyskocil, M. Smrcina, V. Hanus, M. Polasek and P. Kocovsky, *J. Org. Chem.*, 1998, **63**, 7738.
9 A. Herrbach, A. Marinetti, O. Baudoin, D. Guenard and F. Gueritte, *J. Org. Chem.*, 2003, **68**, 4897.
10 P. N. M. Botman, O. David, A. Amore, J. Dinkelaar, M. T. Vlaar, K. Goubitz, J. Fraanje, H. Schenk, I. Hiemstra and J. H. van Maarseveen, *Angew. Chem. Int. Ed.*, 2004, **43**, 3471.
11 T. Hamada and S. L. Buchwald, *Org. Lett.*, 2002, **4**, 999.
12 M. Smrcina, M. Lorenc, V. Hanus and P. Kocovsky, *Synlett.*, 1991, 231.
13 R. A. Singer and S. L. Buchwald, *Tetrahedron Lett.*, 1999, **40**, 1095.
14 Y. N. Belokon, N. B. Bespalova, T. D. Churkina, I. Cisarova, M. G. Ezernitskaya, S. R. Harutyunyan, R. Hrdina, H. B. Kagan, P. Kocovsky, K. A. Kochetkov, O. V. Larionov, K. A. Lyssenko, M. North, M. Polasek, A. S. Peregudov, V. V. Prisyazhnyuk and S. Vyskocil, *J. Am. Chem. Soc.*, 2003, **125**, 12860.
15 N. W. Alcock, J. M. Brown and D. I. Hulmes, *Tetrahedron: Asymmetry*, 1993, **4**, 743.
16 C. W. Lim, O. Tissot, A. Mattison, M. W. Hooper, J. M. Brown, A. R. Cowley, D. I. Hulmes and A. J. Blacker, *Organic Process Research & Development*, 2003, **7**, 379.
17 P. Kocovsky, S. Vyskocil and M. Smrcina, *Chem. Rev.*, 2003, **103**, 3213.
18 P. J. Guiry and C. P. Saunders, *Advanced Synthesis & Catalysis*, 2004, **346**, 497.
19 H. L. Pedersen and M. Johannsen, *J. Org. Chem.*, 2002, **67**, 7982.
20 J. F. Jensen and M. Johannsen, *Org. Lett.*, 2003, **5**, 3025.
21 F. Mathey, *J. Organomet. Chem.*, 2002, **646**, 15.
22 R. Shintani and G. C. Fu, *J. Am. Chem. Soc.*, 2003, **125**, 10778.
23 R. Shintani and G. C. Fu, *Angew. Chem. Int. Ed.*, 2003, **42**, 4082.
24 R. Shintani and G. C. Fu, *Org. Lett.*, 2002, **4**, 3699.
25 K. Tanaka, S. Qiao, M. Tobisu, M. M. C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 9870.
26 K. Tanaka and G. C. Fu, *J. Org. Chem.*, 2001, **66**, 8177.
27 S. Qiao and G. C. Fu, *J. Org. Chem.*, 1998, **63**, 4168.
28 M. Ogasawara, K. Yoshida and T. Hayashi, *Organometallics*, 2001, **20**, 3913.
29 C. Ganter, C. Kaulen and U. Englert, *Organometallics*, 1999, **18**, 5444.
30 X. Sava, L. Ricard, F. Mathey and P. Le Floch, *Organometallics*, 2000, **19**, 4899.
31 M. Melaimi, F. Mathey and P. Le Floch, *J. Organomet. Chem.*, 2001, **640**, 197.
32 C. E. Garrett and G. C. Fu, *J. Org. Chem.*, 1997, **62**, 4534.
33 L. S. Wang and T. K. Hollis, *Org. Lett.*, 2003, **5**, 2543.
34 D. Carmichael, J. Klankermayer, L. Ricard and N. Seeboth, *Chem. Commun.*, 2004, 1144.
35 G. E. Herberich and B. Ganter, *Inorg. Chem. Commun.*, 2001, **4**, 100.
36 C. Burney, D. Carmichael, K. Forissier, J. C. Green, F. Mathey and L. Ricard, *Chem. Eur. J.*, 2003, **9**, 2567.
37 K. Forissier, L. Ricard, D. Carmichael and F. Mathey, *Organometallics*, 2000, **19**, 954.
38 D. Carmichael, F. Mathey, L. Ricard and N. Seeboth, *Chem. Commun.*, 2002, 2976.
39 M. Ogasawara, T. Nagano, K. Yoshida and T. Hayashi, *Organometallics*, 2002, **21**, 3062.
40 S. Holand, N. Maigrot, C. Charrier and F. Mathey, *Organometallics*, 1998, **17**, 2996.
41 S. Holand, M. Jeanjean and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 98.
42 F. G. Mann and M. J. Pragnell, *J. Chem. Soc.*, 1965, 4120.
43 M. V. Bhatt and S. U. Kulkarni, *Synthesis*, 1983, 249.
44 A number of phosphole derivatives having simpler aromatic groups in the 2-position have been shown not to be atropomeric; for example: L. Routaboul, J. Chiffre, G. G. A. Balavoine, J. C. Daran and E. Manoury, *J. Organomet. Chem.*, 2001, **637**, 364.
45 R. S. Paley, L. A. Estroff, D. J. McCulley, L. A. Martinez-Cruz, A. J. Sanchez and F. H. Cano, *Organometallics*, 1998, **17**, 1841.
46 There is precedent for facile racemisation of ligands combining five- and six-membered rings. See for example: T. D. W. Claridge, J. M. Long, J. M. Brown, D. Hibbs and M. B. Hursthouse, *Tetrahedron*, 1997, **53**, 4035.
47 U. Berens, J. M. Brown, J. Long and R. Selke, *Tetrahedron: Asymmetry*, 1996, **7**, 285.
48 C. Hay, M. Sauthier, V. Deborde, M. Hissler, L. Toupet and R. Reau, *J. Organomet. Chem.*, 2002, **643**, 494.
49 H. Brunner and T. Zwack, *Organometallics*, 2000, **19**, 2423.
50 K. Stott, J. Keeler, Q. N. Van and A. J. Shaka, *J. Magn. Reson.*, 1997, **125**, 302.
51 V. S. Dimitrov and N. G. Vassilev, *Magn. Reson. Chem.*, 1995, **33**, 739.
52 C. L. Perrin, *J. Magn. Reson.*, 1989, **82**, 619.
53 S. Macura, B. T. Farmer and L. R. Brown, *J. Magn. Reson.*, 1986, **70**, 493.
54 R. Willem, M. Biesemans, K. Hallenga, G. Lippens, F. Malaisselagae and W. J. Malaisse, *J. Biol. Chem.*, 1992, **267**, 210.
55 I. Pianet, E. Fouquet, M. Pereyre, M. Gielen, F. Kayser, M. Biesemans and R. Willem, *Magn. Reson. Chem.*, 1994, **32**, 617.

56 T. D. W. Claridge, *High Resolution Techniques in Organic Chemistry*, ed. J. E. Baldwin and R. M. Williams, Pergamon, Oxford, 1999.
57 O. Desponds and M. Schlosser, *J. Organomet. Chem.*, 1996, **507**, 257.
58 A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365.
59 A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, 1964, **68**, 651.
60 L. Meca, D. Reha and Z. Havlas, *J. Org. Chem.*, 2003, **68**, 5677.
61 S. Doherty, C. R. Newman, R. K. Rath, H. K. Luo, M. Nieuwenhuyzen and J. G. Knight, *Org. Lett.*, 2003, **5**, 3863.
62 K. Mikami and M. Yamanaka, *Chem. Rev.*, 2003, **103**, 3369.
63 P. J. Walsh, A. E. Lurain and J. Balsells, *Chem. Rev.*, 2003, **103**, 3297.
64 S. Doherty, P. Goodrich, C. Hardacre, H. K. Luo, D. W. Rooney, K. R. Seddon and P. Styring, *Green Chem.*, 2004, **6**, 63.
65 J. J. Becker, P. S. White and M. R. Gagne, *J. Am. Chem. Soc.*, 2001, **123**, 9478.
66 P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2043.
67 C. Elschenbroich, S. Voss and K. Harms, *Z. Naturforsch., Teil B*, 1999, **54**, 209.
68 K. B. Dillon and H. P. Goodwin, *J. Organomet. Chem.*, 1994, **469**, 125.
69 H. W. Kroto, J. F. Nixon, M. J. Taylor, A. A. Frew and K. W. Muir, *Polyhedron*, 1982, **1**, 89.
70 P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati and S. Rizzato, *Organometallics*, 2003, **22**, 5345.
71 Y. Uozumi, K. Kitayama, T. Hayashi, K. Yanagi and E. Fukuyo, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 713.
72 T. Hayashi, H. Iwamura, M. Naito, Y. Matsumoto, Y. Uozumi, M. Miki and K. Yanagi, *J. Am. Chem. Soc.*, 1994, **116**, 775.
73 M. Ogasawara, K. Yoshida and T. Hayashi, *Organometallics*, 2001, **20**, 1014.
74 M. Ogasawara, K. Yoshida and T. Hayashi, *Organometallics*, 2003, **22**, 1783.
75 Unlike classical phosphines, phosphametallocenes can be displaced from $[PtCl_2(PEt_3)]$ centres by relatively poor ligands such as isocyanides: D. Carmichael, L. Ricard and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1994, 1167.
76 C. Daul, H. U. Gudel and J. Weber, *J. Chem. Phys.*, 1993, **98**, 4023.
77 E. Diana, R. Rossetti, P. L. Stanghellini and S. F. A. Kettle, *Inorg. Chem.*, 1997, **36**, 382.
78 S. Doherty, C. R. Newman, R. K. Rath, J. A. van den Berg, C. Hardacre, M. Nieuwenhuyzen and J. G. Knight, *Organometallics*, 2004, **23**, 1055.
79 M. D. Tudor, J. J. Becker, P. S. White and M. R. Gagne, *Organometallics*, 2000, **19**, 4376.
80 D. Carmichael, L. Ricard and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1994, 2459.
81 P. J. Fagan, W. S. Mahoney, J. C. Calabrese and I. D. Williams, *Organometallics*, 1990, **9**, 1843.
82 J. Norinder, H. H. Cotton and J. E. Backvall, *J. Org. Chem.*, 2002, **67**, 9096.
83 U. Kolle, B. Fuss, F. Khouzami and J. Gersdorf, *J. Organomet. Chem.*, 1985, **290**, 77.
84 A. C. Smithies, M. Rycheck and M. Orchin, *J. Organomet. Chem.*, 1968, **12**, 199.
85 A. Breque, F. Mathey and P. Savignac, *Synthesis*, 1981, 983.
86 N. Seeboth, DEA (Masters) Thesis, Ecole Polytechnique, 2001.
87 W. Egan, R. Tang, G. Zon and K. Mislow, *J. Am. Chem. Soc.*, 1971, **93**, 6205.
88 M. Gouygou, O. Tissot, J. C. Daran and G. G. A. Balavoine, *Organometallics*, 1997, **16**, 1008.
89 C Hay, M Sauthier, V Deborde, M Hissler, L Toupet and R Réau, *J. Organomet. Chem.*, 2002, **643**, 494.