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2-(2′-Pyridyl)phosphaferrocenes and analogues: a new type of chelating ligands with planar chirality and π-acceptor phosphorus centres

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Abstract

The reaction of 1-(2′-pyridyl)-3,4-dimethylphosphole with $[CpFe(CO)_2]_2$ under CO pressure at 160 °C affords the 2-(2′pyridyl)-3,4-dimethylphosphaferrocene (**2**) in 65% yield. This compound behaves as a π-acceptor–σ-donor P,N-chelating ligand towards W(0) and Cu(I). The $W(CO)_4$ complex **5** has been characterized by X-ray crystal structure analysis. Some strain within the chelate is obvious from the P–W–N angle of 73°. The analogous 2-(8′-quinolyl)-3,4-dimethylphosphaferrocene (**10**) and 2-(2′-pyridyl)-3,4-dimethylphosphacymantrene (**11**) are also described. © 1997 Elsevier Science S.A. © 1997 Elsevier Science S.A.

Keywords: Phosphaferrocenes; Phosphacymantrenes; Pyridines; Quinolines; P,N-chelating ligands; Phosphole [1,5]-shifts

1. Introduction

Bidentate ligands incorporating a pyridine ring together with an sp^3-phosphorus donor play an ever increasing role in coordination chemistry (two recent reviews are available [1]) and homogeneous catalysis (an efficient process for the industrial synthesis of methyl methacrylate is based upon a 2-pyridylphosphine–palladium catalyst [2]). The recent advances in low coordination phosphorus chemistry [3] suggest the possibility of developing another class of bidentate ligands incorporating an sp^2-phosphorus π-acceptor in lieu of the sp^3 σ-donor. Several applications could be envisaged, such as placing in close proximity electron excessive (soft) and electron deficient (hard) metallic centres. Besides the synthetic challenge, the practical use of such bidentate ligands faces a problem of stability. In general, sp^2-phosphorus species display high reactivity and modest thermodynamic stability. Steric crowding can provide them with some kinetic stability at the expense of coordination ability. But the most attractive solution is to stabilize them by electronic delocalization (a preliminary investigation of phosphinine-based ligands in homogeneous catalysis clearly establishes the interest of this approach [4]). In line with this, we have already started to investigate the chemistry of 2-(2′-pyridyl)phosphinines where the sp^2-phosphorus centre benefits from the 6π-aromatic stabilization of the phosphinine ring [5]. In that case, two drawbacks immediately appeared: firstly, the synthesis is cumbersome and difficult to perform on a sufficient scale; secondly, the reactivity of the phosphinine ring is boosted upon complexation so that, for example, Pd(II) and Pt(II) coordination induces the ready addition of protic reagents onto the formal P=C double bond of the ring. Thus, the sp^2 is converted into an sp^3 phosphorus centre [6]. In this report, we turn our attention towards the possible use of phosphaferrocenes and phosphacymantrenes as stable sp^2-like phosphorus centres. Despite its formal tricoordination, theoretical and experimental studies have amply demonstrated that the phosphorus centre has the electronic characteristics of an sp^2 centre in these species, i.e. a low-energy in-plane phosphorus lone pair and a low-lying π^* LUMO [7].

2. Results and discussion

The synthesis of our model compound, i.e. the 2-(2′-pyridyl)-3,4-dimethylphosphaferrocene (**2**), was based on a transposition of the well-established preparation of 2-phenyl-3,4-dimethylphosphaferrocene [8]. Accordingly, we first prepared 1-(2′-pyridyl)-3,4-dimethylphosphole (**1**) by condensation of the 3,4-dimethylphos-

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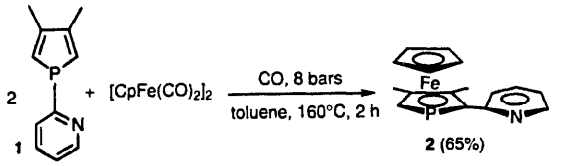
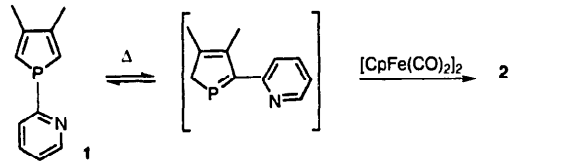
pholide ion with 2-bromopyridine in the presence of CuI as a catalyst in refluxing THF [9]. The phosphole **1** was then allowed to react with $[CpFe(CO_2)_2]_2$ at 160 °C under CO at a pressure of 8 bar (Eq. (1)).



(1)

The mechanism involves a [1,5]-sigmatropic shift of the pyridine ring from phosphorus to the α-carbon of the phosphole ring (Eq. (2)).

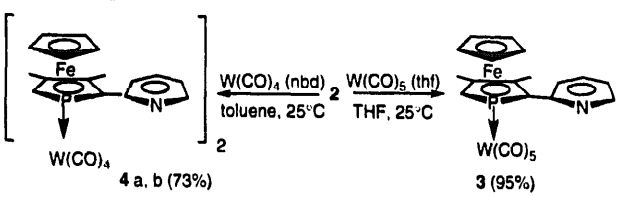


(2)

As previously established for these concerted shifts [10], the substitution position on the migrating heteroarene is retained during the process. The 2*H*-phosphole thus obtained then reacts with $[CpFe(CO)_2]_2$. The CO pressure serves to slow down the complexation reaction so that it does not take place before the shift. Without CO pressure, 3,4-dimethyl-1-phosphaferrocene is formed via the cleavage of the P–py bond.

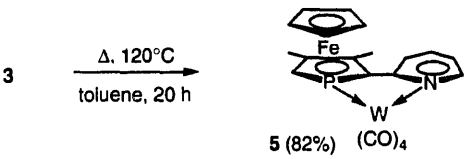
The ^1H, ^{13}C and ^{31}P NMR data of **2** are very close to those of 2-phenyl-3,4-dimethylphosphaferrocene [11]. A closer inspection of the ^{13}C data reveals an interesting effect, except for C_2, all the ^{13}C resonances of the pyridine ring of **2** are displaced to high fields by comparison with those of pyridine itself. In particular, the C_5 resonance displays an upfield shift of −5.5 ppm. Clearly, the phosphaferrocene plays the role of a π-electron releasing substituent towards the pyridine ring, and very likely enhances the σ-donor capacity of nitrogen.

We first investigated the reactivity of **2** towards typical soft transition metal centres. Thus, the reaction of **2** with $[W(CO)_5(thf)]$ and $[W(CO)_4(nbd)]$ at room temperature affords the corresponding *P*-complexes **3** and **4** (Eq. (3)).



(3)

The complexation takes place at phosphorus in both cases as shown by a sizeable downfield shift of the ^{31}P resonance, ca. +25 and +31 ppm respectively. The *cis*-$W(CO)_4$ complex **4** is obtained as a 50:50 mixture of two isomers resulting from the planar chirality of **2**. The magnitude of the ^1J(P–W) coupling constants (256 and 249 Hz respectively) confirms that the phosphorus of **2** is a good π-acceptor. The value for the P–$W(CO)_5$ complex is exactly similar to that recorded for the $W(CO)_5$ complex of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene [12]. Upon heating in refluxing toluene, complex **3** is almost quantitatively converted into the corresponding $W(CO)_4$ chelate **5** (Eq. (4)).



(4)

Complex **5** was characterized by X-ray crystal structure analysis (Fig. 1). The phosphole and pyridine rings are coplanar (angle 4.82 ± 0.7°). The cyclopentadienyl and phosphole planes are parallel (angle 3.01 ± 1.15°). Apparently, the two complexing subunits are independent. The C_5–C_6 bridge has a normal length of 1.472(4) Å, compared with the C–C bridges of free bipyridine [13] and pyridyl–phosphinine $Cr(CO)_4$ chelate [14] (in both cases 1.49 Å). Moreover, the W–P bond is similar in length to that found in a phosphacymantrene–$W(CO)_5$ complex, 2.4592(8) vs. 2.451(3) Å [15], and the W–N bond seems to be weaker than that

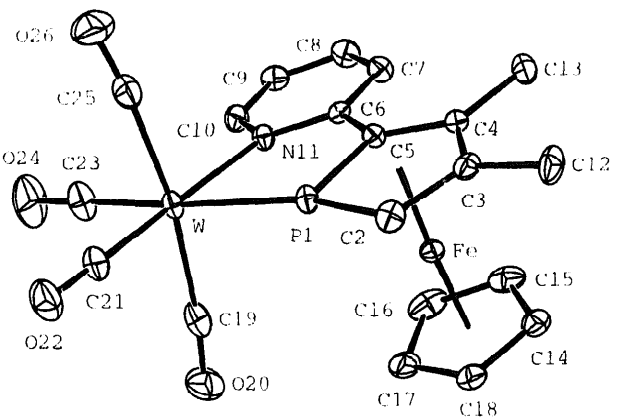
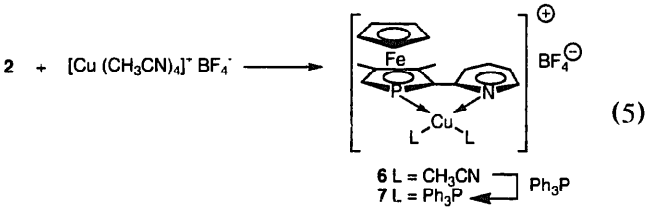


Fig. 1. ORTEP drawing of one molecule of **5**, as determined by a single crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W–P(1) 2.4592(8), W–N(11) 2.332(3), W–C(19) 2.035(4), W–C(21) 1.949(3), W–C(23) 1.970(4), W–C(25) 2.030(4), P(1)–C(2) 1.746(3), P(1)–C(5) 1.761(3), C(2)–C(3) 1.421(5), C(3)–C(4) 1.444(5), C(4)–C(5) 1.443(4), C(5)–C(6) 1.472(4), C(6)–C(7) 1.395(4), C(6)–N(11) 1.376(4), C(7)–C(8) 1.383(5), C(8)–C(9) 1.378(5), C(9)–C(10) 1.379(5), C(10)–N(11) 1.350(4); P(1)–W–N(11) 73.08(7), C(2)–P(1)–C(5) 91.6(2), C(6)–N(11)–C(10) 117.2(3); Fe–C(2)–C(5) mean plane 1.622, Fe–C(14)–C(18) mean plane −1.664.

found in a bipyridine $W(CO)_4$ chelate, 2.332(3) vs. 2.238–2.272(8) Å [16]. The complexation of the phospholyl unit induces a broadening of the intracyclic < CPC angle from 88.4 in 3,4-dimethylphosphaferrocene [17] to 91.6° in **5**. This phenomenon has also been found with phosphinines [18]. Finally, some strain is obvious in the chelate ring as shown by the P–W–N angle of 73°.

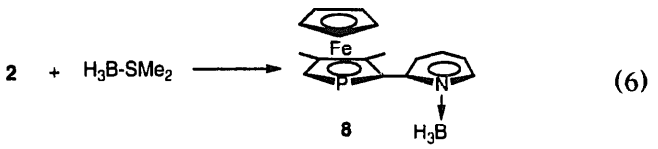
As a preliminary investigation of the behaviour of **2** towards transition metal centres in positive oxidation states, we studied its reaction with copper(I) species. With tetrakis-(acetonitrile)copper(I) cation, an instantaneous substitution of two acetonitrile ligands takes place to give the chelate complex **6**. Further substitution by two molecules of triphenylphosphine affords **7** (Eq. (5)).



(5)

Whereas the relatively low stability of these complexes precludes any analysis by other means than multinuclear NMR, the chelation of the copper centre is obvious from the ^{31}P and ^{13}C data. A strong upfield shift of the ^{31}P resonance indicates that complexation at P has taken place in both **6** and **7**. Besides, the $C_{6'}$ resonance of the pyridine nucleus appears as a doublet in **7** ($^3J(C-P) = 4.3$ Hz) whereas it is a singlet in **2**, thus indicating that nitrogen is coordinated to copper.

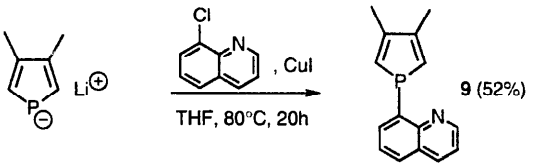
With a typical hard ligand such as borane, complexation takes place at nitrogen as shown by the fact that the ^{31}P resonance of the phosphaferrocene unit is almost unaffected (Eq. (6)).



(6)

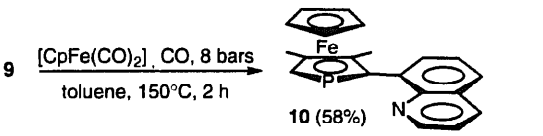
The $C_{4'}$ resonance is downshifted from 135.13 in **2** to 139.74 in **8**, as a result of the electron-withdrawing effect of the borane complexing group. A similar effect was noticed with the copper(I) complexes **6** and **7**.

This preliminary investigation of the coordination chemistry of **2** suggested that a spacer was needed between the pyridine and phosphaferrocene units in order to improve the chelating ability of the system. Hence, we decided to study the possible replacement of the 2-pyridyl by an 8-quinolyl substituent. The starting phosphole **9** was prepared as shown in Eq. (7).



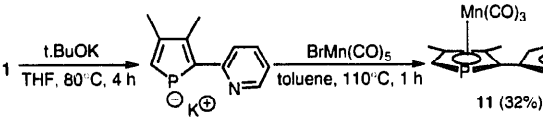
(7)

Heating **9** under CO pressure with $[CpFe(CO)_2]_2$ using the same procedure as for the synthesis of **2** yielded the expected phosphaferrocene **10** (Eq. (8)).



(8)

The purification of **10** proved to be difficult. The characterization of **10** mainly relied on mass and ^{31}P NMR spectroscopy. Owing to its limited purity and stability, we did not investigate the coordination chemistry of **10**. Instead, we decided to study the synthesis of the phosphacymantrene analogue of **2** (**11**) viewed as a stronger π-acceptor version of **2**. We started from the 2-pyridyl-3,4-dimethylphospholide ion made from **1** according to a procedure described elsewhere [9] (Eq. (9)).



(9)

Compound **11** was characterized by ^1H, ^{13}C, ^{31}P NMR and mass spectrometry. All the data are in the normal range for such a compound (see the data of 2-phenyl-3,4-dimethylphosphacymantrene [19]). The coordination chemistry of **11**, whose stability is satisfactory, remains open for investigation.

3. Experimental section

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32 and 81.01 MHz respectively. All chemical shifts are reported in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method. IR were recorded on a Perkin–Elmer Paragon 1000.

Owing to their limited stability upon standing, most of the compounds described hereafter did not give satisfactory analytical data.

3.1. 2-(2'-Pyridyl)-3,4-dimethylphosphaferrocene (2)

1-(2'-Pyridyl)-3,4-dimethylphosphole (1) (3.0 g, 16×10^{-3} mol) and cyclopentadienyl–dicarbonyl–iron dimer (2.81 g, 8×10^{-3} mol) in freshly distilled dry toluene (50 ml) were mixed in an autoclave under pressure of CO (8 bar) and heated for 2 h under stirring at 160 °C. Then, the pressure was released, the mixture was stirred for 1 h more and allowed to cool to room temperature. Solvent was removed and the crude mixture was chromatographed on silica gel with toluene/ethylacetate (70:30) to give 3.2 g (65%) of **2** as a deep orange, partly crystallized oil.

^{1}H NMR ($CDCl_3$) δ: 2.24 (s, CH_3), 2.40 (s, CH_3), 3.91 (d, $^2J_{HP} = 36.3$ Hz, HC=P), 4.14 (s, Cp), pyridyl H: 6.99 (m), 7.42 (m), 8.46 (d, $^3J_{HH} = 4.7$ Hz, $H_{6'}$).

^{13}C NMR ($CDCl_3$) δ: 15.29 (s, CH_3), 16.96 (s, CH_3), 72.95 (s, Cp), 77.31 (d, $^1J_{CP} = 58.4$ Hz, C_5), 92.17 (d, $^2J_{CP} = 3.9$ Hz, C_3 or C_4), 97.14 (d, $^1J_{CP} = 56.6$ Hz, C_2), 97.14 (d, $^2J_{CP} = 6.7$ Hz, C_4 or C_3), 120.09 (s, $C_{5'}$), 124.01 (d, $^3J_{CP} = 7.0$ Hz, $C_{3'}$), 135.13 (s, $C_{4'}$), 148.47 (s, $C_{6'}$), 160.18 (d, $^2J_{CP} = 18.5$ Hz, $C_{2'}$).

^{31}P NMR ($CDCl_3$) δ: −68.05.

Mass spectrum *m/e*: 309 (M^+, 100%).

3.2. [2-(2'-Pyridyl)-3,4-dimethylphosphaferrocene]pentacarbonyl tungsten (3)

A solution of $W(CO)_5 \cdot THF$ prepared from $W(CO)_6$ (0.3 g, 0.85×10^{-3} mol) and THF (150 ml) under irradiation was added to (0.31 g, 1×10^{-3} mol) of **2** to give 0.6 g (95%) of **3**. The characterisation was performed on the crude material.

^{1}H NMR ($CDCl_3$) δ: 2.26 (s, CH_3), 2.30 (s, CH_3), 3.78 (d, $^2J_{HP} = 33.0$ Hz, HC=P), 4.35 (s, Cp), pyridyl H: 7.11 (broad signal), 7.50 (m), 8.50 (broad s, $H_{6'}$).

^{31}P NMR ($CDCl_3$) δ: −43.3 ($^1J_{PW} = 256.0$ Hz).

3.3. Bis-[2-(2'-pyridyl)-3,4-dimethylphosphaferrocene]tetracarbonyl tungsten (4)

(nbd)$W(CO)_4$ (0.93 g, 2.4×10^{-3} mol) and (0.72 g, 2.4×10^{-3} mol) of **2** in toluene (20 ml) were stirred for 16 h at room temperature. Solvent was removed and the crude mixture chromatographed on silica gel with toluene/ethyl acetate (70:30) to give 1.05 g (73%) of two isomers (*a*/*b* = 50/50).

^{1}H NMR ($CDCl_3$) (*a* + *b*) δ: 2.13 (s, CH_3), 2.16 (s, CH_3), 2.24 (s, CH_3), 3.32 (AXX', 2H, $|\Sigma^1 J_{HP}| = 58$ Hz), 4.21 (s, Cp), 4.23 (s, Cp), pyridyl H: 7.07–7.60 (m), 8.47 (d, $^3J_{HH} = 4.4$ Hz).

^{31}P NMR ($CDCl_3$) *a* δ: −37.24, *b* δ: −37.73 ($^1J_{PW} = 249$ Hz).

3.4. [2-(2'-Pyridyl)-3,4-dimethylphosphaferrocene]tetracarbonyl tungsten (5)

(0.6 g, 0.95×10^{-3} mol) of **3** was heated in toluene (5 ml) for 20 h at 120 °C. Solvent was removed and the crude mixture was chromatographed on silica gel with toluene/ethyl acetate (70:30) to give 0.49 g (82%) of **5**.

^{1}H NMR (CD_2Cl_2) δ: 2.34 (s, CH_3), 2.61 (s, CH_3), 4.06 (d, $^2J_{HP} = 35.06$ Hz, HC=P), 4.24 (s, Cp), pyridyl H: 6.98 (m), 7.75 (m), 9.10 (d, $^3J_{HH} = 5.7$ Hz, $H_{6'}$).

^{13}C NMR (CD_2Cl_2) δ: 15.79 (s, CH_3), 17.45 (d, $^2J_{CP} = 4.5$ Hz, CH_3), 66.40 (d, $^1J_{CP} = 6.2$ Hz, C_5), 88.47 (s, C_3 or C_4), 90.87 (d, $^1J_{CP} = 2.9$ Hz, C_2), 96.77 (s, C_4 or C_3), 121.70 (s, $C_{3'}$ or $C_{5'}$), 121.79 (s, $C_{5'}$ or $C_{3'}$), 138.17 (s, $C_{4'}$), 158.24 (d, $^4J_{CP} = 6.0$ Hz, $C_{6'}$), 164.53 (d, $^2J_{CP} = 17.7$ Hz, $C_{2'}$), 198.91 (d, $^2J_{CP} = 8.7$ Hz, CO), 201.11 (d, $^2J_{CP} = 9.8$ Hz, CO), 209.04 (d, $^2J_{CP} = 44.4$ Hz, CO), 211.17 (d, $^2J_{CP} = 4.7$ Hz, CO).

^{31}P NMR (CD_2Cl_2) δ: 17.84 ($^1J_{PW} = 247.8$ Hz).

IR (decalin) ν(CO) 2014.3, 1888.3, 1842.3.

3.4.1. X-ray structure determination for 5

Crystals of **5**, $C_{20}H_{16}FeNO_4PW$ were grown from a solution of the compound in dichloromethane/pentane. Data were collected at -150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallises in space group $P\bar{1}$ (2), $a = 7.055(1)$ Å, $b = 10.425(1)$ Å, $c = 14.001(2)$ Å, $\alpha = 96.84(1)°$, $\beta = 94.28(1)°$, $\gamma = 108.01(1)°$; $V = 965.52(47)$ Å^3; $Z = 2$; $d_{calc} = 2.081$ g cm^{-3}; $\mu = 69.4$ cm^{-1}; $F(000) = 580$. A total of 6021 unique reflections were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 1110 were considered unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 4911 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A 'non-Poisson' weighting scheme was applied with a *p* factor equal to 0.05. The final agreement factors were $R = 0.027$, $R_w = 0.036$, G.O.F. = 1.09.

3.5. [2-(2'-Pyridyl)-3,4-dimethylphosphaferrocene]-bis-(acetonitrile)copper(I) tetrafluoroborate (6)

(0.22 g, 0.71×10^{-3} mol) of the ligand and $[Cu(CH_3CN)_4]^+$, BF_4^- (0.22 g, 0.74×10^{-3} mol) were mixed at room temperature in 3 ml of CH_2Cl_2 and 3 ml of CH_3CN. The chelate (**6**) was thus obtained; solvent was removed and a sample of the crude material was analysed by NMR.

^{1}H NMR (CD_2Cl_2) δ: 2.21 (s, CH_3), 2.36 (s, CH_3), 2.43 (s, CH_3), 4.22 (d, $^2J_{HP} = 34.7$ Hz), HC=P), 4.21 (s, Cp), 4.23 (s, Cp), pyridyl H: 7.36 (broad signal), 7.71 (broad signal), 7.95 (broad signal), 8.09 (broad signal).

^{13}C NMR (CD_2Cl_2) δ: 2.97 (s, CH_3CN), 17.90 (s, CH_3), 17.45 (s, CH_3), 69.53 (broad s, C_5), 74.77 (s,

Cp), 120.07 (s, CN), 124.48 (s, $C_{3'}$ or $C_{5'}$), 126.18 ($C_{5'}$ or $C_{3'}$), 140.09 (s, $C_{4'}$), 150.66 (s, $C_{6'}$), 157.63 (s, $C_{2'}$).

^{31}P NMR (CD_2Cl_2) δ: −102.92.

3.6. [2-(2'-Pyridyl)-3,4-dimethylphosphaferrocene]-bis-(triphenylphosphine)copper(I) tetrafluoroborate (7)

Complex **6** as obtained previously was dissolved in 5 ml of CH_2Cl_2 and PPh_3 (0.38 g, 2 equiv.) was added. Solvent was removed and the crude material was chromatographed on silica gel with ether/ethyl acetate (95:5) to give 0.47 g of **7** (69%).

^{1}H NMR (CD_2Cl_2) δ: 2.24 (s, CH_3), 2.43 (s, CH_3), 3.75 (d, $^2J_{HP}$ = 37.63 Hz, HC=P), 4.02 (s, Cp), 7.14–7.44 (m, Ph), 7.96 (d, $^3J_{HH}$ = 4.1 Hz, $H_{6'}$).

^{13}C NMR (CD_2Cl_2) δ: 14.95 (s, CH_3), 17.49 (s, CH_3), 70.72 (d, $^1J_{CP}$ = 47.7 Hz, C_5), 74.41 (s, Cp), 92.49 (d, $^1J_{CP}$ = 24.8 Hz, C_2), 93.96 (s, C_3 or C_4), 100.44 (d, $^2J_{CP}$ = 7.0 Hz, C_4 or C_3), 122.91 (s, $C_{5'}$), 124.51 (d, $^3J_{CP}$ = 4.0 Hz, $C_{3'}$), 129.14 (s, Ph), 130.75 (s, Ph), 133.57 (s, Ph), 138.54 (s, $C_{4'}$), 150.20 (d, $^3J_{CP}$ = 4.3 Hz, $C_{6'}$), 160.27 (d, $^2J_{CP}$ = 14.6 Hz, $C_{2'}$).

^{31}P NMR (CD_2Cl_2) δ: −80.8, 1.1.

3.7. [2-(2'-Pyridyl)-3,4-dimethylphosphaferrocene]borane (8)

$Me_2S \cdot BH_3$ 1 M (1.0 ml, 1×10^{-3} mol) was added at room temperature to **2** (0.31 g, 1 mmol) in 10 ml of toluene. Solvent was removed and the crude material was chromatographed on silica gel with ether/ethyl acetate (80:20) to give 0.25 g of **8** (78%).

^{1}H NMR (CD_2Cl_2) δ: 1.98 (s, CH_3), 2.28 (s, CH_3), 4.07 (d, $^2J_{HP}$ = 37.0 Hz, HC=P), 4.31 (s, Cp), pyridyl H: 7.32 (m), 7.82 (m), 8.67 (d, $^3J_{HH}$ = 5.5 Hz, $H_{6'}$).

^{13}C NMR (CD_2Cl_2) δ: 15.39 (s, CH_3), 17.17 (s, CH_3), 73.60 (s, Cp), 78.73 (d, $^1J_{CP}$ = 60.99 Hz, C_5), 123.29 (s, $C_{5'}$), 130.77 (s, $C_{3'}$), 139.74 (s, $C_{4'}$), 149.56 (s, $C_{6'}$).

^{31}P NMR (CD_2Cl_2) δ: −64.7.

Mass spectrum *m/e*: 309 ($M^+ - BH_3$, 100%).

3.8. 1-(8'-Quinolyl)-3,4-dimethylphosphole (9)

1-Phenyl-3,4-dimethylphosphole (2.0 g, 10.6×10^{-3} mol) in THF (20 ml) was stirred with Li (0.15 g, 21 mmol) for 2 h. After cooling at 0 °C, $AlCl_3$ (0.25 g, 1.9×10^{-3} mol) was added and, after 30 min, the mixture was heated at 80 °C for 20 h with 8-chloroquinoline (1.75 g, 10.6×10^{-3} mol) and CuI (0.1 g, 0.5×10^{-3} mol). Solvent was removed and the residue chromatographed on neutral alumina with hexane/ether (80:20) to give 1.3 g of **9** (52%).

^{1}H NMR ($CDCl_3$) δ: 1.99 (dd, $^4J_{HH}$ = 0.7 Hz, $^4J_{HP}$ = 3.5 Hz, 6H, CH_3), 6.68 (dd, $^4J_{HH}$ = 0.7 Hz, $^2J_{HP}$ = 36.1 Hz, 2H, HC=P), quinolyl H: 7.20–7.30 (m, 2H), 7.45–7.55 (m, 2H), 7.94 (dd, $^3J_{HP}$ = 8.30 Hz, $^3J_{HH}$ = 1.1 Hz, 1H, $H_{7'}$), 8.89 (dd, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, $H_{1'}$).

^{13}C NMR ($CDCl_3$) δ: 17.73 (d, $^3J_{CP}$ = 3.4 Hz), 127.60 (d, $^1J_{CP}$ = 9.2 Hz, C_2, C_5), 148.11 (d, $^2J_{CP}$ = 9.3 Hz, C_3, C_4), quinolyl C: 121.15 (s, CH), 126.53 (s, CH), 127.70 (s, CH), 131.91 (s, CH), 135.96 (s, CH), 136.55 (d, $^1J_{CP}$ = 9.8 Hz, $C_{8'}$), 148.74 (d, $^2J_{CP}$ = 15.3 Hz, $C_{9'}$), 149.30 (s, CH, H'_1).

^{31}P NMR ($CDCl_3$) δ: −4.5.

3.9. 2-(8'-Quinolyl)-3,4-dimethylphosphaferrocene (10)

1-(8'-Quinolyl)-3,4-dimethylphosphole (0.8 g, 3.3×10^{-3} mol) and cyclopentadienyl–dicarbonyl–iron dimer (0.56 g, 1.7×10^{-3} mol) in freshly distilled dry toluene (30 ml) were mixed in an autoclave under pressure of CO (8 bar) and heated for 2 h under stirring at 150 °C. Then, the pressure was released, the mixture was stirred for 1 h more and allowed to cool to room temperature. Solvent was removed and the crude mixture was chromatographed on neutral alumina with ether/ethyl acetate (90:10) to give 0.7 g (58%) of impure **10**.

^{1}H NMR (CD_2Cl_2) δ: 1.77 (s, CH_3), 2.11 (s, CH_3), 3.58 (d, $^2J_{HP}$ = 36.6 Hz, HC=P), 4.08 (s, Cp), quinolyl H: 7.14–7.91 (m), 8.77 (dd, $^3J_{HH}$ = 4.11 Hz, $^4J_{HH}$ = 4.18 Hz, $H_{1'}$).

^{31}P NMR (CD_2Cl_2) δ: −63.7.

Mass spectrum *m/e*: 359 (M^+, 62%), 294 ($M^+ - Cp$, 79%), 121 (CpFe, 100%).

3.10. 2-(2'-Pyridyl)-3,4-dimethylphosphacymantrene (11)

Phosphole **1** (2 g, 10.6×10^{-3} mol), ^{t}BuOK (1.42 g, 12.7×10^{-3} mol) in diethoxyethane (40 ml) were heated at 80 °C for 4 h. The formation of the anion was controlled in ^{31}P NMR (δ: 80 ppm). $BrMn(CO)_5$ (2.9 g, 10.6×10^{-3} mol) in toluene (10 ml) was added and the mixture heated at 110 °C for 1 h. After cooling at room temperature, solvent was removed and the residue was chromatographed on silica gel with toluene/ether (90:10) to give 1.15 g of **11** (32%).

^{1}H NMR (CD_2Cl_2) δ: 2.20 (s, CH_3), 2.32 (s, CH_3), 4.61 (d, $^2J_{HP}$ = 35.5 Hz, HC=P), pyridyl H: 7.11–7.67 (m), 8.49 (d, $^3J_{HH}$ = 4.0 Hz, H'_6).

^{13}C NMR (CD_2Cl_2) δ: 14.35 (s, CH_3), 16.44 (s, CH_3), 96.75 (d, $^1J_{CP}$ = 61.5 Hz, C_5), 112.43 (d, $^2J_{CP}$ = 6.79 Hz, C_3, C_4), 117.81 (d, $^1J_{CP}$ = 57.75 Hz, C_2), pyridyl C: 123.03 (s, $C_{5'}$), 124.45 (d, $^3J_{CP}$ = 6.4 Hz, $C_{3'}$), 136.83 (s, 224.80 (s, CO), $C_{4'}$), 149.77 (s, $C_{6'}$), 155.78 (d, $^2J_{CP}$ = 18.1 Hz, $C_{2'}$).

^{31}P NMR (CD_2Cl_2) δ: −35.3.

Mass spectrum *m/e*: 327 (M^+, 4.4%), 243 ($M^+ - 3CO$, 100%).

IR (decalin): ν(CO) 2021, 1956, 1942 cm^{-1}.

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