

Studies of how redox chemistry influences the synthesis of transition metal phosphametalloenes: a convenient synthesis of 2,5-diester-substituted phosphametalloenes and 2,2',5,5'-tetraester-substituted-1,1'-diphosphaferrocenes†

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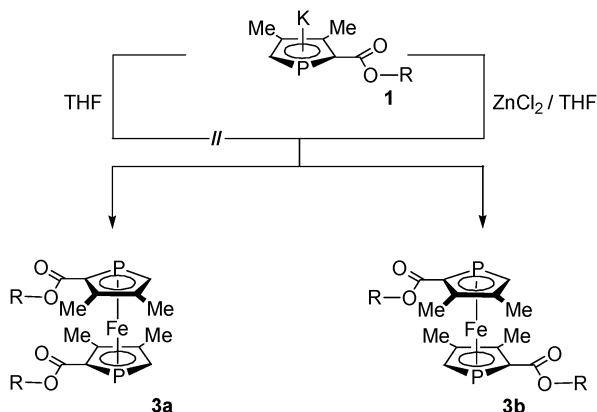
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Convenient syntheses of 2,5-diester-substituted phosphametalloenes and 2,2',5,5'-tetraester-substituted-1,1'-diphosphaferrocenes are described. Studies of the reactivity of alkali metal 3,4-dimethylphospholide, 2-ester-3,4-dimethyl phospholide and 2,5-diester-3,4-dimethylphospholide anions towards iron(II) centres (as $[\text{Fe}(\text{AlCl}_4)_2]$ or $[\text{Fe}(\text{MeCN})_6(\text{BF}_4)_2]$) indicate that the corresponding 1,1'-diphosphaferrocenes are obtained without any complications resulting from redox chemistry at the iron centre.

Introduction

There has been recent interest in the synthesis of difunctional phosphametalloenes, for reasons which reflect their promise¹ as precursors of complex phosphole-derived macrocycles of the sort which have excellent potential as new electronic materials and in catalysis.^{2–9} However, despite previous attempts to prepare 2,5-diketo- or 2,5-diester-functionalised iron,¹⁰ and ruthenium-based¹ phosphametalloenes, these fundamental structures have remained elusive, the most detailed report treating this area being due to Mathey and co-workers who have prepared 2-mono-**1**^{Et} and 2,5-diester-**2**^{Et}-substituted phospholide anions and compared their coordination chemistry. The conclusions of this study were disappointing; the zinc salt of the monoester-substituted phospholide **1**^{Et} readily gave



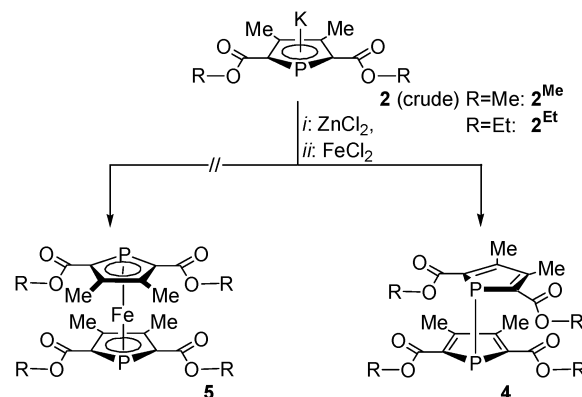
Scheme 1

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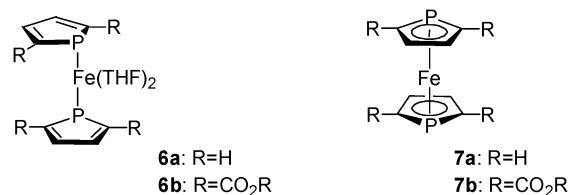
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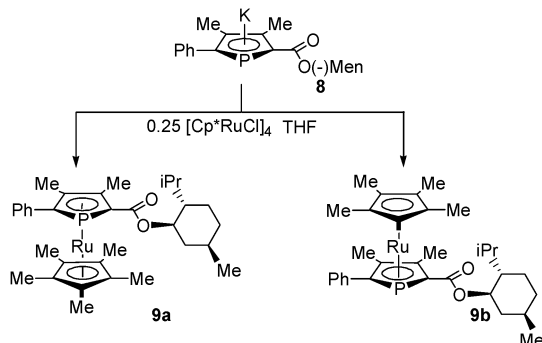


Scheme 2

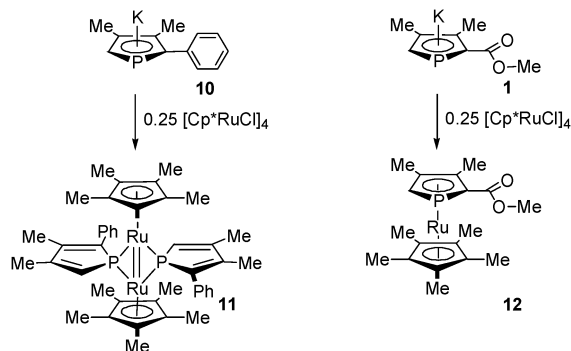
2,2'-diester-1,1'-diphosphaferrocenes **3**^{Et} (Scheme 1) but the corresponding potassium reagent gave intractable mixtures, whilst the 2,5-diester-substituted phospholide **2**^{Et} reacted slowly with ZnCl_2 and then FeCl_2 to generate a crystallographically characterised 1,1'-biphosphole redox product **4**^{Et}, rather than the corresponding 1,1'-diphosphaferrocene **5**^{Et} (Scheme 2).¹⁰ A DFT analysis gave a potential surface minimum for a putative intermediate $[\text{Fe}(\text{THF})_2(\eta^1\text{-phospholide})_2]$ **6a** and it was suggested that **6b** might undergo reductive elimination to the observed 1,1'-biphosphole rather than the corresponding 1,1'-diphosphaferrocene **7b** when ester substituents are present, the suggestion being a mismatch between the MO's of the iron and the phospholide in the ester-substituted case.¹⁰



We have been interested in the coordination chemistry of ester-substituted phospholide ligands for some time and, in



Scheme 3



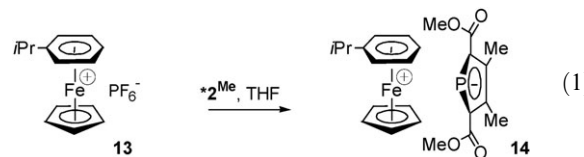
Scheme 4

studies of phosphametalloenes as ligands for enantioselection not cited by Mathey and co-workers (Schemes 3 and 4),^{11,12} have shown that ester functionalities localised in the 2-position of potassium phospholides tend to favour the formation of η^5 -phospharuthenocene complexes (**12**) over μ^2 - η^1 -bridged dimers such as **11**.¹¹ These results suggest that the ester functionality is likely to diminish the potential for initial η^1 -coordination of a phospholide to the metal centre through phosphorus^{11–18} which should therefore disfavour rather than promote the intervention of the postulated intermediates **6**. The doubt cast upon some of our working hypotheses by the results presented in the recent paper,¹⁰ and the unusual proposal that electron-withdrawing ester substituents might induce a reductive elimination pathway from **6** made a further study of this area desirable. It is presented here.

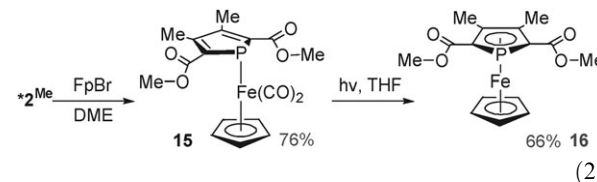
2,5-Diester-substituted monophosphametalloenes

It goes without saying that the presence of the two ester functional groups in the phospholide anion **2** should decrease its reactivity significantly, and this was clearly shown to be the case in experiments. Simple phospholide anions generally react well with half-sandwich precursors such as $[\text{FeCp}^*(\text{arene})]^+\text{X}^-$ ^{18–29} (although for a counterexample, see ref. 1) and, in an early study aimed at preparing a simple monophosphoferrocene complex, the cumene derivative $[\text{FeCp}(\text{C}_6\text{H}_5\text{iPr})]^+\text{PF}_6^-$ was allowed to react with the potassium phospholide **2**^{Me}. Precipitation of KPF_6 occurred cleanly but the anticipated orange phosphoferrocene was not obtained; instead, crystallisation of the crude mixture from THF gave the air-sensitive, pale yellow, charge separated metathesis product **14** wherein the $[\text{FeCp}(\text{C}_6\text{H}_5\text{iPr})]^+$ cation

remained intact and the hexafluorophosphate counteranion was replaced by the phospholide. Redissolution in CD_3CN clearly established the identity of the product, with ^1H and ^{13}C spectra showing both the free anion and cation in a 1 : 1 ratio; the ^{31}P NMR spectrum also features the characteristic chemical shift of the phospholide anion (142.1 for **14**; 142.4 ppm for **2**^{Me} in MeCN) and the absence of PF_6^- resonances. The stability of **14** was confirmed in further experiments, which showed that its evolution to give a secondary product, shown subsequently to be **16**, was extremely slow; a 20 mM solution of **14** showed only ca. 5% conversion upon standing overnight at room temperature in acetonitrile.



An improved access to **16** was therefore desirable and a two step synthesis from $[\text{FeCp}(\text{CO})_2\text{Br}]$ and the phospholide anion **2** was developed; the first-formed η^1 -coordinated intermediate **15** was cleanly decarbonylated under broad-band photolysis to give air-stable orange **16** in 50% overall yield (eqn (2)). **16** shows very different ^1H and ^{13}C NMR data from those of **14**, most particularly in the resonance for the ring carbon lying α -to the phosphorus atom which shows values ($\delta = 81.8$ $^1J_{\text{PC}}$ 60.8, for **16**; $\delta = 136.0$ ppm $^1J_{\text{PC}}$ 33.0 Hz for **14**) that are quite typical of ester-substituted phosphoferrocenes. The molecular structure (Fig. 1) was confirmed crystallographically and is quite normal.[‡]



Clearly, Cp*-derived phosphametalloenes will often be more desirable than their Cp-containing analogues. When allowed to react with Jonas' labile precursor $[\text{FeCp}^*(\text{TMEDA})\text{Cl}]$,³⁰ the potassium phospholide **2**^{Me} gave a very clean conversion into the desired Cp*-substituted phosphoferrocene **17**^{Me} in 69% yield in a

[‡] Crystal data: Crystals were mounted on MicroMounts (MiTeGen) using paratone oil and immediately cooled to 150 K in a stream of cold nitrogen. All data were collected on a Nonius Kappa CCD diffractometer at 150(1) K using MoK α ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. The crystal structures were solved in SIR 97⁴⁴ and refined in SHELXL-94⁴⁵ by full-matrix least-squares using anisotropic thermal displacement parameters for all non-carbon and non-hydrogen atoms. **16**: $\text{C}_{15}\text{H}_{17}\text{FeO}_4\text{P}$, $M = 348.11$, monoclinic, space group $P2_1/c$, $a = 8.213(1)$, $b = 11.074(1)$, $c = 16.621(1)$ Å, $\beta = 101.473(1)^\circ$, $U = 1481.5(2)$ Å³, $Z = 4$, $D_c = 1.56$ g cm⁻³, $F(000) = 720$, $\mu = 1.138$ cm⁻¹. Of 4303 independent reflections from an orange block of $0.24 \times 0.20 \times 0.12$ mm over $h = -11$ to 11 ; $k = -14$ to 15 ; $l = -23$ to 18 , 3710 having $I > 2\sigma(I)$ were refined, $wR_2 = 0.0731$, $R_1 = 0.0268$, $\text{GoF} = 1.040$. **5**^{Me}: $\text{C}_{20}\text{H}_{24}\text{FeO}_8\text{P}_2$, $M = 510.18$, orthorhombic, space group $Ccm2_1$, $a = 7.473(1)$, $b = 21.153(1)$, $c = 13.311(1)$ Å, $U = 2104.2(3)$ Å³, $Z = 4$, $D_c = 1.61$ g cm⁻³, $F(000) = 1056$. Of 7674 independent reflections collected as above from an orange block of dimensions $0.30 \times 0.14 \times 0.14$ mm over $h = -10$ to 10 , $k = -21$ to 29 , $l = -18$ to 16 , 2322 having $I > 2\sigma(I)$ were refined $wR_2 = 0.0654$, $R_1 = 0.0264$, $\text{GoF} = 1.066$.

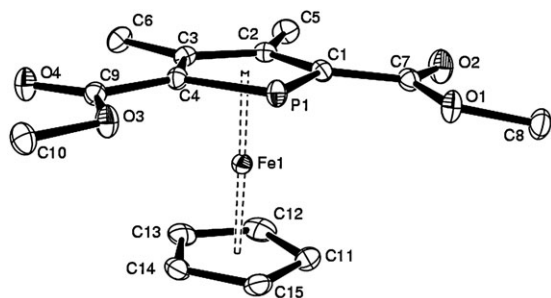
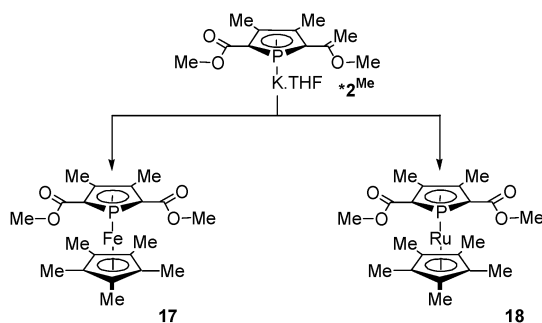


Fig. 1 Molecular structure of **16** (30% probability ellipsoids). Selected bond lengths. P(1)–C(4): 1.787(1); P(1)–C(1): 1.787(1); C(1)–C(2): 1.434(2); C(2)–C(3): 1.431(2); C(3)–C(4): 1.436(2); Fe–Ct(P): 1.628; Fe–Ct(C): 1.659 Å.



Scheme 5

synthesis (Scheme 5) which is operationally much simpler than for the Cp-based system. Again, the product proved to be quite resistant to air and moisture, thus confirming quite adequate stability and implying its potential as a precursor for further chemistry. The Cp**Ru*(II) precursor [RuCp*Cl]₄ also gave rise to the diester-substituted phospharuthenocene **18**^{Me} analogously, as a pale yellow air-stable powder in good yield (81%). The results from this initial phase of the study therefore seem to be very clear: whilst the lack of intrinsic reactivity of the phospholide precursor may sometimes complicate the synthesis of diester-substituted phosphametalloenes, such complexes are inherently quite stable and accessible targets.

2,2',5,5'-Tetraester-substituted-1,1'-diphosphaferrocenes

Mathey and colleagues' earlier study indicates that a combination of the crude phospholide **2**^{Et} and ZnCl₂ reacts with FeCl₂ to give the interesting X-ray diffraction-characterised biphosphole **4**^{Et}, rather than the corresponding 1,1'-diphosphaferrocene (Scheme 2).¹⁰ We conducted a number of experiments which indicated that impure, *in situ*-generated, potassium phospholide **2**^{Me} also reacts with electronic grade FeCl₂ in THF to give the 1,1-biphosphole **4**^{Me}. However, the same batch of FeCl₂ showed very poor reactivity when samples of the phospholide were recrystallised; in such cases no reaction occurred upon heating in THF for several hours. This contrasts strongly with the case of **3a** and **3b** (where the reaction proceeded well between **1**^{Me} and FeCl₂) but resembles the slow evolution of **14**. This obviously raised the possibility that the tetraester-substituted 1,1'-biphosphole product results from side-reactions,

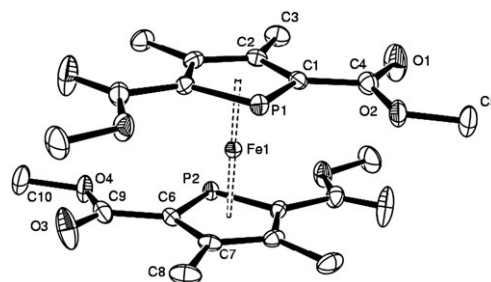


Fig. 2 Structure of tetra(methoxycarbonyl)-1,1'-diphosphaferrocene **5**^{Me} (50% probability ellipsoids). Selected bond lengths: Fe–Ct (P1 ring) 1.658, P(1)–C(1): 1.772(2); C(1)–C(2): 1.435(3); C(2)–C(2'): 1.427(4); Fe–Ct (P2 ring) 1.662, P(2)–C(6): 1.776(2); C(6)–C(7): 1.436(3); C(7)–C(7'): 1.426(4) Å. The non-primed atoms are related to their (unlabelled) primed counterparts by the crystallographically imposed mirror plane bisecting the iron and two phosphorus atoms, so that the primed atoms lie at *x*, *−y*, *z*.

which are occurring under the rather forcing conditions used, rather than a redox process at the iron centre. To examine this eventuality more closely, the recrystallised phospholides **2**^{Me} and **2**^{Et} were allowed to react homogeneously with [Fe(MeCN)₆(BF₄)₂] in acetonitrile, the solvent being chosen so as to provide good solubility for both the iron source and the potassium reagent.³¹ With this system, the potassium phospholides rapidly gave 91 and 65% yields, respectively, of the tetraester-substituted 1,1'-diphosphaferrocenes **5**^{Me} and **5**^{Et} in the form of air-stable orange powders, whose formulation was readily confirmed on the basis of characteristic ³¹P, ¹H and ¹³C spectra. The molecular structure of the tetramethyl ester complex **5**^{Me}, shown in Fig. 2, resembles the ester-free analogue **20**³² in showing the anticipated³³ configuration with the phosphorus atoms of the phospholyl rings oriented at 180° to each other. The slight increase in Fe-centroid difference in **5**^{Me} (*ca.* 1.66 vs. 1.63 Å for the simple tetramethyl analogue **20**) is consistent with the classical “charge separated” Fe²⁺(phospholide[−])₂ description of ferrocenes, with any weakening of the phosphoferrocene skeleton associated with the presence of the ester groups appearing to be small. Therefore it seems, once again, that the stability of 2,2',5,5'-tetraester-substituted-1,1'-diphosphaferrocenes is not in question, but that the synthetic protocol employed will play a crucial role in obtaining them.

Discussion

The possibility of redox chemistry between phospholide anions and late transition metal centres is interesting, and one which is fundamental to the development of good synthetic protocols. In a number of previous papers, it has been shown that additives such as MgCl₂,³² or AlCl₃,³⁴ ZnX₂, SnCl₄, BF₃, TiCl₄, ZrCl₄, TaCl₅, NbCl₅, SbX₃, *etc.*³⁵ or SnBu₃³⁶ increase the yields of 1,1'-diphosphaferrocenes when they are prepared through the classical reaction of *in situ*-generated phospholide anions with FeCl₂.³⁷ This phenomenon has been generally ascribed to a reduction in nucleophilicity of the phenyl anion byproduct as the cation passes from K or Li to the Mg, Al, Zn reagents, *etc.* and to an associated lowering in the tendency of the phospholide to provoke redox reactions as the cation

becomes less electropositive.^{32,34,36,38,39} However, there seems to be no clear literature precedent for redox reactions when purified monophospholide anions react with simple transition metal halides in the M(II) oxidation state^{13–17} and the results here, where the presumably more oxidising “naked” Fe(II) centre in the fluoroborate salt gives much better yields of the 2,2',5,5'-tetraester-1,1'-diphosphaferrocene **5^{Me}** than the corresponding chloride, argue against redox-based reactions at the Fe(II) centre. A more plausible hypothesis seems to be that the addition of suitable metallic salts leads to compound ferr(II)ates whose improved solubility (and/or more dissociated cations) serve to increase the availability of Fe(II) in solution and thus favour the formation of the desired phosphametalocene over slower side-reactions. Two further experiments that we have conducted also argue against the possibility of an inherent tendency towards redox chemistry in such systems: (i) contrary to the literature, the purified monoester-substituted potassium phospholide **1^{Me}** reacts well with FeCl₂ to give the previously reported¹⁰ mixture of diastereomers **3a,b^{Me}** so that the use of zinc additives¹⁰ is not, in fact, required (Scheme 6) and (ii) clean lithium 3,4-dimethylphospholide **19** shows good reactivity towards FeCl₂ to provide the corresponding 1,1'-diphosphaferrocene **20** in about the same yield as the literature case using the corresponding *in situ*-generated phospholyl-lithium–AlCl₃ system (Scheme 7).^{35,37} Further, in our studies with purified phospholides, the only ³¹P NMR resonances observed in the crude phosphaferrrocene product mixtures prior to isolation were those of the products themselves, so that in neither system could the corresponding 1,1'-biphosphole redox product be observed by *in situ* NMR measurements. With respect to the importance of the availability of the iron centre to the phospholide—rather than its susceptibility to redox chemistry—it is noteworthy that the combination of FeCl₂ and AlCl₃ is recommended for the synthesis of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene,³⁴ and we found that the

2,2',5,5'-tetraester-1,1'-diphosphaferrocene **5^{Et}** was obtained in very good yield from the corresponding potassium reagent and the Fe(II) precursor [Fe(AlCl₄)₂]; this reagent was prepared classically, through simple mixing of FeCl₂ and AlCl₃ in acetonitrile prior to reaction.⁴⁰ Therefore, the earlier studies may reflect the accessibility of the iron precursor with respect to the phospholide reagent, rather than any attenuation of redox chemistry.

To conclude this short study, two points seem worthy of note: firstly the new classes of 2,5-diester-substituted phosphametalocene (M = Fe, Ru) and 2,2',5,5'-tetraester-1,1'-diphosphaferrocenes **5** are quite stable; they can be prepared easily from clean potassium phospholides and appropriate precursors and have a particularly rich synthetic potential which will be outlined elsewhere. Second we believe that there is no compelling evidence for redox reactions between simple phospholide reagents and Fe(II) centres.⁴¹ In cases where unexpected chemistry is observed in coordination studies using crude phospholide reagents, reinvestigation may therefore be fruitful.

Experimental

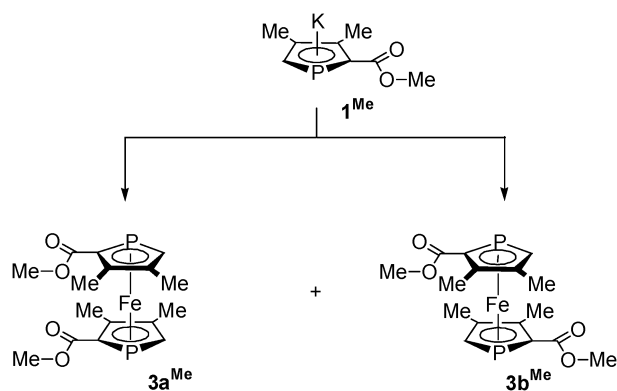
All operations were performed either using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun Labmaster 130 drybox under dry purified argon. **2^{Me}** and **2^{Et}** were prepared according to protocols described previously⁴² and crystallised as 0.75 THF solvates from THF prior to use; **1^{Me}** was prepared according to a protocol described previously and crystallised from THF–pentane,⁴² [FeCp*(TMEDA)Cl] was prepared according to Jonas;³⁰ [RuCp*Cl]₄ after Fagan and co-workers.⁴³ [FeCp(cumene)⁺PF₆[–]] was obtained commercially from Sigma Aldrich and electronic grade FeCl₂ was from Strem. Solvents were distilled under dry nitrogen: THF and ether from sodium benzophenoneketyl, pentane from sodium benzophenoneketyl–tetraglyme, acetonitrile from calcium hydride, methanol from sodium methoxide and dichloromethane from P₄O₁₀. Deuteriochloroform was deacidified through neutral alumina and deuterobenzene was used as received from Aldrich. Other solvents were also used as received. NMR measurements were made on a Bruker Avance 300 spectrometer and are referenced to internal C₆D₅H or CHCl₃ and external H₃PO₄ as appropriate. Mass spectra were obtained from dichloromethane solutions on a Bruker electrospray MicroTOF spectrometer. Infrared spectra on the pure solids were measured by attenuated total reflection on a Perkin Elmer Paragon 1000 spectroscopy.

2^{Me}·0.75 THF

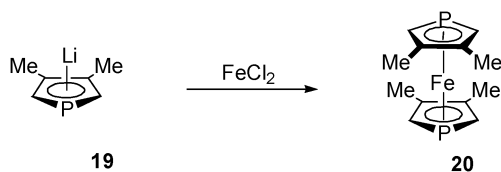
³¹P NMR (CD₃CN): 142.4 ppm. ¹H NMR (CD₃CN): 3.64 (m, 4H, THF), 3.60 (s, 6H, OMe), 2.29 (s, 6H, PCCMe), 1.80 (m, 3H, THF) ppm. ¹³C NMR (CD₃CN): 170.8 (d, *J*_{CP} = 24.6 Hz, COO), 135.7 (d, *J*_{CP} = 33.0 Hz, PCCMe), 134.7 (d, *J*_{CP} = 1 Hz, PCCMe), 68.2 (s, OCH₂ THF), 50.1 (s, OMe), 26.1 (s, OCH₂CH₂, 3H, THF), 15.0 (s, PCCMe) ppm.

3a,b^{Me}

Clean lithium 3,4-dimethylphospholide (7.1 g, 37.8 mmol) (see **20** below) in THF (35 mL) was treated at ice-bath temperature



Scheme 6



Scheme 7

with methylchloroformate (3.0 mL, 38.7 mmol) over a period of two minutes. The reaction was then stirred for five minutes and evaporated to dryness under reduced pressure without warming. The dry residue was taken up in pentane, filtered through dried Celite and evaporated to dryness under reduced pressure. The resulting oil was redissolved in THF (20 mL), heated to 60 °C for 90 minutes and then returned to room temperature. Fresh, finely powdered potassium *tert*-butoxide (3.8 g, 33.6 mmol) was added over a period of 15 minutes with vigorous stirring and the mixture was then returned to 60 °C for 10 minutes. The solution was concentrated to 5 mL under reduced pressure and pentane (15 mL) was added dropwise with vigorous stirring. The mixture was allowed to crystallise for 15 h at –30 °C. **1^{Me}** (4.8 g, 61%).

A solution of **1^{Me}** (540 mg, 2.6 mmol) in THF (3 mL) was treated with a solid sample of anhydrous FeCl₂ (190 g, 2.2 mmol) and the red mixture was stirred vigorously at room temperature for 14 hours. The solvents were then removed under reduced pressure and the dry mixture was extracted into dichloromethane (50 mL). Evaporation to dryness and flash chromatography on neutral alumina in dichloromethane : pentane 2 : 3 gave a crimson band which furnished a 1 : 1.2 mixture of **3a,b^{Me}** (272 mg, 53%). Spectroscopic data as reported previously.¹⁰

5^{Me}

Solid potassium 2,5-dimethoxycarbonyl-3,4-dimethylphospholide-0.75 THF (145 mg, 0.45 mmol) was added under nitrogen to a solution of [Fe(BF₄)₂(MeCN)₆] (105 mg, 0.22 mmol) in acetonitrile (15 mL). The orange precipitate which formed rapidly was rinsed with acetonitrile (2 × 10 mL). The product was filtered, and dried (102 mg, 91%). Crystals suitable for the X-ray diffraction analysis were obtained from diffusion of diethyl ether into a 1,2-dichloroethane solution of **5^{Me}**. ³¹P NMR (CD₂Cl₂): –24.7 ppm. ¹H NMR (CD₂Cl₂): 3.69 (6H, OMe), 2.32 (6H, PCCMe) ppm. The low solubility of this compound in common solvents precluded measurement of its ¹³C NMR spectrum. HRMS: calculated for C₂₀H₂₄FeO₈P₂: 510.0296, found: 510.0290. Elemental analysis: C₂₀H₂₄FeO₈P₂ requires: C, 47.08; H, 4.74; found: C, 47.03; H, 4.66%.

5^{Et}

Anhydrous ferrous chloride (80 mg, 0.62 mmol) and vacuum-sublimed aluminium chloride (180 mg, 1.36 mmol) were stirred in acetonitrile (10 mL) for an hour at room temperature. Solid potassium 2,5-diethoxycarbonyl-3,4-diethylphospholide-0.75 THF (550 mg, 1.58 mmol) was then added to the room temperature solution with rapid stirring and an insoluble orange precipitate formed. This was taken up in dichloromethane (5 mL) and flash chromatographed through a short plug of neutral alumina using dichloromethane. The orange band, when taken to dryness under reduced pressure, gave **5^{Et}** as an orange solid (225 mg, 64%). ³¹P NMR (CD₂Cl₂): –21.7 ppm. ¹H NMR (CD₂Cl₂): 4.13 (m, 8H, CH₂), 2.36 (s, 12H, PCCMe), 1.32 (t, *J*_{HH} = 7.1 Hz, 12H, CH₂CH₃). ¹³C NMR (CD₂Cl₂): 169.8 (d, *J*_{CP} = 18.5 Hz, COO), 103.5 (d, *J*_{CP} = 6.3 Hz, PCCMe), 86.7 (d, *J*_{CP} = 60.2 Hz, PCCMe), 61.2 (s, OCH₂), 14.3 (s, OCH₂Me), 13.2 (s, PCCMe) ppm.

CI-MS (*m/z*, %): 566 ([M]⁺, 100%). HRMS: calculated for C₂₄H₃₂P₂O₈Fe: 566.0922, found: 566.0921. Elemental analysis: C₂₀H₂₄FeO₈P₂ requires: C, 50.90; H, 5.70; found: C, 51.22; H, 5.89%.

14

A suspension of potassium 2,5-dimethoxycarbonyl-3,4-dimethylphospholide-0.75 THF **2^{Me}** (210 mg, 0.66 mmol) in THF (10 mL) was treated with solid [FeCp(cumene)⁺]PF₆[–] (251 mg, 0.65 mmol). The orange solution was stirred for two hours at room temperature (or until the phospholide reagent dissolved) and then cooled to –20 °C overnight. Large pale yellow crystals of **14** were separated from the majority of the KPF₆ by rapid swirling and decanting of the THF, and then separated manually (206 mg, 68%).

³¹P NMR (CD₃CN): 142.1. ¹H NMR (CD₃CN): 6.12–6.06 (m, 3H), 6.06–5.98 (m, 2H), 4.89 (s, 5H, Cp), 3.62 (s, 6H, OMe), 2.94 (sept, *J*_{HH} = 6.9 Hz, 1H, CHMe₂), 2.31 (s, 6H, PCCMe), 1.28 (d, *J*_{HH} = 6.9 Hz, 6H, isopropyl). ¹³C NMR (CD₃CN): 171.1 (d, *J*_{CP} = 24.6 Hz, COO), 136.0 (d, *J*_{CP} = 33.0 Hz, PCCMe), 135.0 (d, *J*_{CP} = 1 Hz, PCCMe), 114.9 (C *ipso*), 88.4 (CH *meta*), 87.8 (CH *para*), 86.9 (CH *ortho*), 77.4 (Cp), 50.3 (s, OMe), 33.7 (CH), 23.2 (Me isopropyl), 15.3 (s, PCCMe).

15

A solution of potassium 2,5-dimethoxycarbonyl-3,4-dimethylphospholide-0.75 THF **2^{Me}** (590 mg, 1.84 mmol) in DME (30 mL) was treated with solid [FeCp(CO)₂Br] (445 mg, 1.73 mmol). After stirring for 1 h at room temperature, the solvent was removed under reduced pressure. The product was purified by flash chromatography in ether on neutral alumina, to give the product as a deep red powder. 533 mg (76%).

³¹P NMR (CD₂Cl₂): –11.7 ppm. ¹H NMR (CD₂Cl₂): 4.71 (s, 5H, Cp), 3.77 (s, 6H, OMe), 2.37 (s, 6H, PCCMe) ppm. ¹³C NMR (CD₂Cl₂): 213.1 (d, *J*_{CP} = 8.5 Hz, CO), 167.8 (d, *J*_{CP} = 20.8 Hz, COO), 153.9 (d, *J*_{CP} = 19.6 Hz, PCCMe), 152.2 (d, *J*_{CP} = 7.7 Hz, PCCMe), 86.2 (d, *J*_{CP} = 0.8 Hz, Cp), 51.4 (d, *J*_{CP} = 0.8 Hz, OMe), 16.6 (d, *J*_{CP} = 2.5 Hz PCCMe) ppm. IR: 2014.5, 1970.2, 1681.9 cm^{–1}. HRMS: calculated for C₁₇H₁₇PO₆Fe: 404.0112, found: 404.0111.

16

Complex **15** (106 mg, 0.26 mmol) was dissolved in THF (50 mL) and placed in a broad-band photoreactor, where it was irradiated at 30 °C for 2 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography in dichloromethane on neutral alumina to give the product as a yellow solid (60 mg, 66%). X-Ray quality crystals grew from a saturated sample in benzene-d₆.

³¹P NMR (C₆D₆): –44.3 ppm. ¹H NMR (C₆D₆): 3.96 (s, 5H, Cp), 3.36 (s, 6H, OMe), 2.41 (s, 6H, PCCMe) ppm. ¹³C NMR (C₆D₆): 172.6 (d, *J*_{CP} = 18.4 Hz, COO), 99.6 (d, *J*_{CP} = 6.4 Hz, PCCMe), 81.8 (d, *J*_{CP} = 60.8 Hz, PCCMe), 75.0 (s, Cp), 51.3 (s, OMe), 15.0 (s, PCCMe) ppm. HRMS: calculated for C₁₅H₁₇PO₄Fe: 348.0214, found: 348.0210. Elemental analysis: required for C₁₅H₁₇PO₄Fe: C, 51.75; H, 4.92; found: C: 51.65, H: 5.17%.

17

A solution of $[\text{FeCp}^*(\text{TMEDA})\text{Cl}]^{30}$ (4.1 g, 12.0 mmol) in THF (100 mL) was added by a cannula over a period of 5 min to a DME (100 mL) solution of potassium 2,5-dimethoxycarbonyl-3,4-dimethylphospholide-0.75 THF $\mathbf{2}^{\text{Me}}$ (4 g, 12.5 mmol). The deep red solution was stirred for an hour at room temperature and then treated with a methanol (1 mL) solution of 2,2'-bipyridine (500 mg, 8.9 mmol). The violet precipitate was discarded, and the solution was purified by rapid chromatography on silica in ethyl acetate. Evaporation to dryness gave the product as a red solid (3.45 g, 69%).

^{31}P NMR (C_6D_6): -30.4 ppm. ^1H NMR (C_6D_6): 3.41 (s, 6H, OMe), 2.62 (s, 6H, Me), 1.53 (s, 15H, Cp*) ppm. ^{13}C NMR (C_6D_6): 171.9 (d, $J_{\text{CP}} = 18.4$ Hz, CO_2Me), 98.6 (d, $J_{\text{CP}} = 6.4$ Hz, PCCMe), 84.8 (Cp*), 83.2 (d, $J_{\text{CP}} = 58.4$ Hz, PC), 50.8 (OMe), 12.3 (PCCMe), 9.2 (Cp*Me) ppm. CI-MS (m/z , %): 419 ($[\text{M} + \text{H}]^+$, 100%) HRMS: calculated for $\text{C}_{20}\text{H}_{27}\text{FeO}_4$ P: 418.0996, found: 418.0998. Elemental analysis: required for $\text{C}_{20}\text{H}_{27}\text{PO}_4\text{Fe}$: C, 57.43; H, 6.51; found C, 57.80; H, 6.57%.

18

A THF (100 mL) suspension of $[\text{RuCp}^*\text{Cl}]_4$ (2.4 g, 2.2 mmol) was added through a wide-bore cannula to a warm (60°C) solution of potassium 2,5-dimethoxycarbonyl-3,4-dimethylphospholide-0.75 THF $\mathbf{2}^{\text{Me}}$ (3.15 g, 9.8 mmol). The black mixture was stirred for an hour at 60°C and then taken to dryness under reduced pressure. The residue was extracted into dichloromethane (200 mL), concentrated, and purified by flash chromatography on neutral alumina in dichloromethane. Evaporation of a very pale yellow band to dryness under reduced pressure gave the product as a pale yellow powder (3.33 g, 81%).

^{31}P NMR (THF): -19.9 ppm. ^1H NMR (C_6D_6): 3.37 (6H, 2 OMe), 2.19 (6H, 2Me), 1.57 (15H, Cp*) ppm. ^{13}C NMR (C_6D_6): 170.8 (d, $J_{\text{CP}} = 18.3$ Hz, CO), 98.1 (d, $J_{\text{CP}} = 6.2$ Hz, PCCMe), 89.9 (Cp*), 84.8 (d, $J_{\text{CP}} = 61.4$ Hz, PC), 50.8 (OMe), 12.0 (PCCMe), 9.8 (Cp*Me) ppm. HRMS: calculated for $\text{C}_{20}\text{H}_{27}\text{O}_4\text{PRu}$: 464.0690, found: 464.0689. Elemental analysis: required for $\text{C}_{20}\text{H}_{27}\text{PO}_4\text{Ru}$: C, 51.83; H, 5.87; found C, 51.44; H, 6.06%.

20

Clean, freshly beaten, lithium foil (ca. 2 g, 290 mmol) was added to a diethyl ether (40 mL) solution of distilled 1-phenyl-3,4-dimethylphosphole (9.7 g, 52 mmol) and the mixture was then stirred vigorously for 5 h at room temperature (or until ^{31}P NMR measurements showed no remaining phosphole). The excess lithium metal was removed and the solution was concentrated to 7 mL under reduced pressure, giving a colourless solid that was collected by filtration under an inert atmosphere and dried. Further washing with cold pentane (-78°C , 5 mL) removed any residual traces of phenyllithium, leaving a colourless sample of unsolvated lithium 3,4-dimethylphospholide which was shown to be clean by ^{31}P , ^{13}C and ^1H NMR spectroscopy (2.43 g, 42%). A sample of this lithium 3,4-dimethylphospholide **19** (240 mg, 2.03 mmol) **19** was then dissolved in THF (30 mL) and treated with anhydrous FeCl_2

(160 mg, 1.26 mmol). After stirring at room temperature for 15 h, the deep orange-red mixture was evaporated to dryness under reduced pressure, extracted into dichloromethane (35 mL) and flash chromatographed in dichloromethane : pentane 1 : 9 on neutral alumina. Evaporation of the red band gave the product **20** as a deep orange-red powder, showing data in full accordance with precedent³² (174 mg, 62%).

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