

# Protonation of the lithio derivatives of the 1,2,4-tri-phosphaferrocenes, $[\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBu})(\eta^5\text{-C}_5\text{R}_5)]$ ( $\text{R} = \text{H}, \text{Me}$ ): Crystal and molecular structure of $[\text{Fe}(\eta^4\text{-P}_3\text{C}_2^t\text{Bu}_2\text{BuH})(\eta^5\text{-C}_5\text{Me}_5)]$

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## Abstract

A new synthetic route is described to generate the 4-centre-5 electron donor ring system ( $\text{P}_3\text{C}_2^t\text{Bu}_2\text{BuH}$ ), *via* protonation of the lithium salts  $[\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBu})(\eta^5\text{-C}_5\text{R}_5)]$  ( $\text{R} = \text{H}, \text{Me}$ ). The molecular structure of  $[\text{Fe}(\eta^4\text{-P}_3\text{C}_2^t\text{Bu}_2\text{BuH})(\eta^5\text{-C}_5\text{R}_5)]$  ( $\text{R} = \text{Me}$ ) has been determined by a single crystal X-ray study.

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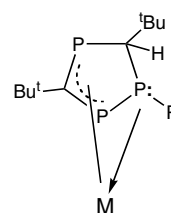
**Keywords:** 4-Centre-5 electron donor; Tri-phosphorus ring; Protonation; Lithium

## 1. Introduction

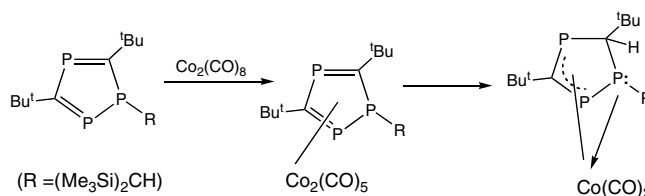
We previously reported [1] a novel intra-molecular hydrogen atom transfer reaction within the  $\eta^4$ -cyclooctadiene- $\eta$ -1,2,4-triphosphole ruthenium(0) complex  $[\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})(\eta\text{-P}_3\text{C}_2^t\text{Bu}_2\text{CH}(\text{SiMe}_3)_2)]$  (see Scheme 1), which afforded a complex containing an  $\eta^5$ -bonded cyclooctadienyl ring and the new  $\text{P}_3\text{C}_2^t\text{Bu}_2\text{H}(\text{CH}(\text{SiMe}_3)_2)$  ring.

The heterocyclic ring can best be considered as a 5e-donor ligand to ruthenium involving an  $\eta^3$ -1,3,-diphosphallyl component augmented by an  $\eta^1$ -interaction (2e-donor) from the  $\sigma^3$ -phosphorus centre as shown below.

We also drew attention [2] to the similar ligating behaviour of this novel 5-electron donor ring system to that of the well-known  $\eta^5$ -cyclopentadienyl ring, e.g. in the cobalt

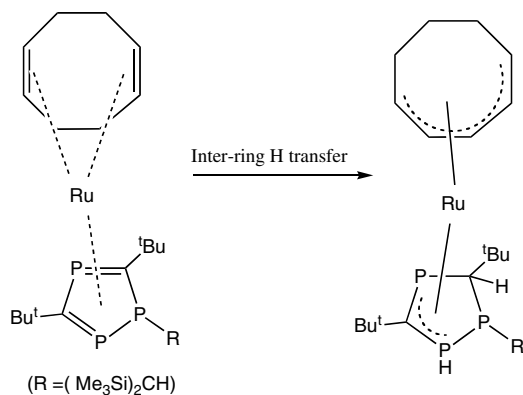


dicarbonyl compounds shown below. The stability of the ring system was illustrated by its formation simply by heating the dinuclear triphosphole complex  $[\text{Co}_2(\text{CO})_5\text{-P}_3\text{C}_2^t\text{Bu}_2\text{R}]$  ( $\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$ ), in which the almost planar triphosphole is acting as 6e-donor towards the two cobalt atoms.

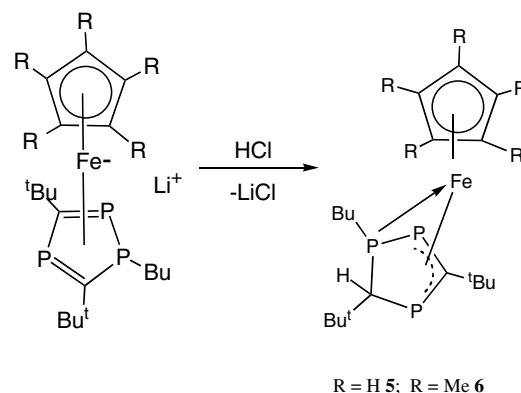


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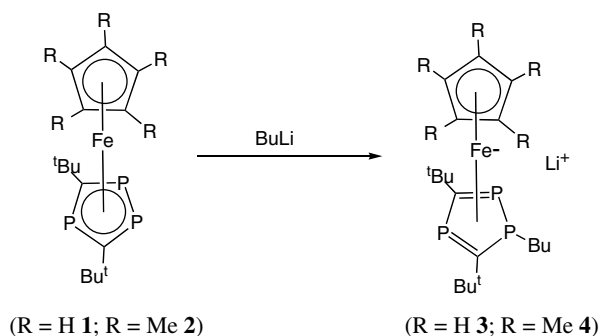


Scheme 1.



Scheme 2.

In the ruthenium system we speculated that the hydrogen transfer from one ring to the other probably proceeded *via* the metal centre [1]. Very recently [3] we described the first examples of lithiation of the tri-phosphaferrocenes **1** and **2** containing the 1,2,4-triphospholyl ring system. These reactions afforded **3** and **4**, respectively and a single crystal X-ray diffraction study reveals that LiFe( $\eta^4$ -P<sub>2</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>-P<sup>Bu</sup>Bu)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> **4** exhibits an unusual dimeric structure in the solid state.



We therefore considered whether the very electron rich iron centres in **3** and **4** would be susceptible to an initial electrophilic attack by a proton; which if then followed by H-migration from the metal to the tri-phosphorus containing ring, might generate the desired  $\eta^4$ -5e-donor (P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>BuH) ring system attached to iron.

## 2. Results and discussion

Treatment of either **3** or **4** with an ether solution of HCl at room temperature immediately gave the products [Fe( $\eta^4$ -P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>BuH)( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)] (R = H **5**, R = Me **6**), respectively, in which the final result of the electrophilic attack of the proton was indeed on the C adjacent to the alkylated P( $\lambda^3\sigma^3$ ) atom of the P<sub>2</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>PBu ring (see Scheme 2). Both products **5** and **6** were fully characterized by multinuclear NMR spectroscopy and in the case of **6** by a single crystal X-ray diffraction study.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [Fe( $\eta^4$ -P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>-BuH)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] **5** gave the expected first-order pattern of lines for an [AMX] spin system for the three different P

environments. The saturated P<sub>A</sub> atom gave rise to a doublet of doublets at -175.5 ppm with a large one bond coupling to the adjacent P<sub>B</sub> (<sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 362.0 Hz) and a smaller coupling to P<sub>C</sub> (<sup>2</sup>J(P<sub>A</sub>P<sub>C</sub>) = 31.5 Hz). The P<sub>B</sub> resonance was a doublet of doublets at 8.2 ppm, exhibiting the same <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) coupling and smaller <sup>2</sup>J(P<sub>B</sub>P<sub>C</sub>) coupling (26.7 Hz). The resonance of P<sub>C</sub> was a doublet of doublets centred at -40.6 ppm. The <sup>1</sup>H NMR spectrum of **5** showed two singlets at 1.49 and 0.69 ppm for the two different <sup>t</sup>Bu groups and a singlet for the five protons of the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> group at 4.46 ppm, with a relative intensity ratio 9:9:5. The mass spectrum showed a peak at 410 (90%) consistent with the [Fe(C<sub>5</sub>H<sub>5</sub>)(P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>HBu)]<sup>+</sup> ion.

As expected both the <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra of [Fe( $\eta^4$ -P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>BuH)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)] **6** are very similar to those of **5**. The <sup>31</sup>P{<sup>1</sup>H} spectrum of **6** showed a doublet of doublets at -166.0 ppm for P<sub>A</sub> (<sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 354 Hz; <sup>2</sup>J(P<sub>A</sub>P<sub>C</sub>) = 33 Hz). P<sub>B</sub> gave rise to the expected doublet of doublets at 1.1 ppm (<sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 354 Hz; <sup>2</sup>J(P<sub>A</sub>P<sub>C</sub>) = 22 Hz) while P<sub>C</sub> occurs as a doublet of doublets at -23.2 ppm with the expected small couplings.

The <sup>1</sup>H NMR spectrum of **6** showed the expected two singlets at 1.60 and 0.76 ppm for the two different <sup>t</sup>Bu groups and a singlet for the protons of the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ring at 1.87 ppm with the intensity ratio 9:9:15, respectively. The resonance of the unique proton was observed and gave a doublet of doublets pattern at 2.29 ppm (<sup>2</sup>J(P<sub>C</sub>H) = 11.75 Hz; <sup>2</sup>J(P<sub>A</sub>H) = 3.66 Hz). The mass spectrum showed a peak at 480 (70%) for the [Fe(P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>)C<sub>5</sub>Me<sub>5</sub>HBu]<sup>+</sup> ion.

The molecular structure of **6** was confirmed by a single crystal X-ray diffraction study (Fig. 1), which reveals that in the coordinated P<sub>3</sub>C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>BuH ring the P(1), P(2), C(2) and P(3) centres all lie in the same plane, which is roughly parallel to that of the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligated ring. The mean Fe-P distance is 2.27 Å. The saturated P(1) is regarded to coordinate to the Fe centre by its electron lone pair, and the Fe-C(2) distance (2.101 Å) is very similar to the average Fe-C(Cp<sup>\*</sup>) distance in the same complex. The distance between the Fe centre and the saturated C(1) of 3.093 Å which is bent out of the P(1)P(2)C(2)P(3) plane is much greater than the sum of the covalent bonding radii of Fe and C.

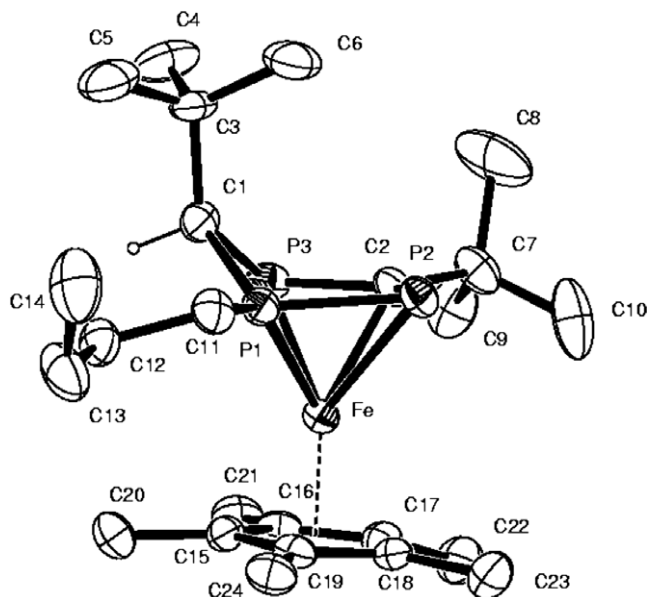
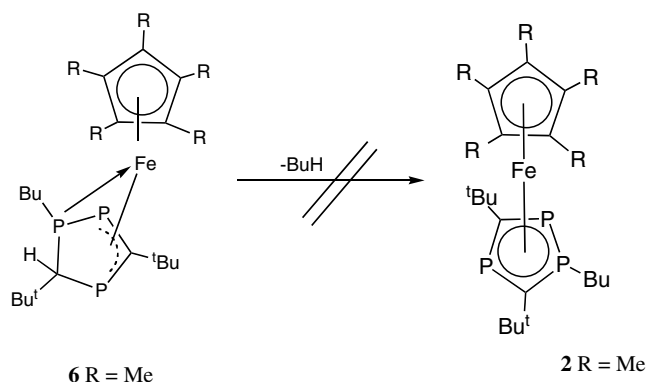


Fig. 1. Molecular structure of  $[\text{Fe}(\eta^4\text{-P}_3\text{C}_2'\text{Bu}_2\text{BuH})(\eta^5\text{-C}_5\text{Me}_5)]$  **6**. Selected bond distances (Å) and angles (°): P(1)–C(1) 1.808(5), C(1)–P(3) 1.914(5), P(3)–C(2) 1.790(5), C(2)–P(2) 1.787(4), P(2)–P(1) 2.1255(17), Fe–P(1) 2.1691(13), Fe–P(2) 2.3393(13), Fe–C(2) 2.101(4), Fe–P(3) 2.3182(14), Fe–M(1) 1.708(4), P(1)–C(1)–P(3) 90.2(2), C(1)–P(3)–C(2) 102.3(2), P(3)–C(2)–P(2) 119.9(2), C(2)–P(2)–P(1) 78.09(15), P(2)–P(1)–C(1) 109.38(17).

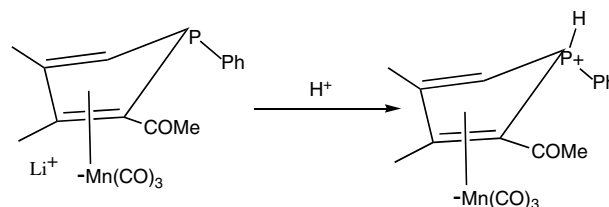
The 5e-4 centre bonding features of the coordinated  $\text{P}_3\text{C}_2'\text{Bu}_2\text{BuH}$  ring in **6** are very similar to those previously reported by us for the analogous rings in both  $[\text{Ru}(\eta^5\text{-C}_8\text{H}_{11})(\eta\text{-P}_3\text{C}_2'\text{BuHCH}(\text{SiMe}_3)_2)]$  and  $[\text{Co}(\text{CO})_2(\eta\text{-P}_3\text{C}_2'\text{BuHCH}(\text{SiMe}_3)_2)]$  [1,2].

Unexpectedly, complex **6** is quite thermally stable and a solution in dekaline showed no decomposition even after heating to 160 °C for 15 h as indicated by monitoring the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The thermal stability of **6** is remarkable, since a likely decomposition pathway involve *n*-butane elimination would readily generate the stable and more fully-delocalised aromatic tri-phosphaferrocene  $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^5\text{-C}_5\text{Me}_5)]$  **2**.



Interestingly Mathey and co-workers [4] found that the protonation of the phosphacyclopentadiene anion shown below, which was obtained from PhLi and 2-acyl-3,4-dim-

ethylphosphacyclopentadiene, occurred exclusively at the phosphorus centre [4].



Likewise, it is noteworthy that alkylation reactions of the lithium salts **3** and **4** were found to occur only at the phosphorus centre [1], so the possibility that the protonation reactions might involve successive H transfers from metal to phosphorus to carbon cannot be ruled out.

### 3. Experimental

All manipulations of air-and/or moisture-sensitive compounds were carried out under rigorously anhydrous and oxygen-free conditions using standard high vacuum Schlenk line techniques or in an inert atmosphere. Glassware and Schlenk tubes were flame dried before used. Solvents were dried and distilled before use. NMR solvents were purified by refluxing over a suitable drying agent, and vacuum-transferred into ampoules.  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra were acquired on a Bruker Avance 300DPX spectrometer operating at 300 MHz for  $^1\text{H}$  measurements, and 121.49 MHz for  $^{31}\text{P}$  measurements.  $^1\text{H}$  NMR spectra are referenced to the residual proton chemical shift of the internal deuterated solvent (which in turn is referenced to TMS).  $^{31}\text{P}$  NMR spectra are referenced to  $\text{H}_3\text{PO}_4$  (87%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$  as an external standard). All spectra were recorded at room temperature. Mass spectra (EI and FAB) were recorded by Dr. A. Abdul-Sada at the University of Sussex. Single crystal X-ray diffraction studies were carried out using the Enraf Nonius KAPPACCD diffractometer.  $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^5\text{-C}_5\text{H}_5)]$  and  $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^5\text{-C}_5\text{Me}_5)]$  were prepared according to the literature procedures [5–7].

#### 3.1. Synthesis of $[\text{Fe}(\eta^4\text{-P}_3\text{C}_2'\text{Bu}_2\text{BuH})(\eta^5\text{-C}_5\text{H}_5)]$ **5**

A solution of  $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^5\text{-C}_5\text{H}_5)]$  (0.40 g, 1.13 mmol) in hexane (10 ml) and BuLi (0.072 g, 1.13 mmol) in hexane was stirred overnight at room temperature.  $[\text{LiFe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{PBu})(\eta^5\text{-C}_5\text{R}_5)]$  was obtained as a beige powder after the solution was filtered. The resulting powder was dissolved in 10 ml of THF, and a solution of HCl in Et<sub>2</sub>O (1.13 mmol) was added. The mixture was stirred overnight, solvent was then removed *in vacuo* and the product was extracted with hexane, the  $[\text{Fe}(\eta^4\text{-P}_3\text{C}_2'\text{Bu}_2\text{BuH})(\eta^5\text{-C}_5\text{H}_5)]$  was obtained as an oil and many attempts to crystallize it were unsuccessful.

Spectroscopic data: ( $C_6D_6$ , 25 °C),  $^{31}P\{^1H\}$  NMR (121.49 MHz):  $\delta P_A = -175.5$  (dd,  $^1J(P_AP_B) = 362.0$  Hz,  $^2J(P_AP_C) = 31.5$  Hz),  $\delta P_B = 8.2$  (dd,  $^2J(P_AP_C) = 26.7$  Hz),  $\delta P_C = -40.6$  (dd).  $^1H$  NMR (300 MHz):  $\delta H(^tBu) = 1.49$  (s, 9H),  $\delta H(^iBu) = 0.69$  (s, 9H),  $\delta H(C_5H_5) = 4.46$  (s, 5H) ppm. Mass spectrum (EI),  $m/z$ : 480 (65%,  $[M]^+$ ), 423 (100%,  $[(M-Bu)^+]$ ).

### 3.2. Synthesis of $[Fe(\eta^4-P_3C_2^tBu_2BuH)(\eta^5-C_5Me_5)]$ **6**

A solution of  $[Fe(\eta^5-P_3C_2^tBu_2)(\eta^5-C_5Me_5)]$  (0.30 g, 0.71 mmol) and BuLi (0.045 g, 0.71 mmol) was stirred overnight in hexane (15 ml) at room temperature. The product  $Li[Fe(\eta^4-P_2C_2^tBu_2PBu)(\eta^5-C_5Me_5)]$  was obtained as a powder after the solution was filtered off, which was dissolved in 10 ml of THF, and a solution of HCl in Et<sub>2</sub>O (0.71 mmol) was added. The mixture was stirred overnight, solvent was then removed *in vacuo* and the product was extracted with hexane, and was crystallised from hexane at -35 °C to give dark red crystals (0.13 g, 40%). Found: C, 60.04; H, 9.08%.  $C_{24}H_{43}P_3Fe$  requires C, 60.01; H, 9.02.

Spectroscopic data  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 25 °C, 121.49 MHz):  $\delta P_A = -166.01$  (dd,  $^1J(P_AP_B) = 354$  Hz,  $^2J(P_AP_C) = 33$  Hz),  $\delta P_B = 1.10$  (dd,  $^2J(P_BP_C) = 22$  Hz),  $\delta P_C = -23.20$  (dd).  $^1H$  NMR ( $C_6D_6$ , 25 °C, 300 MHz):  $\delta H(^tBu) = 1.60$  (s, 9H),  $\delta H(^iBu) = 0.75$  (s, 9H),  $\delta H(Me) = 1.87$  (s, 15H),  $\delta H = 2.29$  (dd,  $^2J(P_CH) = 11.75$  Hz,  $^2J(P_AH) = 3.66$  Hz). MS (EI),  $m/z$ : 480 (65%,  $[M]^+$ ), 423 (100%,  $[M-Bu]^+$ ).

Crystal data for **6**:  $C_{24}H_{43}FeP_3$ ,  $M = 480.34$ , monoclinic, space group  $P\bar{1}$  (No 2),  $a = 11.3007(3)$  Å,  $b = 14.2607(4)$  Å,  $c = 17.7957(5)$  Å,  $\alpha = 67.183(1)$ ,  $\beta = 86.953(1)$ ,  $\gamma = 78.24^\circ$ ;  $V = 2586.98(12)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 4$ ,  $D_c = 1.23$  Mg m<sup>-3</sup>,  $\mu = 0.78$  mm<sup>-1</sup>,  $\lambda = 0.71073$  Å,

$F(000) = 1032$ , crystal size  $0.15 \times 0.10 \times 0.10$  mm<sup>3</sup>, 31376 measured reflections, 8909 independent reflections ( $R_{int} = 0.106$ ), 5731 reflections with  $I > 2\sigma(I)$ , final indices  $R_1 = 0.059$ ,  $wR_2 = 0.108$  for  $I > 2\sigma(I)$ ,  $R_1 = 0.112$ ,  $wR_2 = 0.127$  for all data. Data collection: KappaCCD. Program package WINGX. Refinement using SHELXL-97.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.063](https://doi.org/10.1016/j.jorganchem.2007.11.063).

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