

Redox-active phosphines: synthesis and crystal structures of palladium(II) complexes of a metallaphosphine in two different oxidation states†

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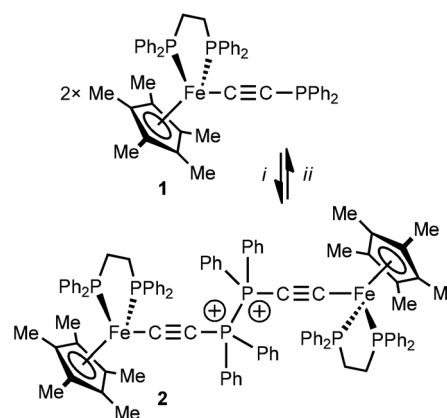
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The redox-active metallaphosphine [Fe(dppe)(η⁵-C₅Me₅)(C≡C-PPh₂)] reacts with [Pd(1,5-cod)Cl₂] to give mono- and bis-phosphine coordinated palladium centres as a function of stoichiometry, and these complexes provide a stable redox-active platform which allows reversible one-electron {Fe(II)→Fe(III)⁺} oxidations within the palladium coordination sphere.

Fine control of architecture and the ability to generate quite specific electronic environments¹ mean that phosphines are exceptionally widely used in many metal-catalysed processes,² and their versatility has driven recent research into areas as varied as self-assembling phosphines for enantioselection,³ supramolecular phosphines allowing unprecedented catalytic selectivities,⁴ and hybrid chemical/biological phosphine-containing systems.⁵ However, there has been comparatively little recent interest in the class of redox-active phosphines,⁶ which should constitute an unusual class of “non-innocent” ligands^{7,8} and have been invoked *inter alia* for the switching of catalytic processes.⁹ We have recently demonstrated that phosphorus centres and redox-active organoiron endgroups can communicate strongly if linked through molecular wires such as acetylenes, and that oxidation of the Fe(II) endgroup in **1** provokes significant reactivity at the phosphorus centre (Scheme 1).¹⁰ This unusual behaviour prompted a study of the coordination chemistry of this metallaphosphine towards Pd(II) centres.

Reaction of the diamagnetic metallaphosphine **1** with one equivalent of [PdCl₂(1,5-cod)] gives a near-quantitative isolated yield of a blue, air-stable dimeric complex [Pd₂Cl₄(**1**)₂] **3** that



Scheme 1 Redox switching of metallaphosphine **1**. Reagents: *i*: [FCH⁺][PF₆⁻], 2 eq., CH₂Cl₂, 20 °C, 1 h; *ii*: [CoCp₂] 3 eq., CH₂Cl₂, 20 °C, 1 h.

shows a classical *trans*-phosphine configuration about a butterfly-configured Pd₂Cl₄ core (Fig. 1, in purple).¹¹ The metalloligand undergoes moderate structural changes upon coordination, with the most significant differences being associated with the alkyne linker (Fig. 1). The C≡C and C-P bond lengths in **3** are slightly longer and shorter respectively than those normally found for simple PdCl₂-coordinated alkynyl-(diaryl phosphines)¹² and the alkynyl ν_{C≡C} stretch falls from 1964 to 1930 cm⁻¹, all of which imply an increased contribution from an iron-vinylidene resonance hybrid.¹³

The cyclic voltammogram for **3** shows two closely spaced reversible oxidations at +0.16 and +0.25 V (both showing ΔE_p = 85 mV in CH₂Cl₂ vs. SCE), which lie within a well-precedented window for the organoiron endgroup;¹³ bulk chemical oxidation using [FCH⁺][PF₆⁻]¹⁴ cleanly and near-quantitatively gave the black, air sensitive, dichloromethane-soluble **4**, whose formulation as the corresponding double oxidation product was confirmed by an X-ray structural analysis (Fig. 1, gold). The crystallographic data confirm an essentially iron-based oxidation, which is reflected in an elongation of (a) the mean

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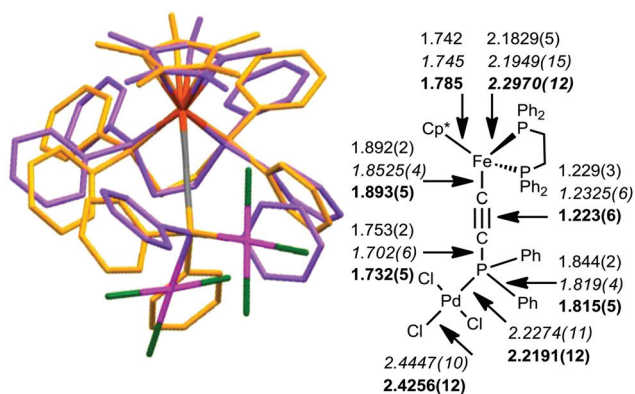


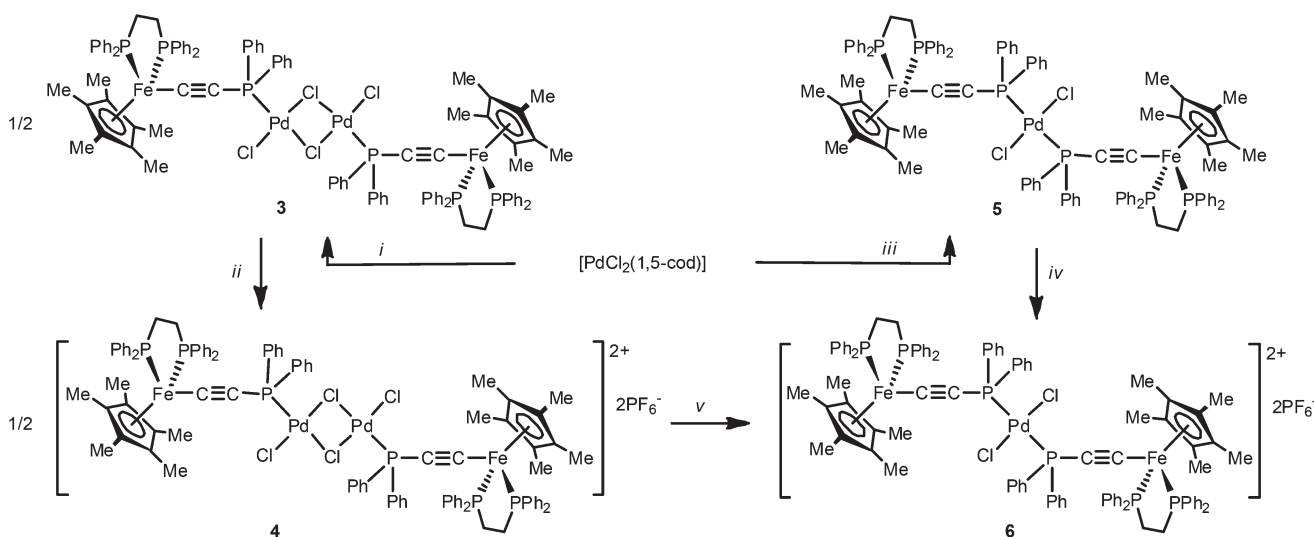
Fig. 1 Left: Superimposed X-ray-structures showing one half of each of the dimers forming the **3**, **4** redox couple, showing ligand superstructure for the neutral complex **3** (purple) and its oxidation product **4** (gold). (Pd in magenta, Fe in orange, Cl in green). See ESI† for individual depictions of these complexes. Right: X-ray structural changes upon passing from free ligand **1** (plain text) to neutral dimer **3** (*italic*) and dication **4** (**bold**). Values are averaged over chemically equivalent sites.

Fe–P distances to the dppe ligand from 2.1949 to 2.2970 Å (+4.7%) and (b) the mean Fe–Cp*_{centroid} distances from 1.745 to 1.785 Å (+2.2%).¹⁵ The oxidation has a significantly smaller effect upon the palladium coordination sphere: a slight shortening of the mean Pd–P distance, from 2.2274(11) to 2.2191(12) Å (–0.4%) and a modest (0.8%) shortening in the *trans*-Pd–Cl distance from 2.4447(10) to 2.4256(12) Å are observed,¹⁶ whilst the sum of the angles made by the organic groups at the Pd-coordinated phosphorus also rises only modestly from 317.6 to 321.8°. The dimeric palladium core of the molecule can be expected to act as “spacer” between the two oxidised [Pd(I⁺)] components and an Evans determination¹⁷ gave a room temperature magnetic moment of 2.21 ± 0.1 BM at 293 K that

is consistent with a ditopic diradical featuring two non-interacting spins.¹⁸

Palladium dimers of type **3** are excellent sources of both homo- and heteroleptic [PdCl₂L₂] complexes¹⁹ and **5**, which offers the possibility of two-electron redox chemistry within a Pd coordination sphere, was found to be accessible through either reaction of two equivalents of **1** with the palladium bridged dimer **3**, or by simple reaction of two equivalents of **1** with [PdCl₂(1,5-cod)] (Scheme 2). Single crystals of the purple, air-stable *trans*-configured **5** revealed metallaphosphine ligands that are very similar to those in **3** and Pd–P distances (2.338(1) Å) which are normal for mutually *trans*-phosphine ligands in a Pd(II) complex (Fig. 2). DFT data (Fig. 3) show a sharp increase in the NBO-calculated positive charge at the Pd-bound phosphorus (+0.62) and a significant rise at the iron-coordinated alkyne carbon (+0.10) upon coordination of a model for **5**²⁰ to PdCl₂, but only negligible changes (<0.04) elsewhere. Again, cyclic voltammetry showed closely-spaced reversible oxidation waves ($E_{1/2}^1 = -0.02$ V, $E_{1/2}^2 = 0.11$ V) and chemical oxidation using two equivalents of [FcH⁺][PF₆[–]] provided a black, air-sensitive product, **6**. Crystals suitable for a diffraction study were not obtained, but comparison of the very similar ¹H NMR data for **4** and **6**,²¹ and an Evans determination showing a value of 2.42 ± 0.1 BM (298 K) that is again classical for two unpaired electrons,¹⁸ imply a bis-Fe(III) complex showing little spin–spin coupling across the palladium centre. A further DFT comparison of NBO charge distributions in models¹⁴ for **5** and **6** confirms an iron based oxidation ($\delta_{Q_{Fe(5\rightarrow6)}} = +0.36$) that causes significant changes in charge at the linker atoms ($\delta_{Q_{Fe-C}} = -0.13$; $\delta_{Q_{P-C}} = +0.21$) but significantly smaller effects at phosphorus and at palladium ($\delta_{Q_{P, Pd}} < 0.02$).

The individual redox steps that occur within the bound couples **3**, **4** and **5**, **6** therefore appear to be well-behaved, but



Scheme 2 Coordination chemistry of **1** and redox reactivity of the resulting Pd(II) complexes **3** and **5**. Reagents and conditions: *i*: compound **1** (1.0 eq.), CH₂Cl₂, 15 h, 97%; *ii*: [FcH⁺][PF₆[–]], CH₂Cl₂, 1 h, >98%; *iii*: compound **1** (2.0 eq.), CH₂Cl₂, 15 h, 96%; *iv*: [FcH⁺][PF₆[–]], CH₂Cl₂, 1 h, >98%; *v*: compound **2** (1.0 eq.), CD₂Cl₂, 15 min, >95%.

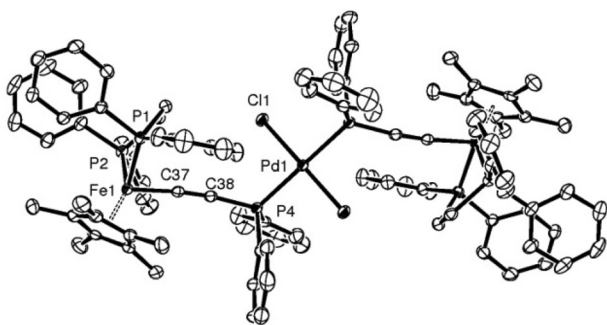


Fig. 2 X-ray structure of the neutral monomeric Pd complex 5.

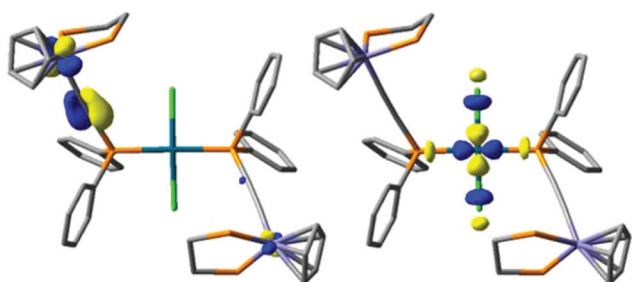
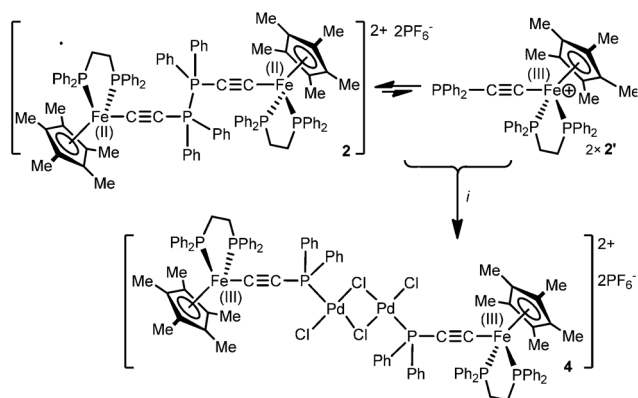


Fig. 3 The B3PW91 calculated HOMO (left) and LUMO (right) for $[\text{PdCl}_2\text{L}_2]$. ($\text{L} = \text{FeCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)\text{C}_2\text{PPh}_2$), a model for 5. Calculated HOMO–LUMO gap: 3.05 eV.



Scheme 3 Reaction of 2 with $[\text{PdCl}_2(1,5\text{-cod})]$ to generate the dicationic dimer 4. Reagents and conditions: (i) $[\text{PdCl}_2(1,5\text{-cod})]$, 2 eq., CH_2Cl_2 , 1 h, 20 °C, >98%.

the chemical reversibility of the system as a whole clearly also rests upon the chemical integrity of any phosphine ligands dissociated from the Pd(II) centres. The stability of 1 is established but our previous study has shown that the iron(III) proligand 2' normally exists as a 1,1'-(biphosphine)dication 2¹⁰ (Scheme 3); this raises the possibility of ligand dissociation from 4 with subsequent dimerisation of the Fe(III) ligand monomers to generate a 1,1'-(biphosphine)dication 2 reservoir and a ligand-deficient solution that deposits $[\text{PdCl}_2]$. Experi-

ments conducted upon isolated 1,1'-(biphosphine)dication 2 and $[\text{PdCl}_2(1,5\text{-cod})]$ indicate that this mixture cleanly generates complex 4 (with 2 eq. of Pd) or 6 (with 1 eq. of Pd), and therefore confirm that ligand dissociation from both systems is reversible. The most likely mechanism involves the transient dissociation of the P–P bond to generate the Fe(III) proligand 2'¹⁰ prior to capture by the Pd centre (Scheme 3).

To conclude, metallaphosphines bearing $[\text{Fe}(\kappa^2\text{-dppe})-(\eta^5\text{-C}_5\text{Me}_5)]$ endgroups bind to Pd(II) in both their neutral and cationic forms and can therefore be used to generate a chemically stable, redox-switchable coordination sphere about PdCl_2 centres. The $[\text{Pd}(\text{II})-(1^+)_2] \leftrightarrow [\text{Pd}(\text{IV})^{2+}-(1)_2]$ valence tautomer is firmly shifted to the left, so the metallaligand brings a potential for varying the overall electron count of the complex without excessively compromising the electronic identity of the palladium(II) centre. Reactivity studies of 3–6 are in progress.

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- 21 See ESI.† Note that the Cp* proton shifts in **4**: –8.5 and **6**: –8.7 ppm are both typical of [Fe^{III}(dppe)(C₅Me₅)]⁺-groups¹³.