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

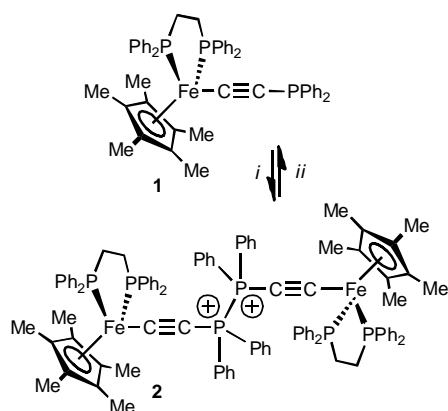
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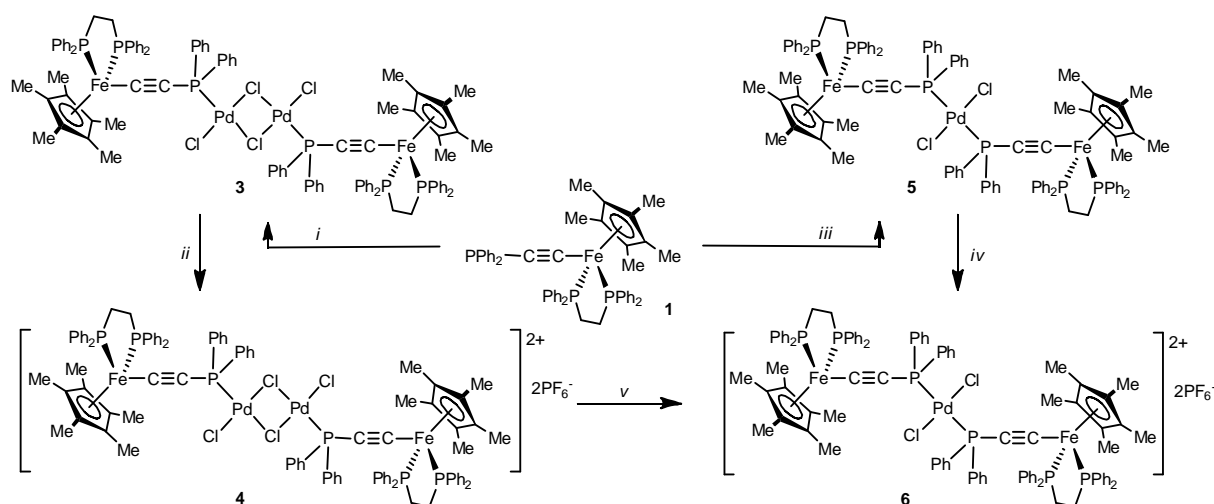
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The redox- active metallaphosphine [Fe(dppe)(η^5 -C₅Me₅) (C≡C-PPh₂)] reacts with [Pd(1,5-cod)Cl₂] give mono- and bis- phosphine complexes as a function of stoichiometry, and these complexes provide a stable redox- active platform which allows reversible 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 means 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 centres (Scheme 1).¹⁰ This unusual behaviour prompted a study of the coordination chemistry of this metallaphosphine towards Pd(II) centres.



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



Scheme 2: Coordination chemistry of **1** and redox reactivity of the resulting Pd(II) complexes **3** and **5**. Reagents and conditions: *i*: $[\text{PdCl}_2(1,5\text{-cod})]$ (1.0eq.), CH_2Cl_2 , 15h, 97%; *ii*: $[\text{FcH}][\text{PF}_6]$, CH_2Cl_2 , 1h, > 98%; *iii*: $[\text{PdCl}_2(1,5\text{-cod})]$ (0.5eq.), CH_2Cl_2 , 15h, 96%; *iv*: $[\text{FcH}][\text{PF}_6]$, CH_2Cl_2 , 1h, > 98%; *v*: Compound **2** (1.0eq.), CD_2Cl_2 , 15mn, > 95%.

Reaction of the diamagnetic metallaphosphine **1** with one equivalent of $[\text{PdCl}_2(1,5\text{-cod})]$ gives a near- quantitative isolated yield of a blue, air-stable dimeric complex $[\text{Pd}_2\text{Cl}_4(\mathbf{1})_2]$ **3** that shows a classical *trans*- phosphine configuration about a butterfly- configured Pd_2Cl_4 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 $\text{C}\equiv\text{C}$ and C-P bond lengths in **3** are slightly longer and shorter respectively than those normally found for simple PdCl_2 - coordinated alkynyl-(diaryl phosphines)¹² and the alkynyl $\nu_{\text{C}\equiv\text{C}}$ stretch falls from 1964 to 1930 cm^{-1} , all of which imply an increased contribution from an iron-vinylidene resonance hybrid.¹³

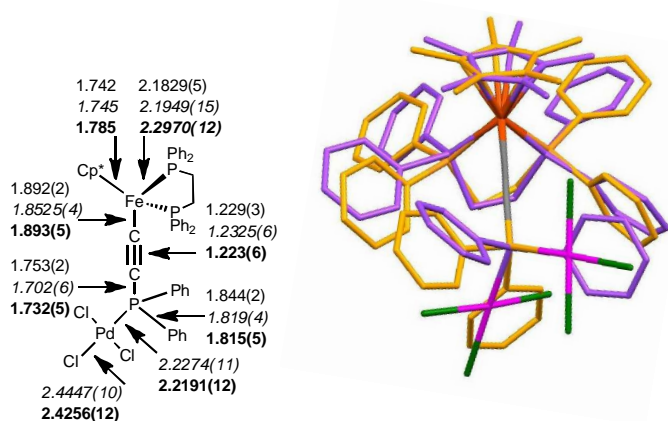


Fig 1. Left: Superimposed X-ray- structures showing one half of each of the dimers forming the **3**, **4** redox couple, showing ligand superstructure for the neutral complex **3** (purple) and its oxidation product **4** (gold). (Pd in magenta, Fe in orange, Cl in green). See supplementary for individual 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.

The cyclic voltammogram for **3** shows two closely spaced reversible oxidations at +0.16 and +0.25 V (both showing $\Delta E_p = 85$ mV in CH_2Cl_2 vs SCE), which lie within a well-precedented window for the organoiron endgroup;¹³ bulk chemical oxidation using $[\text{FcH}][\text{PF}_6]$ 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 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 $[\text{Pd}(\mathbf{1}^+)]$ components and an Evans determination¹⁷ of a room temperature magnetic moment of 2.21 ± 0.1 BM at 293K is consistent with a ditopic diradical featuring two non-interacting spins.¹⁸

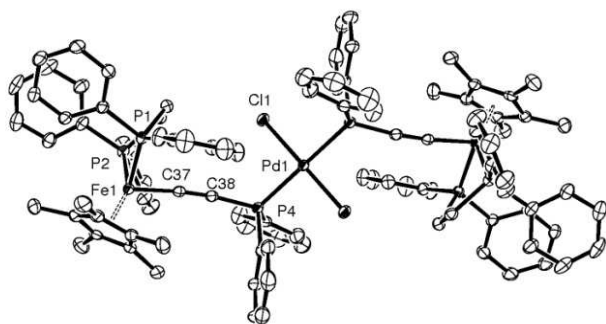


Fig. 2: X-ray structure of the neutral monomeric Pd complex **5**.

Palladium dimers of type **3** are excellent sources of both homo- and heteroleptic $[\text{PdCl}_2\text{L}_2]$ 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 $[\text{PdCl}_2(1,5\text{-cod})]$ (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 from a model for **5**²⁰ (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 but only negligible changes (<0.04) elsewhere. Again, cyclic voltammetry showed closely-spaced reversible oxidation waves ($E^1_{1/2} = -0.02$ V, $E^2_{1/2} = 0.11$ V) and chemical oxidation using two equivalents of $[\text{FcH}][\text{PF}_6]$ 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 DFT comparison of NBO charge distributions in models¹⁴ for **5** and **6** confirms an iron based oxidation ($\delta_{\text{Q}_{\text{Fe}(5 \rightarrow 6)}} = +0.36$) that causes significant changes in charge at the linker atoms ($\delta_{\text{Q}_{\text{Fe-C}}} = -0.13$; $\delta_{\text{Q}_{\text{P-C}}} = +0.21$) but significantly smaller effects at phosphorus and at palladium ($\delta_{\text{Q}_{\text{P, Pd}}} < 0.02$).

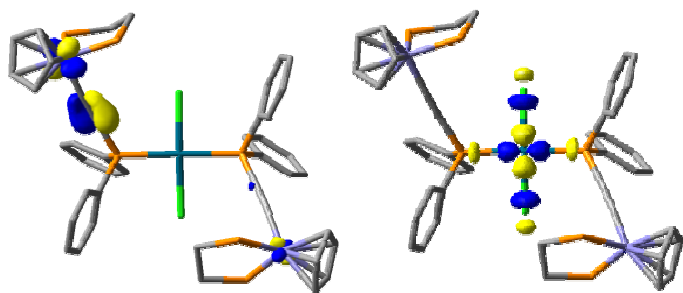
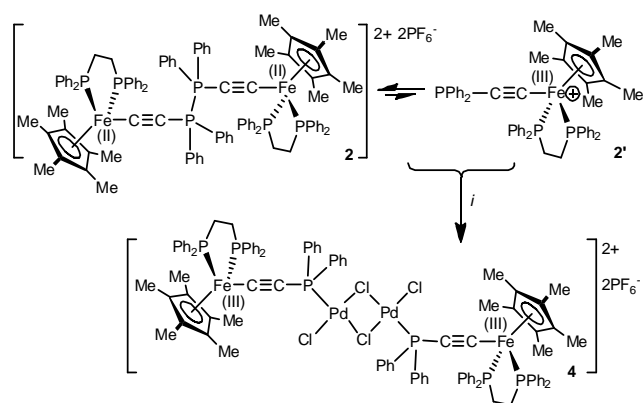


Fig 3: The B3PW91 calculated HOMO (left) and LUMO (right) for $[\text{PdCl}_2\text{L}_2]$, ($\text{L} = \text{FeCp}\{\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2\}\text{C}_2\text{PPh}_2$), a model for **5**. Calculated HOMO- LUMO gap: 3.05eV.

The individual redox steps that occur within the bound couples **3,4** and **5,6** appear to be well-behaved, but the chemical reversibility of the system as a whole clearly also rests upon the integrity of the dissociated ligands. 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 **2**¹⁰ (Scheme 3); this raises the undesirable possibility of the transient dissociation of **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 $[\text{PdCl}_2]$. Experiments 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 2eq of Pd) or **6** (with 1eq 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).



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 , 1h, 20 °C, >98%.

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 $[\text{Pd(II)}-(\mathbf{1}^+)_2] \leftrightarrow [\text{Pd(IV)}^{2+}-(\mathbf{1})_2]$ 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.

Notes and references

† Electronic Supplementary Information (ESI) available: Full experimental, spectroscopic and crystallographic data. See DOI: 10.1039/c4dt00455h.

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- ²¹ See supplementary. Note that the Cp* proton shifts in **4** : -8.5 and **6** : -8.7 ppm are both typical of [Fe^{III}(dppe)(C₅Me₅)]⁺- groups.¹³