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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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The redox-active metallaphosphine [Fe(dppe)(η5-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 environments means that phosphines are exceptionally widely used in many metal-catalysed processes, and their versatility has driven recent research into areas as varied as self-assembling phosphines for enantioselection, supramolecular phosphines allowing unprecedented catalytic selectivities, and hybrid chemical/biological phosphine-containing systems. However, there has been comparatively little recent interest in the class of redox-active phosphines, which should constitute an unusual class of “non-innocent” ligands and have been invoked inter alia for the switching of catalytic processes. 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). 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: [PdCl₂(1,5-cod)] (1.0 eq.), CH₂Cl₂, 15h, 97%; ii: [FcH][PF₆], CH₂Cl₂, 1h, > 98%; iii: [PdCl₂(1,5-cod)] (0.5 eq.), CH₂Cl₂, 15h, 96%; iv: [FcH][PF₆], CH₂Cl₂, 1h, > 98%; v: Compound 2 (1.0 eq.), CD₂Cl₂, 15mn, > 95%.

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 shows a classical trans-phosphine configuration about a butterfly-configured Pd₂Cl₄ core (Fig 1, in purple). 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 and the alkynyl νC≡C stretch falls from 1964 to 1930 cm⁻¹, all of which imply an increased contribution from an iron-vinylidene resonance hybrid.

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 ΔEp = 85 mV in CH₂Cl₂ vs SCE), which lie within a well-precedented window for the organoiron endgroup; bulk chemical oxidation using [FcH][PF₆] 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%). 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, 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 determination 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.

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 [PdCl₂L₂] complexes 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 from a model for 5 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 (E¹/²₁/₂ = -0.02 V, E²₁/₂ = 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 and an Evans determination showing a value of 2.42 ±0.1 BM (298 K) that is again classical for two unpaired electrons, imply a bis-Fe(III) complex showing little spin-spin coupling across the palladium centre. A DFT comparison of NBO charge distributions in models for 5 and 6 confirms an iron based oxidation (δQ_Fe(5→6) = +0.36) that causes significant changes in charge at the linker atoms (δQ_P(Fe-C) = -0.13; δQ_P(C-P) = +0.21) but significantly smaller effects at phosphorus and at palladium (δQ_P(Pd) < 0.02).
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 [PdCl_2]. Experiments conducted upon isolated 1,1’-(biphosphine)dication 2 and [PdCl_2(1,5-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 [PdCl_2(1,5-cod)] to generate the dicationic dimer 4. Reagents and conditions: (i) [PdCl_2(1,5-cod)], 2 eq., CH_2Cl_2, 1h, 20 °C, >98%.

To conclude, metallaphosphines bearing [Fe(κ^2-dppe)(η^5-C_5Me_3)] 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 [Pd(II)-(1')_2] ⇔ [Pd(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.

Notes and references

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

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11 The Pd₂Cl₄ core in 3 shows a fold angle of 35.3°. The butterfly configuration is well-precedented, eg: a) P. Stepnicka, I. Cisarova, and R. Gyepes, Eur. J. Inorg. Chem. 2006, 926, as is the cisoid arrangement of the metallaphosphine Cp* groups eg: b) L. I. Goryunov, J. Grobe, D. Le Van, V. D. Shteingarts, R. Mews, E. Lork and E.-U.


15 The geometric response of arylphosphines to a mono-electronic oxidation of their coordinated metal is well known: a) B. J. Dunne, R. B. Morris and A. G. Orpen, Dalton Trans, 1991, 653; the (marginally statistically valid) shortening of the P-Ph mean lengths (1.838 in 3, 1.832 in 4) that is expected to accompany oxidation of the adjacent metal centre is seen at dppe but not at C$_2$PPh$_2$: b) A. G. Orpen, N. G. Connelly, Organometallics, 1990, 9, 1206.


18 Taking a statistical analysis wherein all the magnetic states are equally populated, an uncoupled biradical should exhibit 75% of the magnetisation that corresponds to its triplet state (3.04 BM here with a g factor of 2.15), leading to an expected value of 2.3 BM.


20 In the models, H$_2$PCH$_2$CH$_2$PH$_2$ ligands replace dppe, and Cp replaces Cp*. B3PW91 with SDD on Fe, Pd and Cl; SDD + polarisation on P; 6-31G** for C and H. See supplementary for full details.

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)(C$_5$Me$_3$)]$^+$- groups.