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 \([\text{Fe(dppe)}(\eta^2-C_5\text{Me}_5)(\text{C} \equiv \text{C} \text{–} \text{PPh}_2)]\) reacts with \([\text{Pd(1,5-cod)Cl}_2]\) 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 \((\text{Fe(II)} \rightarrow \text{Fe(III)+})\) 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” ligands7,8 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 \([\text{PdCl}_2(1,5\text{-cod})]\) gives a near-quantitative isolated yield of a blue, air-stable dimeric complex \([\text{Pd}_2\text{Cl}_4(1)_2]\) 3 that shows a classical trans-phosphine configuration about a butterfly-configured PdCl core (Fig. 1, in purple).11 The metalloligand undergoes moderate structural changes upon coordination, with the most significant differences being associated with the alkynyl 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 νC≡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 ΔEₓ = 85 mV in CH₂Cl₂ vs. SCE), which lie within a well-precedented window for the organoiron endgroup;14 bulk chemical oxidation using \([\text{FcH}^+][\text{PF}_6^-]\) 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(1+)] components and an Evans determination 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.

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 (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 to PdCl2, but only negligible changes (−0.04) elsewhere. Again, cyclic voltammetry showed closely-spaced reversible oxidation waves (E1/2 = −0.02 V, E2/1 = 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 further DFT comparison of NBO charge distributions in models for 5 and 6 confirms an iron based oxidation (δQFe(5→6) = +0.36) that causes significant changes in charge at the linker atoms (δQ(P–C) = −0.13; δQ(P–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 therefore appear to be well-behaved, but
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 2′

\[ \text{Fe}^{(\text{II})} \]

Scheme 3 Reaction of 2 with [PdCl₂(1,5-cod)] to generate the dicaticonic dimer 4. Reagents and conditions: (i) [PdCl₂(1,5-cod)], 2 eq., CH₂Cl₂, 1 h, 20 °C, >98%.

To conclude, metallaphosphines bearing [Fe(κ²-dppe)-[η⁵-C₅Me₅]] 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 PdCl₂ centres. The [Pd(u)-[1⁺]₃] ↔ [Pd(IV)₂⁺-[1]₃] 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.

We thank CNRS and the French ANR (to AT, under contract BLAN 719) for support; S. L. thanks MNERT and ENS (Cachan) for a scholarship.

Notes and references


15 The geometric response of aryolphosphines to a monoelectronic oxidation of their coordinated metal is well known: (a) B. J. Dunne, R. B. Morris and A. G. Orpen, J. Chem. Soc., 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 and N. G. Connelly, Organometallics, 1990, 9, 1206.


18 Assuming 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 ESI† for full details.

21 See ESI†. Note that the Cp* proton shifts in 4: ~8.5 and 6: ~8.7 ppm are both typical of [Fe$^{II}$](dppe)(C$_5$Me$_5$)]$^+$-groups$^{13}$. 
