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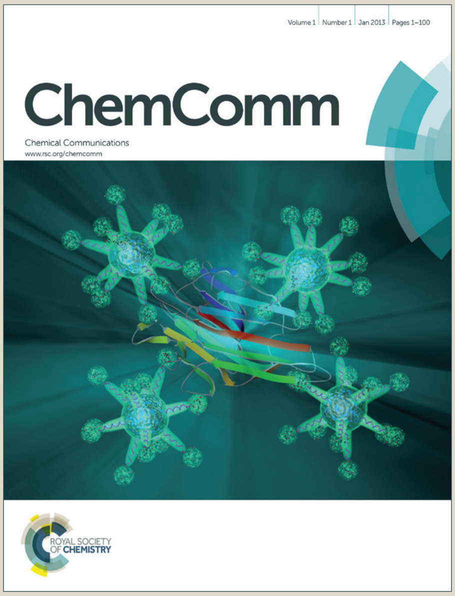

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Easy and Quantitative Access to Fe(II) and Fe(III) Diarylalkynylphosphine Oxides Featuring [Fe(dppe)Cp*] Endgroups: Terminal P=O Functionality Blocks the Dimerisation of the Fe(III) Derivatives

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Dedicated to S. Sinbandhit on the occasion of his retirement.

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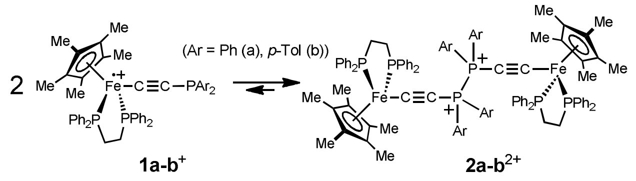
A series of paramagnetic diarylalkynylphosphine oxides 3a-c[PF$_6$] featuring an open-shell [Fe(κ^2-dppe)(η^5-C$_5$Me$_5$)]$^+$ endgroup were obtained by oxidation of their neutral Fe(II) parents 3a-c, themselves obtained in a simple and nearly quantitative fashion from the corresponding Fe(II) metallophosphines 1a-c. The new organometallic radicals were characterised by NMR and ESR and were shown to be perfectly stable in solution, in contrast to species such as 1a-b[PF$_6$] which readily dimerise.

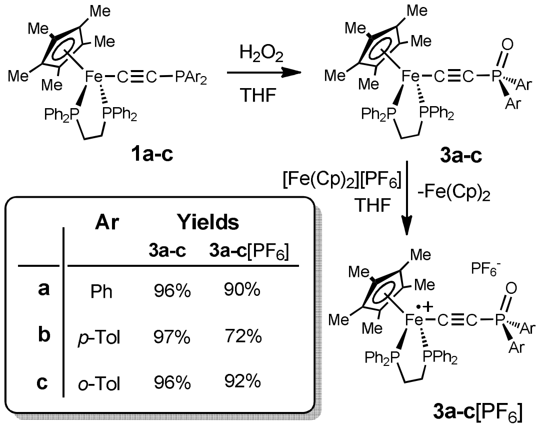
New functional phosphines have always attracted attention because of their outstanding performance in selected metal-catalysed processes,[1] but research in phosphine chemistry has recently extended into many new and non-classical areas, for instance supramolecular phosphines.[2-7] Redox-active metallophosphines,[8, 9] also constitute a subclass that is of current interest because they present appealing potential for switching various kinds of molecular-based processes,[10] including catalysis.[11, 12] In studies to develop metallaphosphines that show relatively emphatic switching, we have shown that oxidising the iron(II) centre in metallophosphines **1a-b** (Ar = Ph and *p*-Tol, resp.) to transiently generate **1a-b**[PF$_6$] switches the electronic properties of the phosphorus atom sufficiently to provoke instant dimerisation to the corresponding *bis*-{Fe(II) phosphonium} di-cations **2a-b**[PF$_6$]$_2$. These were fully characterised (Scheme 1).[13]



(1)

Scheme 1: Equilibrium between the Fe(III) monomer **1**[PF$_6$] and the corresponding bis-Fe(II) dimer **2**[PF$_6$]$_2$

Whilst this result is encouraging, it is probably more interesting for coordination chemists to have a full understanding of the paramagnetic monomers **1a-b**[PF$_6$] than the dimers **2a-b**[PF$_6$]$_2$, because such monomers will constitute the ligands that are generated when a suitable coordination compound of **1a-b** is reduced.[14] Preliminary cyclic voltammetry (CV) and UV-vis measurements indicate that these monomers are probably present in a strongly right-shifted equilibrium with the dimeric species **2a-b**[PF$_6$]$_2$ (Scheme 1) whose massive dominance in solution complicates monomer identification and characterisation. Some electronic signatures that have been tentatively attributed to the monomers have been obtained by spectroscopic studies from very dilute solutions of **2a-b**[PF$_6$]$_2$ (conditions under which the equilibrium (1) is displaced to the left), but an unequivocal confirmation of their nature and properties has proved elusive in the absence of an adequate frame of reference.[13] We therefore present an enlarged study here that aims to treat the properties of the related Fe(III) phosphine oxides (**3a-b**[PF$_6$]), a set of compounds whose saturated phosphorus valence shell is designed to allow the preparation of dimerisation-inert paramagnetic monomer oxides (**3a-b**; Scheme 2).



	Ar	Yields 3a-c	Yields 3a-c[PF$_6$]
a	Ph	96%	90%
b	*p*-Tol	97%	72%
c	*o*-Tol	96%	92%

Scheme 2: Synthesis and one-electron oxidation of **3a-c** to give **3a-c**[PF$_6$].

Despite their low metal oxidation potentials (close to -0.15 V *vs.* SCE),[13] metallaphosphines **1a-c** react cleanly in THF solution with an excess of hydrogen peroxide to provide nearly quantitative yields of the corresponding metallaphosphine oxides in the Fe(II) oxidation state.[15] The absence of any Fe(III) species formed by competitive oxidation of the electron-rich [Fe(κ^2-dppe)(η^5-C$_5$Me$_5$)] centre is noteworthy, given that H$_2$O$_2$ is usually considered to be a powerful oxidant.[16]

The new compounds were fully characterized by MS, CV and normal spectroscopic methods (Table 1). Crystals were obtained for **3a-c** and the single crystal structure was determined for **3a** by X-rays (Figure 1).[15] The presence of the oxide is indicated by the characteristic downfield shift of the terminal phosphorus ^{31}P NMR signal (*ca.* 12 ppm for **3a-b** and *ca.* 28 ppm for **3c** relative to the corresponding free phosphines) and by the appearance of a new absorption corresponding to the ν_{PO} mode (near to 1175 cm^{-1}) in the IR.[17-19] CV of **3a-b** reveals that the Fe$^{II/III}$ oxidation potential lies *ca.* 0.3 V to more positive values than **1a-b**, in line with the enhanced electron affinity of the terminal γ-phosphorus atom that accompanies formation of the PO bond.

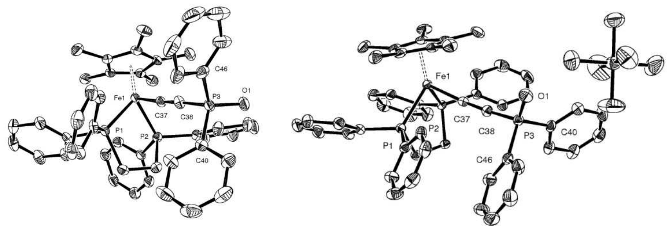


Fig 1. Above: X-ray- structure of the Fe(II) complex **3a**, with hydrogen atoms and an H_2O solvate omitted for clarity. Below: X-ray structure of the Fe(III) parent **3a**[PF_6]. Hydrogen atoms have been omitted for clarity.

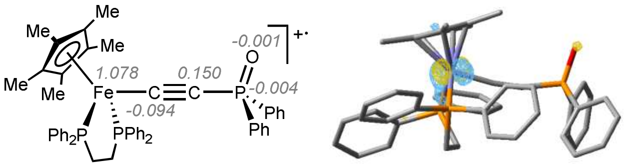
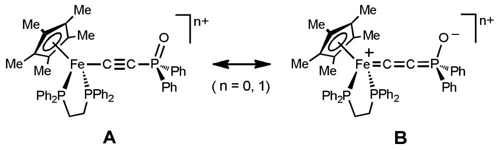


Fig 2. The B3LYP calculated natural spin distribution (a) and SOMO (b) for **3a**[PF_6].

The phosphine oxides **3a-c** were further oxidised at the metal centre by ferricinium hexafluorophosphate to give the corresponding Fe(III) complexes **3a-c**[PF_6]. Unlike the free phosphines **1a-b**[PF_6], the oxides **3a-c**[PF_6] are quite stable in solution and do not evolve further. Again, they were isolated and characterised fully (Table 1) with the structure of **3a**[PF_6] being confirmed by X-ray diffraction (Fig. 1).[15]



Scheme 3: Valence bond representation of **3a**.

The pronounced rhombic symmetry of the *g* tensor (Δ*g* ≥ 0.6) that is observed by ESR for the paramagnetic oxide species **3ac**[PF_6] (Table 1) shows that they are best described as metal-centred organometallic radicals,[20] and this is substantiated by DFT calculations (B3LYP level)[15] which reveal that **3a-c**[PF_6] are low spin (S = ½) Fe(III) complexes.[21] The majority of the spin density is calculated to reside on the metal centre but there is also a significant coefficient at the β-carbon atom (Figure 2). The DFT data predict a relatively small and negative spin density for the oxidised phosphorus centre, which is in accord with the observation of highly downfield shifted ^{31}P NMR resonances at *ca* -800 ppm, and also indicate that less than 1% of the spin density is delocalised onto the aromatic rings of the terminal phosphine oxide. ^{1}H NMR studies, which probed experimental spin densities in **3a-c**[PF_6] further, confirm this. As expected for low-spin Fe(III) metal-based radicals, the paramagnetic ^{1}H NMR shifts of these compounds obey a Curie law in the 300-180K temperature range,[22] and no evidence for nonsymmetrical rotamers was found at low temperatures.[15, 23] A full attribution of all the paramagnetic signals for **3a**[PF_6] could be made through a combination of polarisation transfer experiments and by tracing how the averaged ^{1}H chemical shifts vary under the fast electron exchange conditions that operate when the Fe(II) complex is doped with increasing quantities of the corresponding Fe(III) compound;[15, 22] the methyl-labelled compounds **3b-c**[PF_6] definitively confirmed the assignments of the protons within the aryl rings of the terminal phosphorus atom. The NMR data were in good agreement with the DFT results: the calculations predict a negligible spin density (≤ 0.5%) on the carbon atoms bearing these protons, and this is supported by the very weak (contact) paramagnetic shifts (< 1 ppm) that are observed for the protons of the terminal PAr_2 group by ^{1}H NMR.[24]

The oxidation of the metal to generate **3a**[PF_6] provokes a shift of the $\nu_{C\equiv C}$ stretching mode to higher wavenumbers (Table 1) and an increase in the ν_{PO} stretch. These indicate that the mesomeric form B makes a larger contribution to the valence bond (VB) description of the neutral complex **3a** than it does for **3a**[PF_6], which is indicative of a less electron releasing metal fragment in the Fe(III) form (Scheme 3). The strengthening of the CC and PO bonds upon oxidation to the Fe(III) complex that is implicit in these IR data is reproduced in the DFT calculations, which show that the oxidation reaction induces only small structural changes. Comparison of the X-ray structures of **3a** and **3a**[PF_6] show minor changes in these bond lengths that fall short of significance at the 3σ confidence level, but which are nonetheless fully consistent with this analysis. Thus, slightly shorter triple (1.226(3) *vs.* 1.230(3) Å) and P-O (1.4873(18) *vs.* 1.5008(15) Å) bonds are found in the Fe(III) derivative. The significant lengthening (0.084 Å) of the averaged P-Fe bonds upon oxidation is, however, diagnostic of the redox change at the metal centre.[25]

Table 1. Specific Spectroscopic Signatures of **3a-c** and **3a-c**[PF_6].[a]

Cpnd	CV[b] [V]	$\nu_{C\equiv C}$ [c]	$\nu_{P=O}$ [c] [cm^{-1}]	δ_{dppe} [d]	$\delta_{P=O}$ [ppm]	λ_{max}(Vis) [e] [nm(10^{-3} ε in $M^{-1}cm^{-1}$)] [c]	λ_{max}(NIR) [e]	g_1	g_2	g_3	Δ*g* [f]
3a	0.14	1962	1175	99.0	-8.2 [d]	264 (sh, 21.4), 478 (sh, 0.6)	/	/	/	/	/
3a[PF_6]		1991	1193	*nd*	-797 [e]	409 (3.0), 517(2.2), 602 (sh, 0.3)	1980(0.03)	1.957	2.019	2.574	0.617
3b	0.12	1952	1177	99.6	-7.6 [d]	262 (sh, 20.7), 494 (sh, 0.3)	/	/	/	/	/
3b[PF_6]		1992	1177	*nd*	-790 [e]	404 (2.2), 520 (1.7), 620 (sh, 0.4)	1995(0.02)	1.960	2.022	2.569	0.609
3c	0.11	1968	1174	99.4	-5.2 [d]	264 (sh, 20.2), 488 (sh, 0.5)	/	/	/	/	/
3c[PF_6]		1976	1174	*nd*	-795 [e]	409 (3.0), 519 (2.5), 632 (sh, 0.3)	1990(0.03)	1.960	2.020	2.579	0.619

[a] *nd*: Not detected. [b] CV performed in CH_2Cl_2 (0.1 M [*n*-Bu_4N][PF_6]) and E° values given *vs.* SCE [c] IR Measurements performed in KBr pellets. [d] Measurements performed in C_6D_6. [e] Measurements performed in CH_2Cl_2. [f] ESR measurements performed at 77 K in CH_2Cl_2/1,2-$C_2H_4Cl_2$ glasses.

In the context of generating redox-switchable ligands, a major facet of this work lies in the comparison of the new paramagnetic Fe(III) derivatives **3a-c**[PF_6] with the elusive **1a-b**[PF_6] cations.[13] The natural spin density distributions computed for **3a**[PF_6] and **1a**[PF_6] are almost identical, with the most significant differences being a slight increase on iron (+4%) along with a small decrease on the β-carbon atom (-9%) for **3a**[PF_6]. Except for the absence of a weak NIR d-d band that is present at around 1990 nm in **3a-c**[PF_6],[25] the high dilution UV-vis absorption spectrum of the proposed metallaphosphine **1a**[PF_6] is entirely coherent with the data obtained for **3a-c**[PF_6] (Figure 3), thus substantiating the formulation of **1a**[PF_6] as the Fe(III) alkynylphosphine derivative.[13, 14]

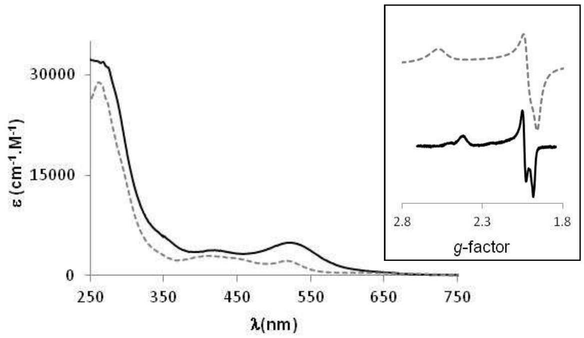


Fig 3. Overlay of the UV-vis spectra of 10^{-5} M solutions of **2a**[PF_6]$_2$ (plain line) and **3a**[PF_6] (dotted line) in CH_2Cl_2 at 298 K. Inset: ESR spectra of frozen solutions of **2a**[PF_6]$_2$ (plain line) and **3a**[PF_6] (dotted line) in CH_2Cl_2/1,2-$C_2H_4Cl_2$ solvent glasses at 77K.

To definitively establish the presence of a metal-centred Fe(III) radical corresponding to **1a**[PF_6] in dilute solutions of **2a**[PF_6]$_2$, we recorded the ESR spectrum of a low concentration solution of **2a**[PF_6]$_2$ trapped in a solvent glass. Gratifyingly, we observed a rhombic tensor (Fig. 3, inset) with g_1 = 1.983, g_2 = 2.038 and g_3 = 2.425 that resembles **3a**[PF_6] except for a slightly lower anisotropy (Δg = 0.442).[20, 25] This more isotropic formulation is predicted by DFT (see ESI) and is to be expected for a less metal-centred radical.[25, 26]

In conclusion, we report the characterisation of three [Fe(κ^2-dppe)(η^5-C_5Me_5)]$^+$-based Fe(III) alkynyl-phosphine oxide derivatives. Sequestering the phosphorus lone pair by a P-O bond clearly stabilises these organometallic species with respect to P-P dimerisation processes and allows their clean isolation. The compound **3a**[PF_6] constitutes a “stable” model for **1a**[PF_6] and provides overwhelming evidence for the formation of the latter in diluted solutions of **2a**[PF_6]$_2$, thereby clarifying the nature of the elusive Fe(III) monomeric species.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental, spectroscopic and selected crystallographic data. See DOI: 10.1039/b000000x/

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Graphic Content Entry

Preventing the Oxidatively-Induced Dimerization of Fe(III) Metalloalkynyl phosphines can be achieved by Sequestring the Phosphorus Lone Pair.