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Redox-Induced Reversible P–P Bond Formation to Generate an Organometallic $\sigma^4 \lambda^4$ -1,2-Biphosphane Dication**

Ayham Tohmé, Guillaume Grelaud, Gilles Argouarch, Thierry Roisnel, Stéphanie Labouille, Duncan Carmichael,* and Frédéric Paul*

Many well-established methods exist for fine-tuning the properties of phosphorus compounds, and these allow the creation of tailored stereoelectronic environments that exert exact and predefined control over systems for catalysis^[1] or molecular electronics.^[2] In principle, the capacity to change the properties of a phosphorus center actively during a process creates further important potential, such as on-off switching in catalysis,^[3] or profound gating of the properties of electronic materials.^[4] Studies of how phosphorus centers can be efficiently modulated using ferrocenes,^[5] cobaltocenes,^[6] TTF derivatives,^[7] or other redox-active groups have appeared; however, these redox-active groups are often spatially close to the phosphorus center, so the electronic outcome of the redox change can be conflated with significant steric effects. This is obviously undesirable if geometrical properties need to be maintained, so the possibility of modulating the properties of a phosphorus atom by a molecular wire^[8] is attractive.^[9] Herein we report a study that concerns metallophosphanes 1a,b (Scheme 1) having a [Fe- $(dppe)(\eta^5-C_5Me_5)$] redox center linked to a σ^3,λ^3 -phosphorus atom by an alkyne that functions as a short molecular wire.^[10] Within such a system, oxidation of the redox-active organoiron(II) center is expected to trigger significant changes at phosphorus because of the very efficient electronic communication that occurs across alkyne bridges.^[11]

The prototype molecular wire-based metallophosphanes **1a,b** were synthesized and characterized.^[12] The crystal structure analysis of **1a** (Figure 1a) reveals a nearly linear Fe-C-C-P arrangement (Fe-C37-C38 178.2(2)°, C37-C38-P3 167.7(2)°), a short C=C distance (1.892(2) Å), and a Ph-P-Ph angle of 98.31(8)°, all of which are well reproduced by DFT calculations at the B3PW91 level (see the Supporting



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Scheme 1. Compounds $1-4[PF_{6}]_{2}$ showing their dominant valence-bond isomers as calculated by B3PW91 DFT calculations.



Figure 1. Crystal structures for the neutral complex 1 a (a) and oxidized dication $4a[PF_{6}]_2$ (b), for which one PF_{6}^- counterion is omitted. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

Information). Comparisons of the calculated structure for **1a** with those for the model organometallic complex **2** and the simple alkynylphosphane $3^{[13]}$ confirm that the complex is uncontroversially characterized by the simple valence-bond formulation given for **1a**,**b**. It therefore shows the characteristics of a classical phosphane and has the metal center in the Fe^{II} state.

Redox reactivity of **1a**,**b** was investigated. [Fe(dppe)(η^{5} -C₅Me₅)(C=C)] endgroups normally undergo chemically reversible oxidations at half-wave potentials between 0 to -0.3 V (in CH₂Cl₂/SCE) to give the corresponding Fe^{III} complexes,^[10] and the cyclovoltammetric analysis of **1a**,**b** under these conditions pointed to the rapid and clean formation of a new species upon oxidation at about -0.1 V (see the Supporting Information).^[14] The corresponding bulk chemical oxidation of **1a**,**b** using [FcH][PF₆] instantaneously gave purple solutions, from which diamagnetic purple dinuclear dications **4a**,**b**[PF₆]₂ could be isolated in yields of about 80% (Scheme 2).



Scheme 2. Interconversion reactions of 1 and $4[PF_6]_2$ complexes. Reagents and conditions: i) [FcH][PF_6], (2 equiv), CH₂Cl₂, 20 °C, 1 h; ii) [CoCp₂] (3 equiv), CH₂Cl₂, 20 °C, 1 h.

The dication $4a[PF_6]_2$ features singlet ³¹P NMR peaks at 95 ppm (dppe) and $-43 \; \text{ppm}$ (PPh_2), a PF_6^{-} multiplet at -144 ppm, and exhibits an apparent diamagnetic proton NMR spectrum showing only pentamethylcyclopentadienyl, aromatic, and methylene components; it also gives an IR stretch at about 1850 cm^{-1.[15]} Its X-ray diffraction structure is given in Figure 1b. The two halves of the dimer are crystallographically identical and almost perfectly staggered about the P-P bond. Dicationic hexacoordinated biphosphanes^[16] are normally expected to show stronger but slightly longer bonds than the corresponding biphosphanes^[16a] (compare P_2Me_4 2.212(1) Å^[17] and $[P_2Me_6]^{2+}$ 2.198(2) Å); in **4a**[PF₆]₂, the very long P-P distance (2.264(4) Å) is significantly greater than in P_2Ph_4 (2.217(1 Å)^[18] and lies close to the value for P_2Mes_4 (2.260(1) Å).^[19] The anticipated lengthening^[16d] of the P-C bonds upon passing from P_2Ph_4 to $4a[PF_6]_2$ is not found, and a small shortening which is on the limit of statistical significance is observed instead (P-C(Ar) mean: 1a 1.845, $4a[PF_6]_2$ 1.825, P_2Ph_4 1.851 Å). Within the alkynyl component, the shortening of the bond to phosphorus upon passing from **1a** to $4a[PF_6]_2$ is pronounced (0.047 Å) but the associated C=C bond lengthening is small, so the linker largely retains the structural characteristics of an alkyne. Simple $[R_3P^+C=C]$ ligands are considered to be strong σ donors and weak π -acceptors,^[20] and the relative charge densities obtained here from B3PW91 DFT studies point clearly to dominant valence-bond structure for $4a^{2+}$ that has Fe^{II} endgroups and a dicationic biphosphane functionality (Figure 2; NPA charges computed for IVa^{2+} : Q_{Fe} –0.14, Q_P + 1.45; for Ia: Q_{Fe} –0.13, Q_P + 0.96).^[21]



Figure 2. B3PW91 calculated Kohn–Sham delocalized orbitals for IVa²⁺. LUMO (left) and HOMO (right).

Cyclic voltammetry experiments performed on isolated $4a,b[PF_6]_2$ are consistent with those performed on 1a,b. However, even when the scan is halted before reaching the expected reduction potential (close to -1 V), the reductive cycle for $4a[PF_6]_2$ gives a persistent peak. This peak is attributed to the reduction of $\mathbf{1a}^+$ and implies that a rapid equilibration of $4a^{2+}$ and $1a^{+}$ occurs in solution. This assignment of a monomer-dimer equilibrium is corroborated by UV/Vis spectra; these show the development of characteristic LMCT transitions that are classically associated with mononuclear $[Fe^{III}(dppe)(\eta^5-C_5Me_5)(C=C)]^+$ species when CH_2Cl_2 solutions of $4a^{2+}$ are diluted to $10^{-5}{\mbox{\sc m}}$ at $20\,{\mbox{\sc oc}}.^{[22]}$ Furthermore, simple exchange experiments showed that redistribution occurs when the two complexes $4a[PF_6]_2$ and $4b[PF_6]_2$ are mixed at room temperature, whereupon a near-statistical equilibrium mixture of the symmetrical starting materials and a new compound assigned as the dissymmetrically substituted dimer $4c[PF_6]_2$ is established over two hours (Scheme 3).^[23]



Scheme 3. Exchange between $4a[PF_{6]_2}$, $4b[PF_{6]_2}$, and $4c[PF_{6]_2}$. Equilibrium established after 2 h at room temperature in dichloromethane.

Calculations to support the formulation of the putative cation $1a^+$ were made upon a simplified model Ia^+ that has $H_2PCH_2CH_2PH_2$ and Cp ligands. The calculations give little spin density at phosphorus for Ia^+ (computed Mulliken spin densities: Fe +1.27, C37 -0.14, C38 +0.16, P -0.01), and they also show that the positive charge increases significantly at iron (by 0.43) but not at phosphorus (-0.01) upon moving from Ia to Ia⁺. The calculations therefore imply that the initial oxidation for 1a is largely metal-centered, and this agrees well with the experimental first electrochemical oxidation poten-

tial for **1a**,**b**, which lies within the region that is classically associated with the Fe^{II} to Fe^{III} oxidation step for [Fe(dppe)- $(\eta^5$ -C₅Me₅)(C=C)] endgroups.^[24]

Finally, a series of experiments conducted at room temperature in CH_2Cl_2 confirmed that treatment of $4a[PF_6]_2$ with cobaltocene leads cleanly and near-quantitatively to the regeneration of the monomeric complex 1a within an hour (Scheme 2).

In conclusion, we report a chemically robust redox system involving a prototypical molecular-wire-based phosphane and demonstrate that initial oxidation of the neutral precursors 1a,b occurs within an electrochemically clement window at the iron center; the products are the complexes $4a,b[PF_6]_2$, which are obtained as isolable dimers.^[25] These compounds show a weak P-P bond and a capacity for redistribution in solution. This redox-induced dimerization established for 1a,b provides support for the involvement of diphosphane intermediates that is often proposed to occur in the complex solution chemistry that follows the oxidation of more classical metallocene-containing phosphanes.^[26] Compound 1a can be regenerated from $4a[PF_6]_2$ by reduction, so that a powerful change in the properties of the phosphorus atom can be effected reversibly through redox chemistry. This process is unprecedented in that none of the few known oxidatively induced dimerization reactions of metal acetylide complexes have yet been found to be reversible.^[27] Work is in progress to investigate further aspects of the chemistry of $4a_{,b}[PF_{6}]_{2}$.

Experimental Section

All of the reactions and workup procedures were carried out under argon using standard Schlenk techniques with freshly distilled solvents.

Synthesis of **1a,b**: $[Fe(Cp^*)(dppe)Cl]^{[28]}$ (625 mg, 1 mmol), HC= C-PAr₂ (Ar = Ph, 4-Tol; 1.2 equiv),^[29] and KPF₆ (184 mg, 1 mmol) were dissolved in THF (15 mL) and MeOH (15 mL) and stirred overnight. After removal of the solvents, the residue was extracted with CH₂Cl₂, concentrated, and precipitated by addition of *n*-pentane. Filtration and drying in vacuo gave the corresponding vinylidene as an orange solid. The vinylidene complex (0.9 mmol) was dissolved in THF (20 mL), and DBU (0.2 mL, 1.3 mmol) was added dropwise. After 2 h of stirring, the solvent was removed and the residue was taken up with toluene and purified on pacified silica gel. After removal of the toluene, the red-orange solid was washed with *n*pentane and dried in vacuo.

1a: Yield 70%. X-ray quality crystals were grown by slow diffusion of methanol into a dichloromethane solution of the complex. The complex **1a** was identified by comparison with published data.^[12] **1b**: Yield 95%. IR (KBr): $\tilde{\nu} = 1964 \text{ cm}^{-1}$ (s, $C \equiv C$). ³¹P NMR (121 MHz, C₆D₆): $\delta = 100.0$ (s, 2P, dppe), -20.1 ppm (s, 1P, *P*(*p*-Tol)₂). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.96$ (t, 4H, *J*_{HH} = 8 Hz, *H*_{Ar}), 7.63 (t, 4H, *J*_{HH} = 8 Hz, *H*_{Ar}), 7.21–6.93 (m, 20H, *H*_{Ar}), 2.56 (m, 2H, CH₂), 2.08 (s, 6H, CH₃), 1.78 (m, 2H, CH₂), 1.47 ppm (s, 15H, C₅(CH₃)₅).

Synthesis of $4a,b[PF_6]_2$: The complex 1a,b (0.25 mmol) and [FcH][PF₆] (0.23 mmol) were dissolved in CH₂Cl₂ (20 mL) and stirred for 1 h. After concentration of the solution to ca. 5 mL, the product was precipitated by addition of *n*-pentane, filtrated, and dried in vacuo to afford a purple solid.

4a²⁺: X-ray quality crystals were grown by slow diffusion of *n*pentane into a dichloromethane solution of the complex. Yield 89%. IR (KBr): $\tilde{\nu} = 1852 \text{ cm}^{-1}$ (vs, C=C-P). ³¹P NMR (121 MHz, CD₂Cl₂): $\delta = 95.0$ (s, 4P, dppe), -42.8 (s, 2P, P-P), -144.4 ppm (sept, $J_{PF} =$ 710 Hz, *P*F₆). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 7.74-6.90$ (m, 60 H, *H*_{Ar}), 2.38 (m, 8 H, C*H*₂), 1.25 ppm (s, 30 H, C₅(C*H*₃)₅). **4b**²⁺: Yield 94%. IR (KBr): $\tilde{\nu} = 1849$ cm⁻¹ (vs, C=C–P). ³¹P NMR (121 MHz, CDCl₃): $\delta = 95.2$ (s, 4P, dppe), -41.4 (s, 2P, P-P), -144.4 ppm (sept, 2P, *J*_{PF} = 710 Hz, *P*F₆). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 7.45-6.86$ (m, 56 H, *H*_{Ar}), 2.46 (s, 12 H, C*H*₃), 2.38 (m, 8 H, C*H*₂), 1.24 ppm (s, 30 H, C₅(C*H*₃)₅).

Reduction of $4a[PF_6]_2$: A solution of $4a[PF_6]_2$ (20 mg, 0.01 mmol) and triphenylphosphane used as internal standard (5 mg, 0.02 mmol) in CH₂Cl₂ was added under argon to cobaltocene (6 mg, 0.03 mmol) and stirred for 1 h. The reaction was monitored by NMR spectroscopy.

Reaction between $4a[PF_6]_2$ and $4b[PF_6]_2$: A solution of $4a[PF_6]_2$ (20 mg, 0.01 mmol) in dry CD_2Cl_2 (0.5 mL) was added under argon to a solution of $4b[PF_6]_2$ (20 mg, 0.01 mmol) in dry CD_2Cl_2 (0.5 mL), and the mixture was left to react for 2 h and checked by NMR spectroscopy.

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