Phosphorus Heterocycles

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From Cyclic Iminophosphoranes to π-Conjugated Materials[**]

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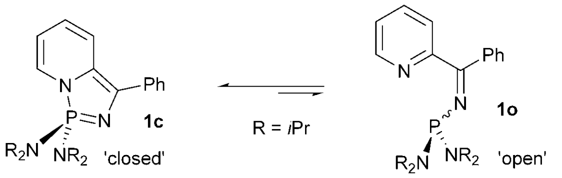
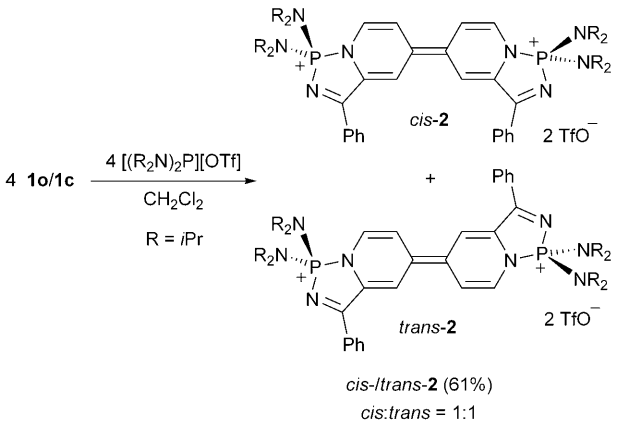
The "closed" benzannulated σ^4-λ^5-[1,3,2]diazaphosphole **1c** has been shown to exist in valance tautomeric equilibrium with its "open" form **1o** (Scheme 1).[1] As a result of the small energy difference between these two isomers, the air- and moisture-sensitive compound **1** exhibits reactivity that is not only commensurate with an iminophosphorane (e.g. cycloaddition at the P=N moiety and Lewis acid coordination at N with **1c**), but also with a P,N chelate ligand (e.g. metal coordination of **1o**), and with a 1,2-dihydropyridine (e.g. cyclobuta[*b*]pyridine formation from **1c**).



Scheme 1. Valence tautomeric equilibrium between the "open" pyridyl-*N*-phosphinoimine **1o** and the "closed" σ^4-λ^5-[1,3,2]diazaphosphole derivative **1c**.

With a view towards exploring further the unusual multifunctional character of **1**, it was of interest to probe its reactivity with an equally versatile substrate. In this regard, σ^2-λ^2-phosphenium ions, R_2P^+, were an attractive choice for study. These dicoordinate cations possess both a phosphorus-centered lone pair and a formally vacant 3p orbital, rendering them "ambiphilic" in terms of their reactivity, something that gives rise to an extensive Lewis acid and cycloaddition chemistry.[2–4]



Scheme 2. Synthesis of diphosphonium salts *cis*- and *trans*-**2**.

Treatment of the equilibrium mixture **1c**/**1o** with an equimolar quantity of the phosphenium salt $[(iPr_2N)_2P]$-[OTf][5] in CH_2Cl_2 affords a new compound **2** as the only phosphorus-containing product (Scheme 2); complete consumption of both starting materials is evident from ^{31}P NMR spectroscopic analysis of the reaction mixture. Following purification, compound **2** was isolated in good yield (61 %) as an air- and moisture-stable green solid, which was found to contain both *cis*- and *trans*-isomers in a 1:1 ratio by multinuclear NMR spectroscopy (δ $^{31}P = +51.9$ and $+51.4$ ppm).[6] No interconversion between the two isomers in solution was observed using selective ^{31}P NMR inversion experiments at 40 °C ([D$_2$]tetrachloroethane).

Recrystallization of *cis*-/*trans*-**2** from a CH_2Cl_2/hexane solution gave crystals of *trans*-**2**·2 CH_2Cl_2 suitable for an X-ray diffraction study.[7] The dicationic component has crystallographic C_i symmetry (Figure 1) and is comprised of a 1*H*,1′*H*-

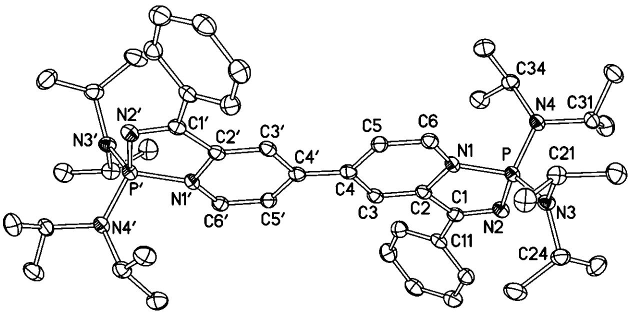


Figure 1. X-ray molecular structure of the dication of *trans*-**2** (primed atoms are generated by an inversion centre).[7] H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P–N(1) 1.687(2), P–N2 1.657(2), P–N3 1.619(2), P–N4 1.612(2), N1–C2 1.407(3), N2–C1 1.306(4), C1–C2 1.468(4), C2–C3 1.355(4), C3–C4 1.433(4), C4–C5 1.457(4), C5–C6 1.343(4), C4–C4′ 1.394(5), C6–N1 1.402(3), C1–C11 1.478(4); N1-P-N2 95.6(1), N1-C2-C1 108.1(2), C2-C1-N2 115.5(2), C1-N2-P 110.7(2).

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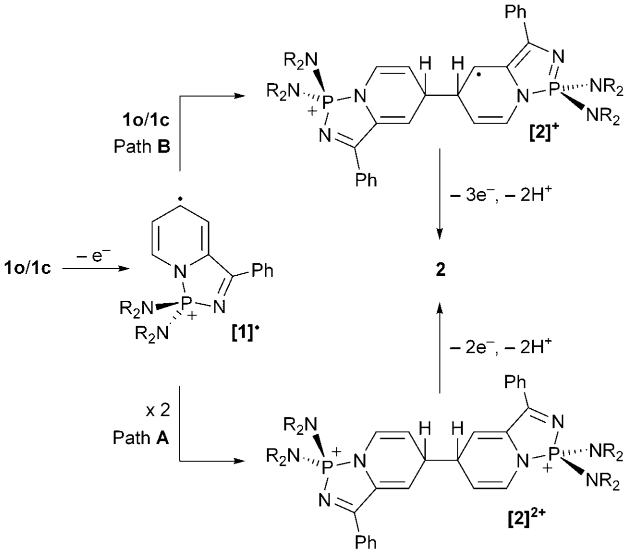
4,4′-bipyridylidene core bearing two benzannulated σ^4-λ^4-[1,3,2]diazaphosphole fragments at each terminus; each phosphorus atom has a distorted tetrahedral environment. Both the 4,4′-bipyridylidene unit and the diazaphosphole rings show substantially localized bonding patterns and are planar within ± 0.04 and ± 0.03 Å, respectively, with an angle of 6.5° between the two planes of the ring systems. The phenyl rings are inclined to the bipyridylidene core by 38°. The C(4)–C(4′) distance, 1.394(5) Å, is consistent with a pseudo-quinoidal structure and compares well with the central C–C distance of 1.381(3) Å reported for the two-electron reduced bis(trimethylsilyl)dihydro-4,4′-bipyridine, (cf. localized 4,4′-bipyridine, 1.486 Å).[8]

X-Ray analysis of a selection of individual crystals revealed each to be *trans*-**2**. However, the ^{31}P NMR spectrum (CD_2Cl_2) of this small sample of crystalline material consistently showed the presence of both *cis* and *trans* isomers in an approximately 1:1 ratio, with the exact proportions being sample-dependent. Since the two isomers of **2** do not interconvert in solution (see above), this suggests that *cis*-**2** is present in amorphous form alongside crystalline *trans*-**2**. Although repeated attempts were made to separate *cis-/trans*-**2** by fractional crystallization and by chromatography, these proved unsuccessful.[6]

The mechanism for the formation of diphosphonium salt **2** from reaction of [(iPr$_2$N)$_2$P][OTf] with **1o/1c** is not readily apparent. Despite extensive efforts no phosphorus-containing by-products could be detected in the reaction mixture, prior to purification, by ^{31}P NMR spectroscopy.[6] Most likely the unaccounted for material is lost in the form of intractable oligomeric products that are removed during the purification of **2**, something consistent with the observation of [iPr$_2$NH$_2$][OTf] formed by P–N bond cleavage (see below).[6]

Elucidation of the mechanistic pathway by which **2** is formed is further complicated by the ambiphilic nature of the phosphenium ion.[2] However, a hydride abstraction process can be ruled out since: 1) no (iPr$_2$N)$_2$PH[9] was detectable from the reaction of [(iPr$_2$N)$_2$P][OTf] with **1o/1c**, and 2) no reaction takes place on treating **1o/1c** with an equimolar quantity of the trityl salt [Ph$_3$C][B(C$_6$F$_5$)$_4$].[6] Thus, in order to reduce the complexity of the system, an alternative cationic Lewis acid/oxidant, namely a ferrocenium salt, was employed. Indeed, treatment of a CH_2Cl_2 solution of **1o/1c** with one equivalent of [Cp$_2$Fe][OTf][10] (Cp = cyclopentadienyl) resulted in the near-instantaneous formation of a blue-green solution from which *cis-/trans*-**2** (1:1) was isolated in 39% yield following purification.[6]

Together, these observations suggest that the formation of **2** from **1o/1c** involves a radical-based process, which may be regarded as a variant of the intermolecular Scholl reaction (i.e. a Friedel–Crafts aryl coupling).[11] Although the mechanism for this type of transformation is not well-established, the intermediacy of a radical cation has been implicated.[12–14] Indeed, such a process was invoked to account for the formation of *N,N*′-disilyldihydropyridines through silylation of pyridine in the presence of Pd/C.[15] Consequently, two reaction pathways for the formation of **2** are proposed here (Scheme 3). Both depend on the initial formation of the radical cation **[1]**$^{\bullet}$, which then undergoes either a two-radical coupling followed by double deprotonation (pathway **A**) or, reaction with a second equivalent of **1o/1c** generating **[2]**$^+$, which is subject to elimination of H$^+$ and oxidation to yield **2** (pathway **B**). Both pathways are supported by the observed formation of sub-stoichiometric quantities of [iPr$_2$NH$_2$][OTf] resulting from the generation of acid following reaction of **1o/1c** with either [(iPr$_2$N)$_2$P][OTf] or [Cp$_2$Fe][OTf].[6] Furthermore, both paths **A** and **B** involve singly-bonded biaryl species consistent with the formation of a 1:1 mixture of *cis-/trans*-**2**; this is supported by a DFT study (B3LYP/6-31G*), which revealed that *trans*-**2** is only 1.8 kJ mol^{-1} lower in energy than *cis*-**2**.[6]



Scheme 3. Proposed mechanisms for the formation of **2** from **1**.

From a structural standpoint, the dihydro-4,4′-bipyridine core of the dicationic component of **2** resembles that of the doubly-reduced *N,N*′-dimethyl-4,4′-bipyridinium dication, known commonly as “reduced viologen”, MV^0.[16] Initially developed as herbicides, the viologens constitute a well-known class of redox-active compound, which give rise to intensely colored, stable radical monocations.[16] The extensive electrochromic behavior reported for the viologens has led to their use in a range of applications including as electron relays, redox mediators in catalytic cycles, and molecular-scale devices.[17–19] Thus, it was of interest to further probe the electronic character of dication **2** and the extent of its similarity with MV^0.

A computational study using time-dependent density functional theory (TD-DFT) methods (B3LYP/6-31G*) gave an optimized structure for the dication of **2** that was in excellent agreement with that obtained by X-ray crystallography.[6,20] The computed absorption maxima ($\lambda_{max} = 761$ nm, $\varepsilon = 20\,000$ dm^3 mol^{-1} cm^{-1}) correspond well with those determined experimentally (see below), with the band at 761 nm being comprised largely of a transition from the HOMO to the LUMO (73%). As expected, the computed HOMO and LUMO for **2** extend across the whole of the dication and are consistent with a quinoidal-type structure, although only a small orbital component is located at the two formally

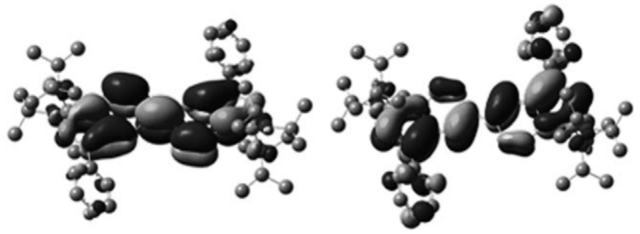


Figure 2. HOMO (left) and LUMO (right) for *trans*-**2** dication determined by DFT methods at the B3LYP/6-31G* level of theory.

cationic phosphorus centers as would be expected (Figure 2). For the HOMO–LUMO transition it is calculated that the electron density shifts from the central quinoidal core (P,N1,C6,C5,C4) to the imine moiety (C1,N2), which is consistent with previous reports of the reduction of iminopyridines.[21] The HOMO–LUMO gap of 1.7 eV for **2** is considerably smaller than those reported for other *N,N′*-R$_2$-dihydropyridines (e.g. R = Me, 3.0 eV;[22] R = Ph,[23] 2.7 eV; R = B(mesityl)$_2$, 2.6 eV[24]), consistent with the π-conjugation extending across the two imino groups as well as the bipyridylidene moiety. Overall, this DFT study highlights the remarkable similarity between the composition of the HOMO of **2** with the HOMO of the doubly-reduced *N,N′*-dimethyl-4,4′-bipyridinium dication (MV^0),[6,22] although the LUMOs of the two compounds differ as would be expected.

The UV/vis absorption spectra of dication **2** measured in a variety of solvents were found to be anion-independent, but solvatochromic, with a hypsochromic shift being displayed with increasing solvent dielectric constant (Table 1).[6] In all solvents two bands are observed in the visible region at ca. 400 and ca. 740 nm, with the latter agreeing well with that determined by TD-DFT.[6] Molar extinction coefficients of log ε ≈ 4.3 were determined in each of the different solvents.

Table 1: UV/vis spectroscopic data for **2** in various solvents.

Solvent	ε_r[a]	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε
THF	7.5	398	4.00	772	4.30
CH_2Cl_2	9.1	392	3.96	740	4.31
MeOH	32.6	380	3.96	720	4.33

[a] Dielectric constant data from ref. [25].

Since much of the importance of the viologens stems from their electrochemistry,[16,26] it was of interest to explore the redox properties of **2**. The cyclic voltammogram of **2** in CH_2Cl_2 solution (Figure 3) showed that it readily undergoes two reversible, one-electron reduction steps, with reduction occurring at −0.55 and −0.46 V.[6] An irreversible oxidation was observed at + 0.79 V, most likely as a result of decomposition.

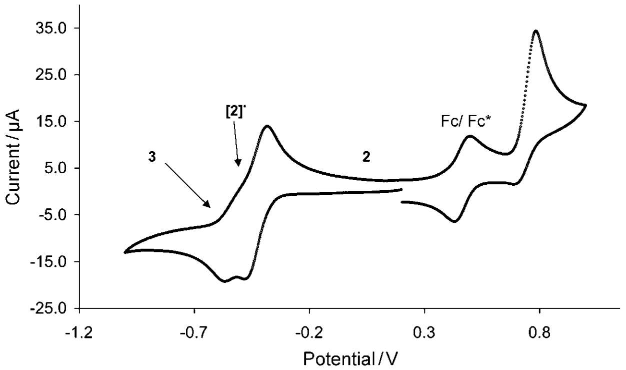


Figure 3. Cyclic voltammogram of *cis-/trans*-**2**, 10^{-4} M in CH_2Cl_2/10^{-1} M Bu_4NBF_4 at μ = 100 mV s^{-1} (versus ferrocene/ferrocenium, Fc/Fc$^+$).

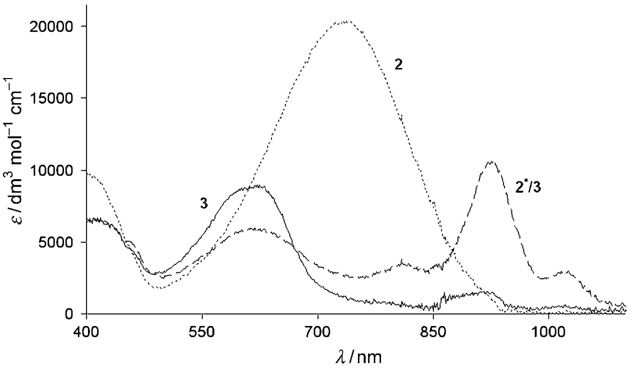
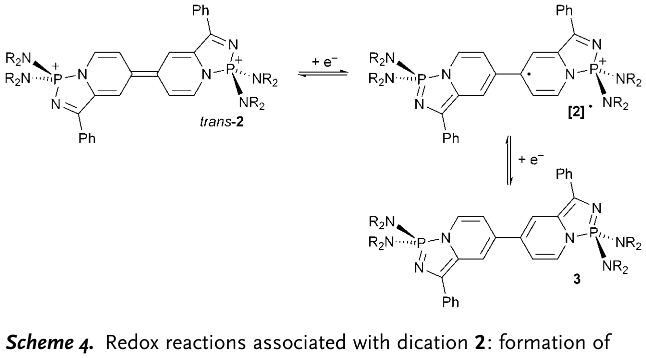


Figure 4. UV/vis spectroelectrochemistry of the two one-electron reduction processes for **2** in CH_2Cl_2 (dotted line) affording **3** (solid line), and **[2]**•/**3** (dashed line). Due to the small difference in reduction potential between **[2]**• and **3**, a clean spectrum of the **3** could not be obtained.

These two reduction processes were monitored for **2** in CH_2Cl_2 solution by means of spectroelectrochemistry (Figure 4). In an initial reaction the pseudo-quinoidal dication **2** is reduced to what is proposed to be the radical monocation **[2]**• with λ_{max} = 925 nm (Scheme 4). This is followed by a further one-electron reduction to afford the neutral linked benzannulated σ^4-λ^5-[1,3,2]diazaphosphole **3**, giving rise to a feature centered at λ_{max} = 610 nm. In order to probe the identity of **3**, chemical reduction of **2** was undertaken using metallic Na in THF solution.[6] Following this reaction by ^{31}P NMR spectroscopy revealed the clean formation of a single product **3** after 2 d at ambient temperature, accom-



Scheme 4. Redox reactions associated with dication **2**: formation of radical cation **[2]**• and bis(benzannulated diazaphosphole) **3**. For clarity, only *trans*-**2** is shown.

panied by a change in color of the solution from green-blue to dark blue. The ^{1}H and ^{31}P NMR spectra of **3** are entirely consistent with its formulation as the neutral bis(benzannulated diazaphosphole), giving rise to a singlet resonance at $\delta(^{31}P) = +39.1$ ppm ([D$_8$]THF), which is in excellent agreement for the chemical shift for the annulated σ^4-1λ^5-[1,3,2]diazaphosphole derivative **1c**, $\delta(^{31}P) = +40.4$ ppm ([D$_8$]THF).[1]

Intriguingly, irradiation of a dilute (1×10^{-6} M) CH_2Cl_2 solution of **2** at 635 nm induces a comparatively weak, anion-independent emission in the near-infrared (NIR) centered at 922 nm, with a Stokes shift of 2670 cm^{-1}; the normalized emission spectrum is given in the Supporting Information.[6] Unfortunately, the low sensitivity of the detector in this spectral region and, hence large correction factors required, precludes a determination of the quantum efficiency.

In summary, this work demonstrates that the "multifunctional" pyridyl-*N*-phosphinoimine/σ^4-1λ^5-[1,3,2]diazaphosphole **1o**/**1c** equilibrium mixture may be homocoupled in a novel variant of a Scholl-type reaction, which exploits a phosphenium salt as an oxidant. The resulting air- and water-stable salt **2** possesses a 4,4′-dihydropyridine core bearing two conjugated imino moieties, giving an extended π-conjugated material, which emits in the NIR spectral region. Notably, **2** is one of only a very small number of stable, neutral "extended viologens".[27] This work continues to highlight the importance of phosphorus-containing building blocks for the preparation of "tuneable" extended π-conjugated materials, an area that has developed over the last decade.[28–30] Such systems are starting to find application as components of sensors and of single- and multilayer OLEDs (organic light-emitting diodes), something that in light of their photophysical properties is particularly attractive for compounds **2** and **3**, respectively.[31–33] These areas, together with an in-depth mechanistic study, are being actively explored.

Experimental Section

All reactions/manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and glovebox techniques.

*cis-/trans-***2**: A solution of **1o**/**1c** (207 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was added slowly to a solution of [(iPr$_2$N)$_2$P][OTf] (190 mg, 0.50 mmol) in CH_2Cl_2 (5 mL). After 7 d the solution was layered with hexane causing a green solid to precipitate slowly. This material was isolated by filtration and washed with H_2O (3 × 3 mL) then Et_2O (3 × 3 mL) and dried in vacuum affording a 1:1 mixture of *cis-/trans-***2** as a green solid (168 mg, 61 %).

3: A solution of *cis-/trans-***2** (50 mg, 0.02 mmol) in [D$_8$]THF (0.5 mL) was treated with excess finely divided Na metal (250 mg) and left to stand for 2 d at ambient temperature. Complete conversion of **2** to **3** was indicated by ^{31}P NMR spectroscopy.

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[7] Crystal data: *trans*-**2**: $[C_{48}H_{72}N_8P_2][CF_3O_3S]_2\cdot 2\,CH_2Cl_2$; $M = 1291.07$; monoclinic; space group $P2_1/c$ (No. 14); $a = 9.6074(15)$, $b = 17.592(3)$, $c = 18.132(3)$ Å; $\beta = 90.94(2)°$; $V = 3064.1(8)$ Å^3; $Z = 2$; $\mu(Mo_{K\alpha}) = 0.33$ mm^{-1}; $T = 120$ K; 35703 reflections collected; $R_{int} = 0.069$; $R(F) = 0.051$ for 4485 data with $I > 2\sigma(I)$, $\omega R(F^2) = 0.147$ for all 5392 independent data. CCDC 686757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[11] Spin trapping experiments using 2,2,6,6-tetramethylpiperidin-oxyl (TEMPO) were attempted to probe the role of radical intermediates in the formation of **2**. However, the experiments were inconclusive since the phosphenium salt was found to react with TEMPO to form a number of, as yet, unidentified products, although sequential reaction of **1o**/**1c** with [(iPr$_2$N)$_2$P][OTf], followed by addition of TEMPO did afford **2** as the only phosphorus-containing product.[6]

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