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Through-conjugation of two phosphaalkyne ('C≡P') moieties mediated by a bimetallic scaffold †

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Through-conjugation of two phosphaalkyne moieties within an isolable molecule is demonstrated for the first time with the synthesis of $[\{Ru(dppe)_2\}_2\{\mu\text{-}(C{\equiv}C)_2C_6H_4\text{-}p\}(C{\equiv}P)_2]$, *via* base-induced desilylation of $[\{Ru(dppe)_2\}_2\{\mu\text{-}(C{\equiv}C)_2C_6H_4\text{-}p\}(\eta^1\text{-}P{\equiv}CSiMe_3)_2]^{2+}$. The nature of the cyaphide ligands and their influence upon the bimetallic core are studied electrochemically.

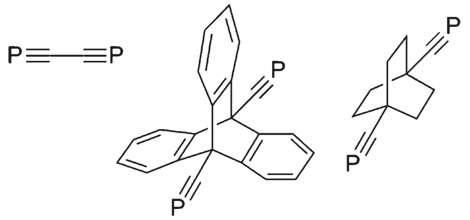

Chart 1 Known bis-phosphaalkynes.[12,13]

Phosphaalkynes ($RC{\equiv}P$)[1] are archetypal models of the phosphorus–carbon analogy,[2] being both isolobal and isoelectronic with alkynes. Though dichotomous in nature – by virtue of the polarity and lone-pair imparted by phosphorus – their chemical analogy to alkynes is well-established, with a prevalence of cycloaddition/oligomerisation reactions, while both η^2-*CP* (*cf.* alkynes) and η^1-*P* (*cf.* nitriles, alkynyls) complexes with transition metals are known.[3] Notwithstanding, an enduring omission lies with the incorporation of the discrete 'C≡P' moiety into architectures featuring extended conjugation (*cf.* the prevalence of polyacetylides), a desirable target – particularly from an organometallic standpoint[4] – given extensive interest in acetylenic and phosphorus-containing moieties in the context of developing molecular electronic components.[5–7] Indeed, the conjugation of phosphaalkyne ('C≡P') moieties with other π-systems is limited to the small range of aromatic phosphaalkynes: $PhC{\equiv}P$,[8] $2,6\text{-R-}C_6H_3C{\equiv}P$ (R = Mes, ^{t}Bu),[9] $2,6\text{-R-4-R'-}C_6H_2C{\equiv}P$ (R = ^{t}Bu, R′ = OMe, NMe_2;[9b] R=R′ = ^{t}Bu,[10] CMe_2Et[11]) and the putative $P{\equiv}C\text{–}C{\equiv}E$ (E = CH, N,[12a,b] P[12c–e]), which were generated (transiently) and observed in the gas phase. The latter ($P{\equiv}C\text{–}C{\equiv}P$) is also among a very limited range of compounds to feature two 'C≡P' moieties (Chart 1),[13] and is the sole precedent example for which their mutual conjugation might reasonably be invoked (albeit unstudied).

Though a small number of transition metal complexes featuring *trans*-disposed η^1-phosphaalkynes has been reported,[14] *viz.* $[M(L)_2(P{\equiv}C^tBu)_2]$ (M = Mo, L = dppe, depe, $R_2PC_2H_4PR_2$, R = Tol, ClC_6H_4); (M = W, L = dppe), $[Mo(depe)_2(P{\equiv}CAd)_2]$ and $[Mo(dppe)_2(P{\equiv}CSiMe_3)_2]$,[15] even the concept of metal-mediated conjugation (*cf.* bis-alkynyl complexes) was unexplored prior to our recent report of the unprecedented cyaphide–alkynyl complexes *trans*-$[Ru(dppe)_2(C{\equiv}CR)(C{\equiv}P)]$ (R = CO_2Me, *p*-An).[16] Herein, we extend this conceptual framework to consider, for the first time, extended conjugation between multiple 'C≡P' moieties, mediated by a bimetallic, redox-active, core; we also elucidate the electronic and redox nature of these complexes.

The sequential treatment of the bisethynylbenzene-bridged bimetallic complex $[\{Ru(dppe)_2\}_2\{\mu\text{-}(C{\equiv}C)_2C_6H_4\text{-}p\}Cl_2]$ (**1**) with two equivalents of AgOTf and $P{\equiv}CSiMe_3$ facilitates installation of two terminal phosphaalkyne moieties to afford $\mathbf{2}^{2+}$ (Scheme 1). Formation of $\mathbf{2}^{2+}$ is evident from characteristic spectroscopic signatures indicative of a coordinated phosphaalkyne (δ_P 111.4, J_{PP} 34 Hz) in proximity to the dppe scaffold (δ_P 42.2 (1 : 4 ratio)), while the carbon-rich bridge remains apparent from $^{13}C\{^1H\}$ NMR and infrared ($\nu_{C{\equiv}C}$ 2054 cm^{-1}) spectroscopic data. Retention of the silyl moieties follows from heteronuclear ($^1H\text{–}^{29}Si$) correlation, while the triflate counter-ion is observed in the ^{19}F-NMR spectrum (δ_F −78.9); bulk composition is affirmed by microanalysis.

The connectivity of $\mathbf{2}^{2+}$ is further supported by X-ray diffraction data (Fig. 1).[17] The internal geometry is largely unremarkable, exhibiting only slight deviations from linearity about the metal centres (∠ P–Ru–C 173.4(2), 175.3(2)°) and in the bridge

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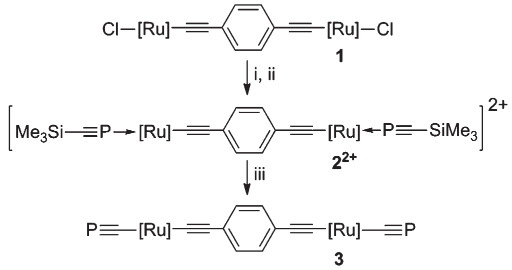

Scheme 1 Reagents and conditions: (i) CH_2Cl_2, 2 AgOTf, (ii) 2 $P{\equiv}CSiMe_3$ in toluene, 1 h.; (iii) thf, 2 KO^tBu, 1 h. [Ru] = $Ru(dppe)_2$.

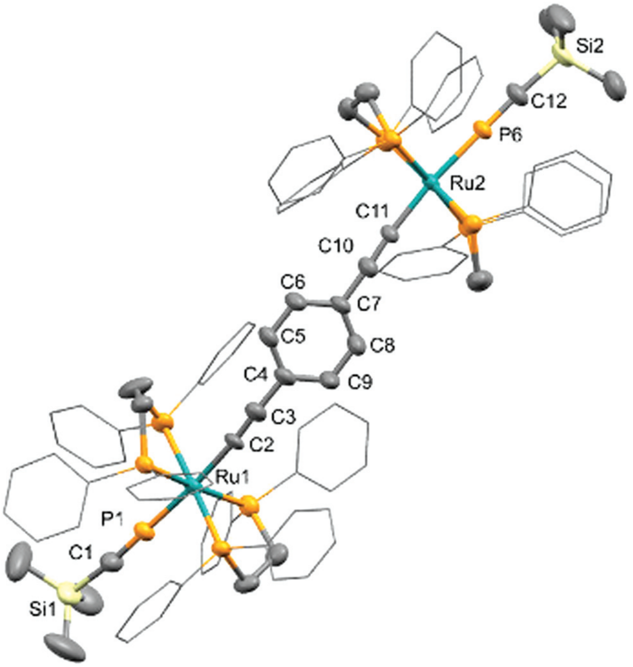

Fig. 1 Molecular structure of 2^{2+}; 50% thermal ellipsoids, hydrogen atoms omitted, and phenyl rings reduced for clarity. Selected bond distances (Å) and angles (°): Ru1–P1 2.264(1), Ru1–C2 2.035(4), Ru2–P6 2.269(1), Ru1–C11 2.022(4), P1–C1 1.526(5), C2–C3 1.203(6), C3–C4 1.443(6)m P6–C12 1.526(5), C10–C11 1.214(6), C10–C7 1.441(6); P1–Ru1–C2 175.23(13), P6–Ru2–C11 173.38(12), C1–P1–Ru1 179.3(2), C12–P6–Ru2 177.3(2), Ru1–C2–C3 174.2(4), Ru2–C11–C10 174.5(4), C2–C3–C4 171.7(5), C11–C10–C7 174.8(5).

(∠ Ru–C≡C 174.5(4), 174.2(4); ∠ C≡C–C 174.5(5), 172.7(5)°) characteristic, respectively, of other bis-alkynyls[18] and the limited range of structurally characterized complexes comprising the '$Ru_2\{\mu\text{-}(C{\equiv}C)_2C_6H_4\text{-}p\}$' and related cores.[19] The coordinated phosphaalkyne moieties are similarly consistent with related analogues.[14–16,20]

Table 1 Comparative experimental and calculated NMR spectroscopic data[a]

	$\delta_{P(CP)}$	$\Delta\delta_{P(CP)}$[b]	$\delta_{C(CP)}$	$\Delta\delta_{C(CP)}$[b]
2^{2+}	111.4	—	189.8	—
3	159.7	48.3	281.8	92.0
$[\{Ru\}(C_2R)(P{\equiv}CSiMe_3)]^+$	108.4	—	192.6	—
$[\{Ru\}(C_2R)(C{\equiv}P)]$ (R = CO_2Me)	168.5	60.0	279.1	86.5
$[\{Ru\}(C_2R)(P{\equiv}CSiMe_3)]^+$	112.8	—	188.2	—
$[\{Ru\}(C_2R)(C{\equiv}P)]$ (R = *p*-An)	159.5	46.7	281.9	93.7
$[\{Ru\}H(P{\equiv}CSiPh_3)]^+$ [20a]	143.8[c]	—	175.1	—
$[\{Ru\}H(C{\equiv}P)]$[20a]	165.0	21.3	287.1	112.0
2^{2+} (calc)[d]	118.4	—	188.8	—
3 (calc)[d]	166.4	48.0	271.4	82.6

[a] {Ru} = $Ru(dppe)_2$. [b] $\Delta\delta$ on conversion from η^1-$P{\equiv}CR$ to terminal cyaphide. [c] Increase in δ_P due to $SiPh_3$ *vs.* $SiMe_3$. [d] GIAO method with the PBE functional (lanl2dz for Ru; 6-31G** for all other atoms); referenced to H_3PO_4 or Me_4Si at the same level of theory.

Conversion of the η^1-$P{\equiv}CSiMe_3$ moieties to terminal cyaphide ligands ('–C≡P') proceeds upon treating 2^{2+} with 2 equiv. KO^tBu,[21] affording **3** in moderate yield (Scheme 1). While single crystals of **3** can be grown, their rapid desolvation during mounting (even at low temperature) has precluded the acquisition of X-ray diffraction data. Nonetheless, the identity of **3** is readily established from the characteristic spectroscopic features and changes that accompany the desilylative rearrangement of η^1-$P{\equiv}CSiMe_3$ to cyaphide;[16,20a] *viz.* (i) reduction in frequency of the C≡P stretch ($\Delta\nu_{C{\equiv}P}$ ~ −12 cm^{-1}); (ii) loss of NMR resonances for silyl and ^-OTf moieties; (iii) increase in frequency ($\Delta\delta_P$ 48) for the phosphaalkynic P-centres, with reduced magnitude of the P_{CP}–P_{dppe} coupling (precluding its resolution); (iv) increased frequency ($\Delta\delta_c$ 92) for the cyaphidic carbon resonance, consistent with formation of an organometallic linkage (*cf* M–CO, M–CN). These data compare well with those we have noted previously[16] and those for Grutzmacher's seminal complex $[RuH(dppe)_2(C{\equiv}P)]$;[20a] they also concur with data calculated for **3** using the PBE functional (Table 1).

The optimized gas-phase geometries of 2^{2+} and **3** (see ESI†)[22] both exhibit slightly greater linearity about the metal centres and bridge when compared with the solid-state structure of 2^{2+}, alongside marginally longer C≡P linkages (~1.58 Å). These features are consistent with a prevalence of packing effects in the solid state, as noted previously for several η^1-$P{\equiv}CR$ complexes,[20,23] and for our precedent cyaphide–alkynyls.[16] The calculated C≡P stretching mode for **3** (asym. $\nu_{C{\equiv}P}$ 1224 cm^{-1}) also compares well with experiment ($\nu_{C{\equiv}P}$ 1247 cm^{-1}). Notably, the experimentally observed frequency reflects a slightly stronger C≡P linkage for **3** than in $[RuH(dppe)_2(C{\equiv}P)]$ ($\nu_{C{\equiv}P}$ 1239 cm^{-1}),[20a] attributable to competition with the *trans*-alkynyl for Ru → π* donation. Indeed, we noted this previously for cyaphide–alkynyls, though to a greater extent ($\nu_{C{\equiv}P}$ 1255, 1260 cm^{-1}),[16] suggesting a reduced competition within the bimetallic scaffold.

The frontier orbitals of 2^{2+} and **3** (Fig. 2) show similarities, the HOMO in each case being dominated by the bridging π-system (76%, 2^{2+}; 54% **3**) with a modest contribution from the metals (14% 2^{2+}; 26% **3**). Notably, the HOMO of **3** also includes contributions from $\pi_{C{\equiv}P}$ (14%), which engage in out-of-phase mixing with the Ru (d_{xy}, d_{xz}), $\pi_{C{\equiv}C}$ and π_{Ar} orbitals, consistent with some level of through-conjugation. The contri-

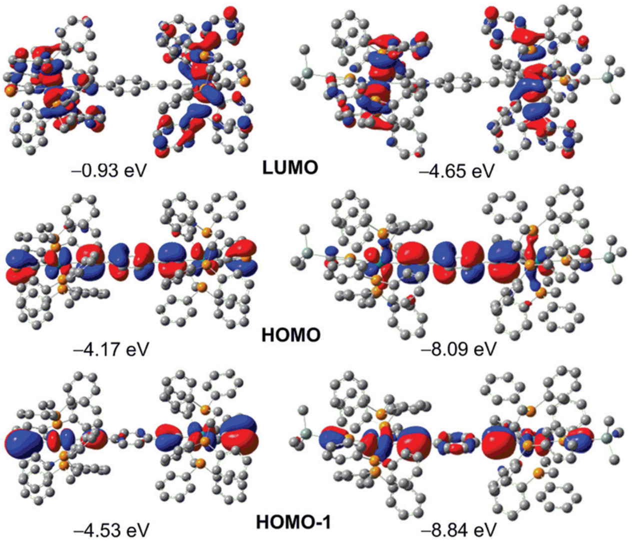

Fig. 2 Frontier orbitals for **3** (left) and $\mathbf{2}^{2+}$ (right), with relative energies (see also ESI†).

Table 2 Electrochemical (CV) data and comproportionation constants[a,b]

	E_{pa}/V	E_{pc}/V	$E_{1/2}(\Delta E_{\mathrm{pp}})$/V	ΔE_{pa}/V	K_{c} [b]
1	−0.268 0.081	−0.348 0.004	−0.308 (80) 0.043 (77)	0.351	8.9×10^5
$\mathbf{2}^{2+}$	0.705 0.995	0.565	0.635 (140)	0.290	0.8×10^5
3	−0.210[c] −0.020[c]	−0.780[d]	—	0.190	1.7×10^3

[a] CH_2Cl_2/0.1 M $[NBu_4]PF_6$ using 1 mM analyte solutions at (25 °C), with Pt disc (1 mm) working electrode, Pt wire counter electrode and Ag wire pseudo-reference at 100 mV s^{-1}. Potentials relative to the FcH/FcH$^+$ couple (0.00 V), referenced using internal Fc*H/Fc*H$^+$ (−0.56 V (E_{pp} 78 mV) *vs.* Fc/Fc$^+$). [b] $K_{\mathrm{c}} = 10^{\Delta E/59\ \mathrm{mV}}$ at 298 K. [c] Irreversible oxidation. [d] Irreversible reduction.

butions from $\pi_{\mathrm{C{\equiv}P}}$ increase appreciably in the mutually degenerate HOMO−1 and HOMO−2 (~25%, see ESI†), lying 0.36 eV below the HOMO, albeit without involvement of the bridging arene (1%). In marked contrast, there is negligible contribution (<10%) from the η^1-P≡CSiMe$_3$ moieties of $\mathbf{2}^{2+}$ to any occupied frontier orbitals, their involvement becoming significant only in the appreciably stabilized HOMO−3 and HOMO−4, lying *ca.* 1.4 eV below the HOMO. Finally, in respect of **3**, we note that the terminal cyaphidic lone-pairs manifest in the HOMO−14 and HOMO−15, being stabilised by *ca.* 2 eV relative to the HOMO. This is entirely consistent with expectation, being similar to our previous observations,[16] and those for phosphaalkynes more generally.[24] Additionally, NBO calculations suggest these to reside in orbitals of *ca.* 75% *s* and 25% *p* character, as is typical of phosphaalkynes.

As is typical of complexes with the Ru(dppe)$_2$ scaffold, the latter dominates the virtual orbitals of **3**, which are mostly centred on the dppe ligands; the bridge contributes marginally to LUMO+12 and LUMO+14, lying 4 eV above the HOMO. In contrast, while the LUMO/LUMO+1 of $\mathbf{2}^{2+}$ are again dominated by the Ru(dppe)$_2$ framework, LUMO+2 is centred on the unsaturated core, with appreciable contributions from $\pi^*_{\mathrm{C{\equiv}P}}$ (60%) and the bridge (15%). This is reflected in the electronic spectrum of $\mathbf{2}^{2+}$, assigned in comparison with those derived from TD-DFT studies,[25] calculating the first 200 excited states. This offers a fair approximation of the observed UV spectra for $\mathbf{2}^{2+}$ and **3** (within limitations of the model), providing sufficient correlation to assist in the assignment of some key features. Thus, a feature at 350 nm (28 571 cm^{-1}) includes significant contribution from LLCT bands ($\pi_{\mathrm{C{\equiv}C}} \rightarrow \pi^*_{\mathrm{Ar}}$ and $\pi_{\mathrm{C{\equiv}C}} \rightarrow \pi^*_{\mathrm{C{\equiv}P}}$) with marginal involvement of intraligand CT ($\pi_{\mathrm{C{\equiv}C}} \rightarrow \pi^*_{\mathrm{C{\equiv}C}}$), alongside the dominant MLCT and LLCT associated with excitation from the HOMO/HOMO+1 to low-lying dppe-based orbitals. A second feature around 260 nm (38 462 cm^{-1}) is primarily composed of ILCT within the dppe scaffold (<HOMO−10 → LUMO), but with additional contribution from $\pi_{\mathrm{C{\equiv}P}} \rightarrow \pi^*_{\mathrm{C{\equiv}P}}$ ILCT and $\pi_{\mathrm{Ar}} \rightarrow \pi^*_{\mathrm{C{\equiv}P}}$ LLCT (HOMO−3 → LUMO+5). In contrast, features in the UV/Vis spectrum of **3** around 370 nm (27 027 cm^{-1}) and 250 nm (40 000 cm^{-1}) are wholly dominated by MLCT and LLCT transitions to the dppe scaffold, with marginal contributions from ILCT within the bridging π-framework; contributions from transitions to the high-lying $\pi^*_{\mathrm{C{\equiv}P}}$ (LUMO+36 to LUMO+39) are negligible.

The redox behaviours of $\mathbf{2}^{2+}$ and **3** were explored using cyclic voltammetry (Table 2 and ESI†), both compounds exhibiting two distinct oxidative events, which can be assigned (trivially[26]) to sequential generation of the $\mathrm{Ru^{III}/Ru^{II}}$ and $\mathrm{Ru^{III}/Ru^{III}}$ species. For $\mathbf{2}^{2+}$ an initial quasi-reversible oxidation occurs at significantly more anodic potential than the corresponding (reversible) feature of **1**, presumably a corollary of its cationic nature. The second (irreversible) oxidation is similarly shifted to more positive potential,[27] and demonstrates an appreciable stability for the mixed valence state $[\mathbf{2}^{2+}]^+$, K_{c} being comparable in magnitude to that of $[\mathbf{1}]^+$ and related terminal alkynyls.[19e,28]

In the case of **3**, two irreversible oxidations are observed, the initial event showing a slight anodic shift relative to **1**, and indeed related alkynyl systems;[19e,28] the second occurs at lower potential than the corresponding oxidation of $[\mathbf{1}]^+$. On the reverse scan, an irreversible reduction process is observed at heavily cathodic potential. Notably, the diminished separation of the oxidative events indicates a reduced stability for the mixed valence state ($[\mathbf{3}]^+$) in comparison to $[\mathbf{1}]^+$ and, indeed, related alkynyl complexes and $[\mathbf{2}^{2+}]^+$, K_{c} being two-orders of magnitude lower than for its counterparts.[19e,28] Notwithstanding, some stability is apparent, which implies some retention of the electronic coupling characteristic of the "Ru$_2${μ-(C≡C)$_2$C$_6$H$_4$-*p*}" scaffold, albeit diminished by the seemingly electron-acceptor character of the cyaphide ligand.

Conclusions

In conclusion, we have described the first isolable compound to incorporate two 'C≡P' moieties as part of the same conjugated scaffold, *viz.* $[Ru_2\{\mu\text{-}(C{\equiv}C)_2C_6H_4\text{-}p\}(C{\equiv}P)_2]$ (**3**). The electronic spectrum shows a dominance of LLCT and MLCT transitions from the bridge and phosphacarbon moieties to the dppe scaffold, with negligible ILCT within the π-system. The redox properties of **3** are more interesting and suggest some electron-acceptor character for the cyaphide ligand. While its presence leads to irreversible redox behaviour and serves to destabilize the mixed-valent state $[\mathbf{3}]^+$, the retention of electronic coupling within the bimetallic core provides initial conceptual validation for the incorporation of the cyaphide ligand into electro-active complexes. This will require engineering of appropriately stabilizing ancillary scaffolds, a challenge with which we are currently engaged.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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21 Sub-stoichiometric KO^{t}Bu affords statistical mixture of $\mathbf{2}^{2+}$ and **3**, with no evidence for the asymmetric (mono-desilylated) product. While separation of the mixture has not been effected, computed NMR data indicate signatures for the asymmetric species to be distinct from those of $\mathbf{2}^{2+}$ and **3**.

22 Geometries were optimized from an initial model based on the solid state structure of $\mathbf{2}^{2+}$, using the B3LYP functional (lanl2dz for ruthenium; 6-31G** for all other atoms). See ESI† for full details.

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26 Though commonly attributed to sequential Ru^{II}/Ru^{III} couples, the oxidation events have heavy involvement from the carbon-rich bridge, due to extensive orbital mixing in the HOMO. These are thus more properly considered as sequential mono-oxidations of the bimetallic core.

27 Though mindful of previous reports of **1** (and related systems) that describe the irreversible oxidation of $[\mathbf{1}]^{2+}$ close to 1 V,[28b–e] in the present case we are confident in our assignment of this feature to oxidation of the mixed-valence complex $[\mathbf{2}^{2+}]^{+}$ to $[\mathbf{2}^{2+}]^{2+}$, the initial event being more consistent with a 1-electron process.

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