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

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Through-conjugation of two phosphalkyne moieties within an isolable molecule is demonstrated for the first time with the synthesis of $[\{\text{Ru}(\text{dppe})_2\}_2\{\mu-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4\text{-p}\}(\text{C}\equiv\text{P})_2]$, via base-induced desilylation of $[\{\text{Ru}(\text{dppe})_2\}_2\{\mu-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4\text{-p}\}(\eta^1\text{-P}\equiv\text{CSiMe}_3)_2]^{2+}$. The nature of the cyaphide ligands and their influence upon the bimetallic core are studied electrochemically.

Phosphalkynes ($\text{RC}\equiv\text{P}$)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 $\eta^2\text{-CP}$ (*cf.* alkynes) and $\eta^1\text{-P}$ (*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 polyacetylenes), a desirable target – particularly from an organometallic standpoint⁴ – given extensive interest in acetylenic and phosphorus-containing moieties in the context of developing molecular electronic components.^{5–7} Indeed, the conjugation of phosphalkyne ('C≡P') moieties with other π -systems is limited to the small range of aromatic phosphalkynes: $\text{PhC}\equiv\text{P}$,⁸ 2,6- $\text{R-C}_6\text{H}_3\text{C}\equiv\text{P}$ ($\text{R} = \text{Mes}$, tBu),⁹ 2,6- $\text{R-R}'\text{-C}_6\text{H}_2\text{C}\equiv\text{P}$ ($\text{R} = \text{tBu}$, $\text{R}' = \text{OMe}$, NMe_2 ;^{9b} $\text{R}=\text{R}' = \text{tBu}$,¹⁰ $\text{CMe}_2\text{Et}^{11}$) and the putative $\text{P}\equiv\text{C-C}\equiv\text{E}$ ($\text{E} = \text{CH}$, N ,^{12a,b} P^{12c-e}), which were generated (transiently) and observed in the gas phase. The latter ($\text{P}\equiv\text{C-C}\equiv\text{P}$) 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 -phosphalkynes has been reported,¹⁴

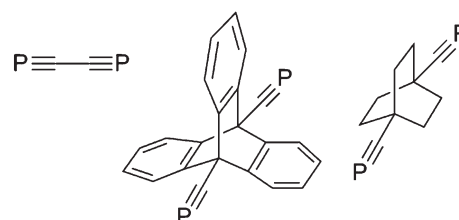


Chart 1 Known bis-phosphalkynes.^{12,13}

viz. $[\text{M}(\text{L})_2(\text{P}\equiv\text{C}^t\text{Bu})_2]$ ($\text{M} = \text{Mo}$, $\text{L} = \text{dppe}$, depe , $\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2$, $\text{R} = \text{ToI}$, ClC_6H_4); ($\text{M} = \text{W}$, $\text{L} = \text{dppe}$), $[\text{Mo}(\text{depe})_2(\text{P}\equiv\text{CAd})_2]$ and $[\text{Mo}(\text{dppe})_2(\text{P}\equiv\text{CSiMe}_3)_2]$,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*- $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\text{C}\equiv\text{P})]$ ($\text{R} = \text{CO}_2\text{Me}$, *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.

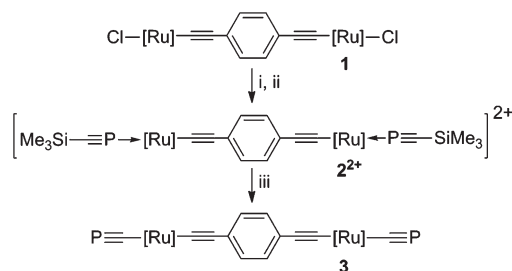
The sequential treatment of the bisethynylbenzene-bridged bimetallic complex $[\{\text{Ru}(\text{dppe})_2\}_2\{\mu-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4\text{-p}\}\text{Cl}_2]$ (**1**) with two equivalents of AgOTf and $\text{P}\equiv\text{CSiMe}_3$ facilitates installation of two terminal phosphalkyne moieties to afford **2**²⁺ (Scheme 1). Formation of **2**²⁺ is evident from characteristic spectroscopic signatures indicative of a coordinated phosphalkyne (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 $^{13}\text{C}\{\text{H}\}$ NMR and infrared ($\nu_{\text{C}\equiv\text{C}}$ 2054 cm^{-1}) spectroscopic data. Retention of the silyl moieties follows from heteronuclear (^1H – ^{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 **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 ($\angle \text{P-Ru-C}$ 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 $\text{P}\equiv\text{CSiMe}_3$ in toluene, 1 h.; (iii) thf, 2 KO^tBu , 1 h. $[\text{Ru}] = \text{Ru}(\text{dppe})_2$.

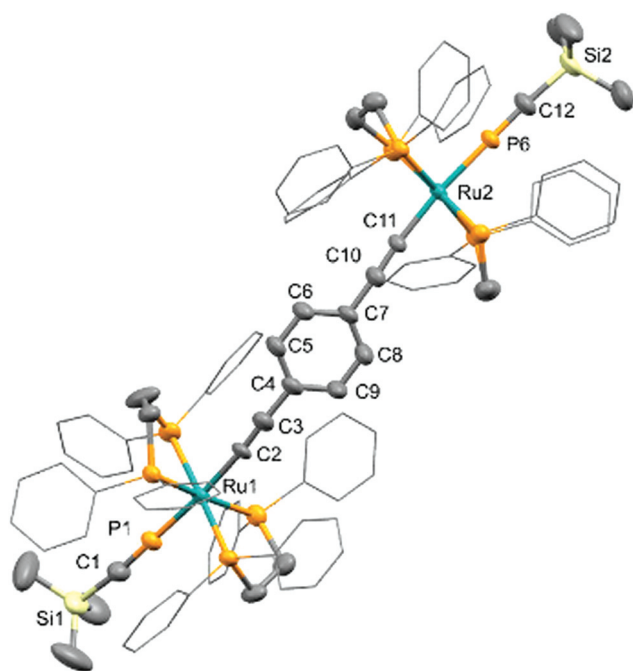


Fig. 1 Molecular structure of 2^{2+} ; 50% thermal ellipsoids, hydrogen atoms omitted, and phenyl rings reduced for clarity. Selected bond distances (Å) and angles ($^\circ$): Ru1–P1 2.264(1), Ru1–C2 2.035(4), Ru2–P6 2.269(1), Ru1–C11 2.022(4), P1–C1 1.526(5), C2–C3 1.203(6), C3–C4 1.443(6), P6–C12 1.526(5), 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).

($\angle \text{Ru}-\text{C}\equiv\text{C}$ 174.5(4), 174.2(4); $\angle \text{C}\equiv\text{C}-\text{C}$ 174.5(5), 172.7(5) $^\circ$) characteristic, respectively, of other bis-alkynyls¹⁸ and the limited range of structurally characterized complexes comprising the ' $\text{Ru}_2\{\mu-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4-p\}$ ' and related cores.¹⁹ The coordinated phosphalkyne moieties are similarly consistent with related analogues.^{14–16,20}

Conversion of the $\eta^1\text{-P}\equiv\text{CSiMe}_3$ moieties to terminal cyaphide ligands ($-\text{C}\equiv\text{P}$) 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

Table 1 Comparative experimental and calculated NMR spectroscopic data^a

	$\delta_{\text{P}(\text{CP})}$	$\Delta\delta_{\text{P}(\text{CP})}^b$	$\delta_{\text{C}(\text{CP})}$	$\Delta\delta_{\text{C}(\text{CP})}^b$
2 ²⁺	111.4	—	189.8	—
3	159.7	48.3	281.8	92.0
$[\{\text{Ru}\}(\text{C}_2\text{R})(\text{P}\equiv\text{CSiMe}_3)]^+$	108.4	—	192.6	—
$[\{\text{Ru}\}(\text{C}_2\text{R})(\text{C}\equiv\text{P})]$ (R = CO_2Me)	168.5	60.0	279.1	86.5
$[\{\text{Ru}\}(\text{C}_2\text{R})(\text{P}\equiv\text{CSiMe}_3)]^+$	112.8	—	188.2	—
$[\{\text{Ru}\}(\text{C}_2\text{R})(\text{C}\equiv\text{P})]$ (R = <i>p</i> -An)	159.5	46.7	281.9	93.7
$[\{\text{Ru}\}\text{H}(\text{P}\equiv\text{CSiPh}_3)]^{+20a}$	143.8 ^c	—	175.1	—
$[\{\text{Ru}\}\text{H}(\text{C}\equiv\text{P})]^{20a}$	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 $[\text{Ru}] = \text{Ru}(\text{dppe})_2$. ^b $\Delta\delta$ on conversion from $\eta^1\text{-P}\equiv\text{CR}$ 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.

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 $\eta^1\text{-P}\equiv\text{CSiMe}_3$ to cyaphide;^{16,20a} viz. (i) reduction in frequency of the $\text{C}\equiv\text{P}$ stretch ($\Delta\nu_{\text{C}\equiv\text{P}} \sim -12 \text{ cm}^{-1}$); (ii) loss of NMR resonances for silyl and ^-OTf moieties; (iii) increase in frequency ($\Delta\delta_{\text{P}}$ 48) for the phosphalkynic P-centres, with reduced magnitude of the $\text{P}_{\text{CP}}\text{-P}_{\text{dppe}}$ coupling (precluding its resolution); (iv) increased frequency ($\Delta\delta_{\text{C}}$ 92) for the cyaphidic carbon resonance, consistent with formation of an organometallic linkage (*cf* $\text{M}-\text{CO}$, $\text{M}-\text{CN}$). These data compare well with those we have noted previously¹⁶ and those for Grutzmacher's seminal complex $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$;^{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 $\text{C}\equiv\text{P}$ linkages ($\sim 1.58 \text{ Å}$). These features are consistent with a prevalence of packing effects in the solid state, as noted previously for several $\eta^1\text{-P}\equiv\text{CR}$ complexes,^{20,23} and for our precedent cyaphide-alkynyls.¹⁶ The calculated $\text{C}\equiv\text{P}$ stretching mode for **3** (asym. $\nu_{\text{C}\equiv\text{P}}$ 1224 cm^{-1}) also compares well with experiment ($\nu_{\text{C}\equiv\text{P}}$ 1247 cm^{-1}). Notably, the experimentally observed frequency reflects a slightly stronger $\text{C}\equiv\text{P}$ linkage for **3** than in $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$ ($\nu_{\text{C}\equiv\text{P}}$ 1239 cm^{-1}),^{20a} attributable to competition with the *trans*-alkynyl for $\text{Ru} \rightarrow \pi^*$ donation. Indeed, we noted this previously for cyaphide-alkynyls, though to a greater extent ($\nu_{\text{C}\equiv\text{P}}$ 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 $\pi_{\text{C}\equiv\text{P}}$ (14%), which engage in out-of-phase mixing with the Ru (d_{xy} , d_{xz}), $\pi_{\text{C}\equiv\text{C}}$ and π_{Ar} orbitals, consistent with some level of through-conjugation. The contri-



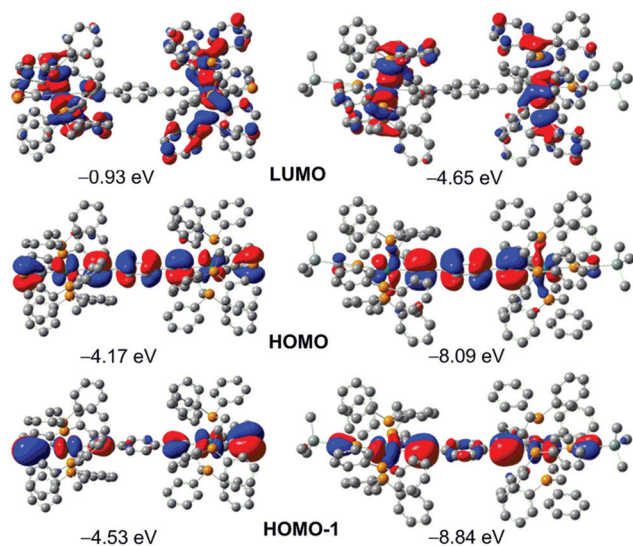


Fig. 2 Frontier orbitals for **3** (left) and **2²⁺** (right), with relative energies (see also ESI†).

Contributions from $\pi_{C\equiv P}$ 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 $\eta^1\text{-P}\equiv\text{CSiMe}_3$ moieties of **2²⁺** 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 phosphalkynes more generally.²⁴ Additionally, NBO calculations suggest these to reside in orbitals of *ca.* 75% *s* and 25% *p* character, as is typical of phosphalkynes.

As is typical of complexes with the $\text{Ru}(\text{dppe})_2$ 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 **2²⁺** are again dominated by the $\text{Ru}(\text{dppe})_2$ framework, LUMO+2 is centred on the unsaturated core, with appreciable contributions from $\pi^*_{C\equiv P}$ (60%) and the bridge (15%). This is reflected in the electronic spectrum of **2²⁺**, 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 **2²⁺** 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 ($\pi_{C\equiv C} \rightarrow \pi^*_{Ar}$ and $\pi_{C\equiv C} \rightarrow \pi^*_{C\equiv P}$) with marginal involvement of intraligand CT ($\pi_{C\equiv C} \rightarrow \pi^*_{C\equiv C}$), 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

Table 2 Electrochemical (CV) data and comproportionation constants^{a,b}

	E_{pa}/V	E_{pc}/V	$E_{1/2}(\Delta E_{pp})/V$	$\Delta E_{pa}/V$	K_c^b
1	−0.268 0.081	−0.348 0.004	−0.308 (80) 0.043 (77)	0.351	8.9×10^5
2²⁺	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 $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}_4]\text{PF}_6$ 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 $\text{Fc}^*\text{H}/\text{Fc}^*\text{H}^+$ (−0.56 V (E_{pp} 78 mV) vs. Fc/Fc^+). ^b $K_c = 10^{\Delta E/59 \text{ mV}}$ at 298 K. ^c Irreversible oxidation. ^d Irreversible reduction.

primarily composed of ILCT within the dppe scaffold (<HOMO–10 → LUMO), but with additional contribution from $\pi_{C\equiv P} \rightarrow \pi^*_{C\equiv P}$ ILCT and $\pi_{Ar} \rightarrow \pi^*_{C\equiv P}$ 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 $\pi^*_{C\equiv P}$ (LUMO+36 to LUMO+39) are negligible.

The redox behaviours of **2²⁺** and **3** were explored using cyclic voltammetry (Table 2 and ESI†), both compounds exhibiting two distinct oxidative events, which can be assigned (trivially²⁶) to sequential generation of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}$ species. For **2²⁺** 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 [**2²⁺**]⁺, K_c being comparable in magnitude to that of [**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 [**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 ([**3**]⁺) in comparison to [**1**]⁺ and, indeed, related alkynyl complexes and [**2²⁺**]⁺, 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 “ $\text{Ru}_2\{\mu\text{-(C}\equiv\text{C)}_2\text{C}_6\text{H}_4\text{-p}\}$ ” 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 ‘ $\text{C}\equiv\text{P}$ ’ moieties as part of the same conju-



gated scaffold, viz. $[\text{Ru}_2\{\mu\text{-(C}\equiv\text{C)}_2\text{C}_6\text{H}_4\text{-p}\}\{\text{C}\equiv\text{P}\}_2]$ (**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 $[\text{3}]^+$, 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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- 17 CCDC 1811689† Crystals grown from CH₂Cl₂/hexane at –20 °C. See ESI† for data.
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