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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

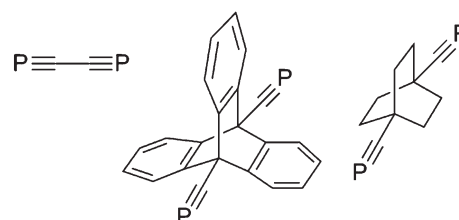


Chart 1 Known bis-phosphalkynes.^{12,13}

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.

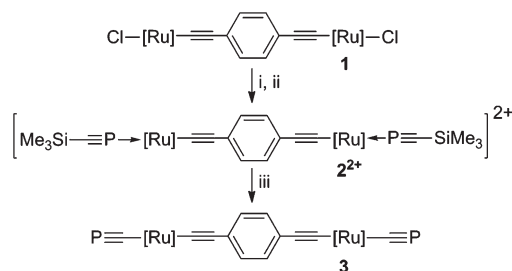
The sequential treatment of the bisethynylbenzene-bridged bimetallic complex $[\{\text{Ru}(\text{dppe})_2\}_2\{\mu-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4\text{-p}\}\text{Cl}_2]$ (**1**) with two equivalents of AgOTf and $\text{P}\equiv\text{CSiMe}_3$ facilitates installation of two terminal phosphalkyne 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. $[\text{Ru}] = \text{Ru}(\text{dppe})_2$.

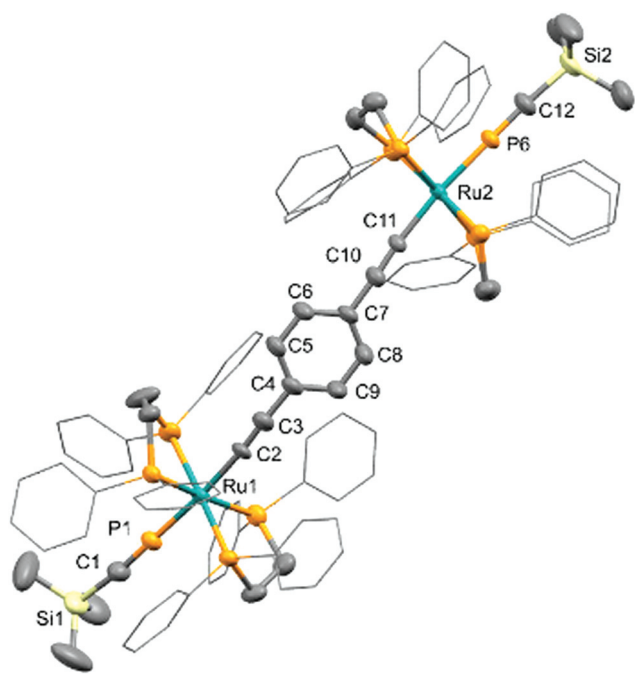


Fig. 1 Molecular structure of 2^{2+} ; 50% thermal ellipsoids, hydrogen atoms omitted, and phenyl rings reduced for clarity. Selected bond distances (Å) and angles ($^\circ$): Ru1–P1 2.264(1), Ru1–C2 2.035(4), Ru2–P6 2.269(1), Ru1–C11 2.022(4), P1–C1 1.526(5), C2–C3 1.203(6), C3–C4 1.443(6), P6–C12 1.526(5), 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 ' $\text{Ru}_2\{\mu-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4\text{-p}\}$ ' 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 ($\sim 1.58 \text{ \AA}$). 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-



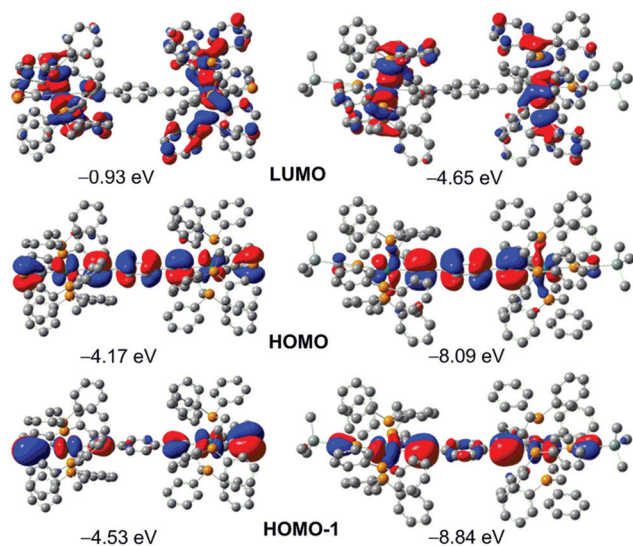


Fig. 2 Frontier orbitals for **3** (left) and **2⁺** (right), with relative energies (see also ESI†).

butions 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 **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 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 **2⁺** 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 **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 **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 ($\pi_{C\equiv C} \rightarrow \pi^*_{Ar}$ 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
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 $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}_4]\text{PF}_6$ 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 **2⁺** 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 **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 [**2⁺**]⁺, 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 [**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 “ $\text{Ru}_2\{\mu\text{-(C}\equiv\text{C)}_2\text{C}_6\text{H}_4\text{-p}\}$ ” 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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Notes and references

- For reviews of phosphacarbon and phosphalkene chemistry see: (a) F. Mathey, *Angew. Chem., Int. Ed.*, 2003, **42**, 1578–1604; (b) R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990; (c) L. N. Markovski and V. D. Romanenko, *Tetrahedron*, 1989, **45**, 6019–6090; (d) R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731–744.
- K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998.
- (a) J. F. Nixon, *Coord. Chem. Rev.*, 1995, **145**, 201–258; (b) J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327–1362.
- See for example and reviews: (a) C. Schubert, J. T. Margrat, T. Clark and D. M. Guidi, *Chem. Soc. Rev.*, 2015, **44**, 988–998; (b) P. J. Low, *Dalton Trans.*, 2005, 2821–2824; (c) M. I. Bruce and P. J. Low, *Adv. Organomet. Chem.*, 2004, **51**, 179–444; (d) M. I. Bruce and P. J. Low, *Adv. Organomet. Chem.*, 2001, **48**, 71–288; (e) F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431–509; (f) I. R. Whittall, A. J. McDonagh and M. G. Humphrey, *Adv. Organomet. Chem.*, 1998, **42**, 291–362; (g) N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21–38.
- (a) M. A. Shameem and A. Orthaber, *Chem. – Eur. J.*, 2016, **22**, 10718–10735; (b) T. Baumgartner, *Acc. Chem. Res.*, 2014, **47**, 1613–1622; (c) T. Baumgartner and R. Reau, *Chem. Rev.*, 2006, **106**, 4681–4727 and references therein.
- (a) X.-L. Geng, Q. Hu, B. Schafer and S. Ott, *Org. Lett.*, 2010, **12**, 692–695; (b) E. Oberg, B. Schafer, X.-L. Geng, J. Pettersson, Q. Hu, M. Kritikos, T. Rasmussen and S. Ott, *J. Org. Chem.*, 2009, **74**, 9265–9273; (c) B. Schafer, E. Oberg, M. Kritikos and S. Ott, *Angew. Chem., Int. Ed.*, 2008, **47**, 8228–8231; (d) V. A. Wright, B. O. Patrick, C. Schneider and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **126**, 8836–8844; (e) C.-W. Tsang, B. Baharloo, D. Riendi, M. Yam and D. P. Gates, *Angew. Chem., Int. Ed.*, 2004, **43**, 5682–5685; (f) C.-W. Tsang, M. Yam and D. P. Gates, *J. Am. Chem. Soc.*, 2003, **125**, 1480–1481.
- (a) X. He, J. Borau-Garcia, A. Y. Y. Woo, S. Trudel and T. Baumgartner, *J. Am. Chem. Soc.*, 2013, **135**, 1137–1147; (b) Y. Ren and T. Baumgartner, *Dalton Trans.*, 2012, **41**, 7792–7800; (c) P.-A. Bouit, A. Escande, R. Szucs, D. Szieberth, C. Lescop, L. Nyulaszi, M. Hissler and R. Reau, *J. Am. Chem. Soc.*, 2012, **134**, 6524–6527; (d) A. Bruch, A. Fukazawa, E. Yamaguchi, S. Yamaguchi and A. Studer, *Angew. Chem., Int. Ed.*, 2011, **50**, 12094–12098.
- (a) C. Mueller, R. Bartsch, A. Fischer, P. G. Jones and R. Schmutzler, *J. Organomet. Chem.*, 1996, **512**, 141–148; (b) R. Appel, G. Maier, H. P. Reisenauer and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 197–197.
- (a) C. Jones and M. Waugh, *J. Organomet. Chem.*, 2007, **692**, 5086–5090; (b) K. Toyota, S. Kawasaki and M. Yoshifuji, *J. Org. Chem.*, 2004, **69**, 5065–5070.
- (a) A. S. Ionkin, W. J. Marshall, B. M. Fish, A. A. Marchione, L. A. Howe, F. Davidson and C. N. McEwen, *Eur. J. Inorg. Chem.*, 2008, 2386–2390; (b) G. Markl and H. Sejpka, *Tetrahedron Lett.*, 1986, **27**, 171–174.
- M. Yoshifuji, H. Kawanami, Y. Kawai, K. Toyota, M. Yasunami, T. Niitsu and N. Inamoto, *Chem. Lett.*, 1992, **21**, 1053–1056.
- (a) T. A. Cooper, H. W. Kroto, J. F. Nixon and O. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1980, 333–334; (b) H. W. Kroto, J. F. Nixon and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 512–516; (c) M. Brönstrup, J. Gottfriedsen, I. Kretzchmar, S. J. Blanksby, H. Schwarz and H. Schumann, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2245–2250; (d) L. A. Jones, E. P. F. Lee, P. Soldan and T. G. Wright, *Phys. Chem. Chem. Phys.*, 1999, **1**, 391–395; (e) F. M. Bickelhaupt and F. Bickelhaupt, *Chem. – Eur. J.*, 1999, **5**, 162–174.
- (a) F. Brodkorb, M. Brym, C. Jones and C. Schulten, *J. Organomet. Chem.*, 2006, **691**, 1025–1029; (b) M. Brym and C. Jones, *Dalton Trans.*, 2003, 3665–3667.
- P. B. Hitchcock, M. J. Maah, J. F. Nixon, J. A. Zora, G. J. Leigh and M. A. Bakar, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 474–475.
- S. M. Mansell, M. Green and C. A. Russell, *Dalton Trans.*, 2012, **41**, 14360–14368.
- N. Trathen, M. C. Leech, I. R. Crossley, V. K. Greenacre and S. M. Roe, *Dalton Trans.*, 2014, **43**, 9004–9007.



- 17 CCDC 1811689† Crystals grown from CH₂Cl₂/hexane at –20 °C. See ESI† for data.
- 18 (a) M. C. B. Colber, J. Lewis, N. J. Long, P. R. Raithby, A. J. P. White and D. J. Williams, *Dalton Trans.*, 1997, 99–104; (b) N. D. Jones and M. O. Wolf, *Organometallics*, 1997, **16**, 1352–1354; (c) C.-Y. Wong, C.-M. Che, M. C. W. Chan, J. Han, K.-H. Leung, D. L. Phillips, K.-Y. Wong and N. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 13997–14007; (d) A. Vacher, F. Barriere, T. Roisnel, L. Piekara-Sady and D. Lorcy, *Organometallics*, 2011, **30**, 3570–3578.
- 19 (a) S. Sporler, L. Muller, A. R. Waterloo, R. R. Tykwinski and N. Burzlaff, *J. Organomet. Chem.*, 2016, **821**, 122–129; (b) X. Wang, X. You, Z.-P. Shang and J. Xia, *J. Organomet. Chem.*, 2016, **803**, 111–118; (c) J. Xia, Y.-P. Ou, D. Wu, G. J. Jin, J. Yin, G.-A. Yu and S. H. Liu, *Dalton Trans.*, 2013, **42**, 14212–14222; (d) M. A. Fox, B. Le Guennic, R. L. Roberts, D. A. Brue, D. S. Yufit, J. A. K. Howard, G. Manca, J.-F. Halet, F. Hartl and P. J. Low, *J. Am. Chem. Soc.*, 2011, **133**, 18433–18446; (e) L. D. Field, A. M. Magill, T. K. Shearer, S. B. Colbran, S. T. Lee, S. J. Dalgarno and M. M. Bhadbhade, *Organometallics*, 2010, **29**, 957–965; (f) D. J. Armit, M. I. Bruce, M. Gaudio, N. N. Zaitseva, B. W. Skelton, A. H. White, B. L. Guennic, J.-F. Halet, M. A. Fox, R. L. Roberts, F. Harlt and P. J. Low, *Dalton Trans.*, 2008, 6763–6775.
- 20 (a) J. G. Cordaro, D. Stein, H. Ruegger and H. Grutzmacher, *Angew. Chem., Int. Ed.*, 2006, **45**, 6159–6162; (b) T. Groer, G. Baum and M. Scheer, *Organometallics*, 1998, **17**, 5916–5919.
- 21 Sub-stoichiometric KO^tBu affords statistical mixture of 2²⁺ 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 2²⁺ and 3.
- 22 Geometries were optimized from an initial model based on the solid state structure of 2²⁺, using the B3LYP functional (lanl2dz for ruthenium; 6-31G** for all other atoms). See ESI† for full details.
- 23 C. Jones, C. Schulten and A. Stasch, *Eur. J. Inorg. Chem.*, 2008, 1555–1558.
- 24 J. C. T. R. Burckett-St. Laurent, M. A. King, H. W. Kroto, J. F. Nixon and R. J. Suffolk, *J. Chem. Soc., Dalton Trans.*, 1983, 755–759.
- 25 TD-DFT calculations were performed at the B3LYP level using lanl2dz for Ru and 3-21G* for all other atoms, without addition of a solvent model. Though a relatively low level of theory (constituting a balance against the complexity of the system and number of required excited states), such has previously proven suitable to provide a general guide to assignment.
- 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 [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 [2²⁺]⁺ to [2²⁺]²⁺, the initial event being more consistent with a 1-electron process.
- 28 (a) E. Wuttke, Y.-M. Hervault, W. Polit, M. Linseis, P. Erler, S. Rigaut and R. F. Winter, *Organometallics*, 2014, **33**, 4672–4686; (b) A. Benameur, P. Brignou, E. D. Piazza, Y.-M. Hervault, L. Norel and S. Rigaut, *New J. Chem.*, 2011, **35**, 2105–2113; (c) C. Olivier, B. Kim, D. Touchard and S. Rigaut, *Organometallics*, 2008, **27**, 509–518; (d) A. Klein, O. Lavastre and J. Fielder, *Organometallics*, 2006, **25**, 635–643; (e) M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, M. Younus, A. J. P. White, D. J. Williams, N. N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury and R. H. Friend, *Organometallics*, 1998, **17**, 3034–3043; (f) S. K. Hurst, M. P. Cifuentes, A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs and A. Persoons, *J. Organomet. Chem.*, 2002, **642**, 250–267; (g) O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet and P. H. Dixneuf, *Organometallics*, 1997, **16**, 184–189.

