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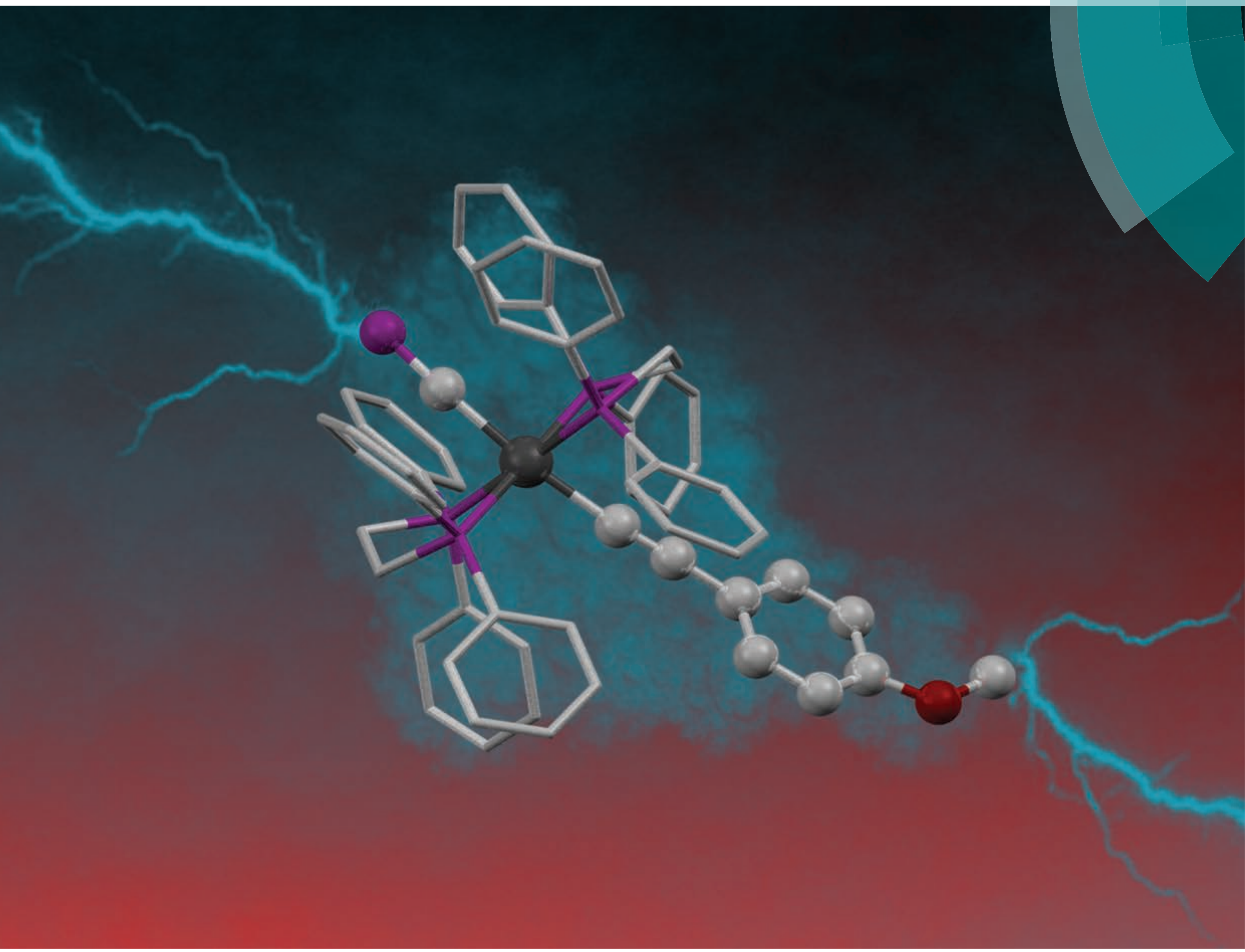

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Synthesis and electronic structure of the first cyaphide-alkynyl complexes

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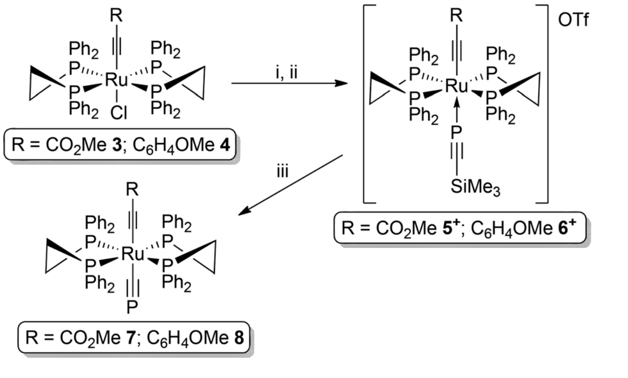
The novel complexes *trans*-[Ru(dppe)$_2$(C≡CR)(C≡P)] (R = CO_2Me, C_6H_4OMe), the first to incorporate cyaphide as part of a conjugated system, are obtained in facile manner. The electronic structure of these compounds is probed by X-ray, DFT and UV/Vis studies.

Low coordinate phosphacarbons (*e.g.* RC≡P, R_2C=PR′) have long been a source of intrigue,[1] being isolobal and isoelectronic analogues of more familiar carbo-centric and nitrogenous species, yet still embodying appreciable dichotomies. For instance, the chemistry of phosphaalkynes and phosphaalkenes is dominated by the high-energy π-systems (HOMO) akin to classical alkynes and alkenes, yet the lone pairs remain accessible (*cf.* nitriles and imines) to engage in reactivity,[2] albeit that those of phosphaalkynes are appreciably stabilised. Such varied facets render low-coordinate phosphacarbons attractive moieties to incorporate into electro-active and conducting molecules as a means of moderating orbital distributions and energies, and thus the molecular electronic properties. Indeed, this is illustrated by numerable examples[3] of phosphaalkene[4] and phosphole-based[5] systems, which exhibit enhanced electrochemical and photo-electronic responses in comparison to carbo-centric and nitrogen-doped analogues.

In respect of phosphaalkynes, however, such application has yet to be realised, a direct corollary of a lack of intrinsic kinetic stability within the C≡P moiety and resulting difficulties in accessing appropriate derivatives. Indeed, even complexes of the notionally simple cyaphide ligand (C≡P$^-$), a direct analogue of the ubiquitous cyanide, have long evaded isolation.[6] Though first observed by Angelici in 1992, in the complex "Cl(Et$_3$P)$_2$Pt(C≡P)",[7] later trapped as [Cl(Et$_3$P)$_2$Pt(μ-η^1-η^2-C≡P)Pt(PEt$_3$)$_2$],[7,8] only in 2006 was Grützmacher able to isolate the first unequivocal example of a terminal cyaphide complex, *viz.* [RuH(dppe)$_2$(C≡P)] (**1**),[9] obtained from the η^1-phosphaalkyne complex [RuH(dppe)$_2$(P≡CSiPh$_3$)]$^+$ (**2**$^+$) by base-induced desilylative rearrangement.[9,10] Since this seminal report, no further examples have been described, though Russell and co-workers recently inferred the *in situ* formation of *trans*-[Mo(dppe)$_2$(P≡CSiMe$_3$)(C≡P)]$^-$,[11] albeit unisolated.

We are interested in the chemical and electronic properties of organometallics that comprise low-coordinate phosphacarbons,[12] particularly those involving metal-centred conjugation. To this end, Grützmacher's methodology presented an intriguing opportunity. Herein, we report the synthesis and isolation of the first compounds to incorporate the cyaphide ligand as part of an extended π-system; we also outline preliminary investigations into the electronic structure of these molecules.

The ruthenium alkynyl complexes [Ru(dppe)$_2$(C≡CR)Cl] (R = CO_2Me **3**,‡ [13] *p*-C_6H_4OMe **4**) were converted *in situ* to the respective triflate salts by reaction with AgOTf, subsequent treatment with Me_3SiC≡P affording [Ru(dppe)$_2$(η^1-P≡CSiMe$_3$)-(C≡CR)]$^+$ (R = CO_2Me **5**$^+$, *p*-C_6H_4OMe **6**$^+$) in good yields (Scheme 1).



Scheme 1 *Reagents and conditions*: (i) AgOTf, CH_2Cl_2; (ii) P≡CSiMe$_3$, CH_2Cl_2/C_7H_7; (iii) KO^{t}Bu, thf.

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† Electronic supplementary information (ESI) available: Full synthetic details and characterising data for all compounds, computational details, UV/Vis data, crystallographic data in CIF format and ellipsoid plot of **3**. CCDC 962350, 962351 and 990881. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01108b

The identities of 5^+ and 6^+ follow convincingly from multinuclear NMR spectroscopic data. Thus, the $^{31}P\{^1H\}$ NMR spectra exhibit quintet and doublet resonances (5^+: δ_P 108.6; 6^+: δ_P 113.1) in 1 : 4 ratio, with mutual couplings of *ca.* 30 Hz. A singlet resonance corresponding to the $SiMe_3$ group is apparent in the ^1H NMR spectra, in each case integrating consistently with the dppe backbone, and exhibiting correlation (HMBC) with a characteristic doublet in the $^{13}C\{^1H\}$ NMR spectra ($\delta_C \sim 190$) attributed to the phosphaalkynic centre, and thus confirming the $P{\equiv}CSiMe_3$ moiety.

Retention of the alkynyl functionality is similarly confirmed, as is the presence of triflate (δ_F −78.9), while bulk purity was established by microanalysis. The spectroscopic data resemble those reported for 2^+, differences in chemical shift being attributable to a more electron withdrawing nature for the metal fragments of 5^+ and 6^+, and thus differing polarization of the alkynic P and C centres.

The molecular connectivity was further supported by isolation of X-ray quality crystals of **5·OTf**, obtained by slow cooling of a saturated $CDCl_3$ solution of the salt (Fig. 1).[14] The cation exhibits the anticipated geometry, with the *trans*-disposed alkynyl and phosphaalkyne adopting near perfect linearity (∠C–Ru–P 177.0(3), ∠Ru–C≡C 178.0(10); ∠Ru–P≡C 175.7(4)°); this contrasts the situation observed in 2^+ and Jones' $[RuH(dppe)_2(\eta^1\text{-}P{\equiv}CMe)]$,[15] both of which exhibit appreciably bent geometries for the phosphaalkyne unit (∠Ru–P≡C 165.5(2)[8] and 153.7(2)° respectively), attributed to steric encumbrance. The internal geometry of 5^+ is largely unremarkable; the C≡P linkage (1.528(11) Å) is comparable to those of 2^+ (1.530(3) Å)[9] and Russell's *trans*-$[Mo(dppe)_2(\eta^1\text{-}P{\equiv}CSiMe_3)_2]$ (1.540(2) Å),[11] which are consistent with prior examples.[15,16] A somewhat short C≡C distance is noted (1.153(15) Å; *cf.* 1.16–2.25 Å from a CCDC search[17]), but is mirrored in the parent alkynyl **3** (1.136(10) Å), and presumably results from disorder within this unit.

Treatment of 5^+ or 6^+ with a single equivalent of KO^tBu in thf solution effects desilylative rearrangement to afford the cyaphide complexes **7** and **8** respectively, isolated in excess of 60% yield. Notably, this reaction proceeds to completion within 1 h under ambient conditions; this contrasts the case of **1**, for which extended reaction times (14 h) were required. Moreover, while Grützmacher observed a kinetically-favoured "intermediate" (believed to be $[Ru(dppe)_2\{C(SiPh_3){=}P(OPh)\}]$ (**A**), formed by reversible attack of ^-OPh at phosphorus) no comparable species are apparent in the formation of **7** or **8**. Indeed, even *in situ* NMR studies at −78 °C failed to reveal any intermediates, or significantly slow the reaction. Since **A** was not considered to lie on the pathway leading to cyaphide,[10] we reason that the faster reactions can be attributed to its absence, which is presumably the result of diminished electrophilicity at phosphorus in $5^+/6^+$, combined with enhanced facility of direct nucleophilic attack at the smaller $SiMe_3$ (*cf.* $SiPh_3$).

Formation of the cyaphide complexes is convincingly established from spectroscopic data, supported in the case of **8** by an X-ray diffraction study (Fig. 2).[18] Spectroscopically, a significant shift to higher-frequency is noted for both alkynic and dppe phosphorus centres (**7**: δ_P 161.5, 52.7; **8**: δ_P 159.5, 50.8) when compared to 5^+ and 6^+, with concomitant reduction in the mutual spin–spin coupling constant (to ∼4 Hz), consistent with increased separation of the interacting nuclei (*i.e.* $^3J_{PP}$ *vs.* $^2J_{PP}$). A significant shift is also noted for the phosphaalkynic carbon centre ($\Delta\delta_C \sim 86$), similar to that observed by Grützmacher. The ^1H and $^{13}C\{^1H\}$ spectra confirm loss of the $SiMe_3$ group and retention of the respective alkynyl ligands, which is further supported by infrared data (**7**: ν_{CO} 1660 cm^{-1} ν_{CC} 2040 cm^{-1}; **8**: ν_{CC} 2032 cm^{-1}); the C≡P stretching mode is also observed in both infrared and Raman spectra (**7**: 1255 cm^{-1}; **8**: 1261 cm^{-1}) and is in good agreement with that

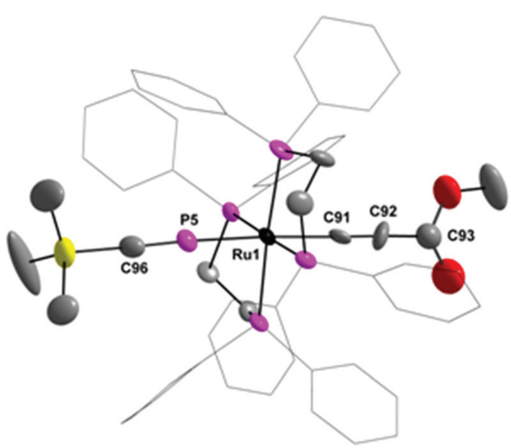

Fig. 1 Molecular structure of 5^+ in crystals of **5·OTf**, DCM solvate. Hydrogen atoms are omitted and phenyl rings reduced for clarity; 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): Ru(1)–C(91) 2.082(11), C(96)–P(5) 1.528(11), C(96)–Si(1) 1.858(12), C(91)–C(92) 1.153(15), C(92)–C(93) 1.450(18), P(5)–C(96)–Si(1) 178.3(6), C(96)–P(5)–Ru(1) 175.7(4), P(5)–Ru(1)–C(91) 177.0(3), C(91)–C(92)–C(93) 171.9(12).

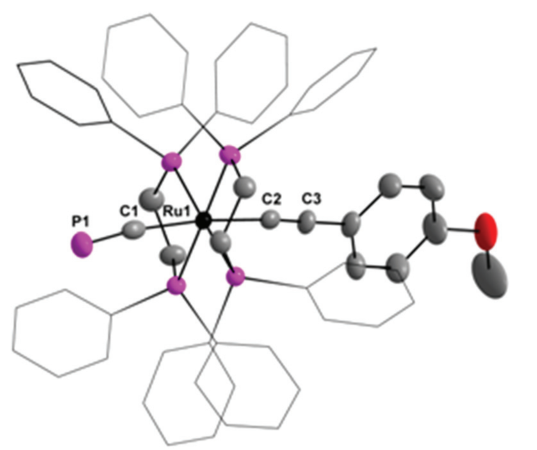

Fig. 2 Molecular structure of **8**. Hydrogen atoms omitted and phenyl rings reduced for clarity; 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): C(1)–P(1) 1.544(4), Ru(1)–C(1) 2.065(4), Ru(1)–C(2) 2.084(3), C(2)–C(3) 1.205(5), Ru(1)–C(1)–P(1) 172.3(2), Ru(1)–C(2)–C(3) 174.4(3), C(1)–Ru(1)–C(2) 171.91(14), C(2)–C(3)–C(4) 178.5(4).

reported for **1** (1239 cm^{-1}) and those calculated for **7** and **8** (~1240 cm^{-1}; see ESI†).

In the solid state, **8** exhibits slight distortion from linearity (∠Ru–C≡C 174.4(3)°; ∠Ru–C≡P 172.3(2)°), as previously noted for other *trans*-bisalkynyls.[19] A shorter C≡P (1.544(4) Å) and very slightly longer Ru–CP (2.065(4) Å) bond are noted as compared with **1** (1.573(2) and 2.057(2) Å respectively), presumably reflecting diminished $d_{\pi}\rightarrow\pi^*_{(C\equiv P)}$ retrodonation within **8**, due to the competing *trans*-alkynyl. It is, however, noteworthy that DFT studies§ indicate greater linearity within the conjugated system of **8**, together with a longer C≡P linkage (1.58 Å), a situation that is mirrored for **7**; this would perhaps imply incidence of packing effects in the solid state.

The frontier orbitals of **7** and **8** (Fig. 3) are similar to those typically seen in alkynyl and bis(alkynyl) complexes.[20] Thus, the HOMO and HOMO−1 in each case derive from the out-of-phase mixing of the Ru (d_{xy}, d_{xz}), C≡C (π) and C≡P (π) orbitals, with an appreciable contribution from the cyaphide moiety. This is most pronounced for **7** (50% $\pi_{(C\equiv P)}$, 35% Ru) in which the electron-withdrawing methylpropiolate ligand contributes only *ca.* 10% to either orbital. In contrast, the more donating $C\equiv CC_6H_4OMe$ ligand contributes significantly to the HOMO of **8** (24% $\pi_{C\equiv C}$, 17% π_{Ar} *cf.* 30% Ru, 24% $\pi_{C\equiv P}$), leading to reduced involvement of the cyaphide, which in turn dominates the orthogonally-lying HOMO−1 (43% $\pi_{C\equiv P}$, 35% Ru, 14% $\pi_{C\equiv C}$), lying 0.2 eV lower in energy (*cf.* 0.01 eV for **7**). The LUMO of each molecule is appreciably separated from the HOMO (Δ*E* 3.45 eV **7**, 3.7 eV **8**) and centred on the dppe ligands (*ca.* 75%) and Ru $d_{x^2-y^2}$ orbital (25%), with appreciable Ru–P antibonding character. Higher energy orbitals (up to LUMO+10) are almost exclusively ligand (dppe) based, while the C≡P π* orbitals do not contribute appreciably until LUMO+18/19; the C≡C (and for **8** Ar) π* orbitals feature from LUMO+11.

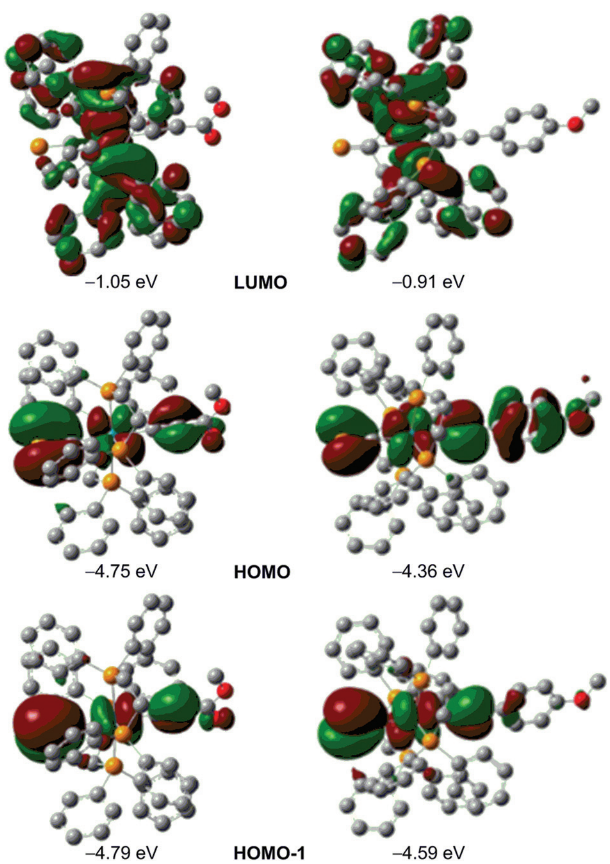

Fig. 3 Frontier molecular orbitals for **7** (left) and **8** (right).

It is noteworthy that the lone-pair of the cyaphide moiety is appreciably stabilised with respect to the π-system, lying *ca.* 1.6 eV below the HOMO (HOMO−6 in **7**, HOMO−7 in **8**). In each case, NBO calculations reveal the lone-pair to be held in an orbital of *ca.* 75% s and 25% p character, with polarisation of the C≡P moiety in the sense $P^{\delta+}$–$C^{\delta-}$. In this regard, the cyaphide closely resembles classical phosphaalkynes.

Both **7** and **8** were further studied by a combination of UV/Vis spectroscopy and TD-DFT (calculating the first 100 excited states; see ESI† for details). Both exhibit strong absorptions around 250 nm (40 000 cm^{-1}) arising from ligand → ligand charge transfer (LLCT) between the π-CP/CC and dppe π* orbitals. For **7**, a further feature around 275 nm (36 363 cm^{-1}) is again dominated by LLCT transitions but also involves some intraligand transitions (ILCT) centred on $\pi_{(C\equiv P)}\rightarrow\pi^*_{(C\equiv P)}$. A weaker feature around 300 nm (33 333 cm^{-1}) is again dominated by LLCT. In contrast, while a dominance of LLCT is also apparent for **8**, a strong feature around 298 nm (33 550 cm^{-1}) involves significant contributions from ILCT, centred on π→π* transitions of the alkynyl (HOMO→LUMO+11) and C≡P (HOMO→LUMO+18/19) ligands; a smaller contribution from metal→ligand charge transfer (MLCT) is evident between ruthenium and the dppe π* orbitals (HOMO→LUMO+5, 9, 10).

In conclusion, we have described the first organometallic complexes to incorporate the terminal cyaphide ligand as part of an extended π-system; this also represents only the second unequivocal report of a terminal metal-cyaphide complex. Structural and theoretical studies reveal a modestly screened cyaphide moiety with a stabilised, but nonetheless accessible, lone-pair akin to classical phosphaalkynes. The cyaphide contributes significantly to the HOMO and HOMO−1, with an influence that is clearly moderated by the *trans*-alkynyl ligand. The molecules absorb strongly in the UV region, their electronic spectra being dominated by LLCT transitions to the dppe ligands, though ILCT π→π* transitions within the C≡P moiety also contribute, most significantly so in **8** for which further ILCT occurs within the $C\equiv CC_6H_4OMe$ ligand. These molecules are the first of a novel class of conjugated, organometallic hetero-ynyl complexes that we continue to explore and develop.

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Notes and references

‡ The novel complex **3** was prepared by a modification of established synthetic routes to ruthenium alkynyl complexes. See ESI† for full details and characterising data.[13]

§ Calculations used the B3LYP hybrid-functional, with the lanl2dz basis set for Ru and 6-31G** for all other atoms; see ESI† for full details.

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