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Cyphide-alkynyl complexes: Metal-ligand conjugation and the influence of remote substituents†

Samantha K. Furfari, Matthew C. Leech, Nicola Trathen, Madeleine C. Levis and Ian R. Crossley*

A homologous series of novel trans-cyphide-alkynyl complexes, viz. trans-[Ru(dppe)_2](C=CR)(C=CC_H(R-R)) (R = Me, H, F, CO_2Me, NO_2) is prepared and comprehensively characterised, alongside their parent phosphaalkyne-complex cations trans-[Ru(dppe):(η^1-P=CSiMe_3)(C=CC_H(R-R))]. Structural data for trans-[Ru(dppe):(C=CC_H(R-R)) (R = Me, F) and trans-[Ru(dppe):(η^1-P=CSiMe_3)(C=CC_H(R-R))] (R = F, CO_2Me) are described, along with that for the previously reported trans-[Ru(dppe):(C=CR)] (R = C(CO_2Me)). NMR spectroscopic data indicate significant influence of the remote aromatic substituent over the properties of the cyphide ligand, in line with the Hammett parameter (σ_p), suggesting appreciable ‘communication’ along the through-conjugate chain. Cyclic voltammetry data indicate irreversible oxidative behaviour, at more anodic E_peak than in the respective alkynyl-chloride complexes, though apparently moderated by the remote substituent.

Introduction

Phosphaalkynes are among the best established and most studied classes of low-coordinate phosphacarbon.¹ Their chemistry epitomizes the phosphorus-carbon analogy² with a prevalence of alkyne-like behaviour, a corollary of the π-centred HOMO and heavily stabilised phosphorus lone-pair. Thus, extensive cycloaddition and oligomerisation chemistry is known,³ and exploited en-route to organophosphorus architectures. In an organometallic context, metal-centred cyclization is common,⁴ resulting from the preferential adoption of the η^1-P=C-R coordination mode, albeit that nitrile-like η^1-P coordination can be induced within encumbered coordination spheres.⁵ Indeed, steric encumbrance is widely invoked to achieve kinetic stability of the core ‘P=C’ fragment, albeit that electronic factors are now recognised to be equally important,⁶ as clearly illustrated by recent prevalent activity with the phosphaethynyloate ion ‘OC=CR=²⁷’.

Notwithstanding, the simplest phosphacarbon fragment, viz. the cyphide (‘C=P’) moiety, a direct analogue of terminal ethynyl (‘C≡CH’), long remained elusive, the free anion being computed to be intrinsically unstable.⁸ Only in 1992 was this ligand first described, with Angelici’s in situ observation of trans-Pt(P(C≡CMe)_2)(C≡CR)⁹ albeit only isolable by coordination of the reactive π-system within the structurally characterised [{Et_2P}PtCl(μ-η^1:η^2-C≡CR)Pt(P(C≡CMe)_2)]²⁰. The unequivocal observation of a terminal cyphide ligand was finally achieved in 2006, with Grützmacher’s seminal report of trans-[RuH(dppe):(C=CR)] (1).¹¹ obtained by desilylative rearrangement of the parent trans-[RuH(dppe):(η^1-P=CSiPh_3)] (2). The stability of 1 was attributed to the steric protection afforded by the ‘M(dppe)_2’ scaffold, which has also featured heavily in subsequent efforts to tame this elusive ligand, albeit with initially limited success, the complex anion trans-[Mo(dppe):(η^1-P=CSiMe_3)(C≡CR)] being finally inferred by Russell in 2012.¹² More recently, Meyer reported the synthesis of a uranium cyphide complex (Figure 1), derived from deoxygenation of an ‘OC=CR’ ligand,¹³ which exhibits a less encumbered coordination sphere, suggesting a greater than anticipated stability for the terminal M–C≡CR moiety.

Inspired by Grützmacher’s report of 1,¹¹ we sought to explore and exploit the potential ‘ethynyl-like’ character of cyphide, through its incorporation into complexes of the type trans-[Ru(dppe):(C≡CR)] (C≡CR), akin to classical ruthenium bis(acetylides). We thus reported in 2014 complexes 3 and 4, stilbene-like derivatives of 1.

Figure 1: Meyer’s uranium-cyphide complex¹⁴
(R = CO₂Me) and 4 (R = C₆H₄OMe-p), and more recently the homobimetallic [(P=CC(dppe)Ru)d(R=CCH₆H₂-p)] (5), the first compound to incorporate two ‘C=P’ moieties within the same conjugate scaffold. In each case, through-conjugation of the acetylenic and cyaphidic ρ-systems is apparent in both the HOMO and HOMO-1, reminiscent of bis-alkynyl analogues. For 3 and 4 these fragments contribute Intra-Ligand Charge Transfer (ILCT) events (π→π* and π→π*) to the electronic spectra (ca. 270 nm), which are otherwise dominated by Metal to Ligand, and Ligand to Ligand Charge Transfers (MLCT/LLCT) from HOMO & HOMO-1 to the low-lying virtual orbitals of the dppe scaffold (LUMO & LUMO+1). The influence of cyaphide upon redox behaviour is also apparent, electrochemical studies of 5 demonstrating a reduced stability of the mixed valence form 5⁺ (cf. the parent dichloride and analogous alkynyl systems) with concomitant loss of reversibility for both redox events (5→5⁺ and 5⁺→5²⁺).

Following from these preliminary studies, we have sought to develop a deeper understanding of the nature and influence of the cyaphide ligand, and its interaction with trans-alkynyl moieties. To this end we describe herein the synthesis of a homologous series of trans-cyaphide-alkynyls, and explore the interplay of cyaphide, alkynyl and metal fragments. Aspects of this work have appeared in preliminary form.  

Results and discussion

Synthesis

The ruthenium-alkynyl precursors trans-[Ru(dppe)₂(Cl)(C=CR)Cl] (6, R = C₆H₄Me-p a, C₆H₅ b, C₆H₄F-p c, C₆H₄(CO₂Me)-p d, C₆H₄(NO₂)-p e, CO₂Et f), are conveniently obtained either directly from literature methods, or by their simple modification. Thereafter, halide abstraction in the presence of Me₃Si=P affords good yields of trans-[Ru(dppe)₂(η¹-P=SiMe₃)(C=CR)]⁺ (Scheme 1, 7a-f), obtained as either the triflate or hexafluorophosphate salts. In all cases, the identities of 7⁺ follow from spectroscopic data, each exhibiting characteristic resonances in the 3P(H)/H NMR spectrum associated with the η¹-phosphaalkyne (δP ~ 110) and dppe (δP ~ 40) ligands. Retention of the SiMe₃ and alkynyl moieties is in each case apparent from the respective NMR spectroscopic signatures, as is the associated counter-ion (δP ~ 78, OTf; δP ~ 73.6, δP ~ 142.1 (νP = 712 Hz) PF₆). For 7a* and 7c* single-crystal X-ray diffraction data (vide infra) confirmed the structure of the molecular cation.

The conversion of each of 7⁺ to the respective cyaphide complexes (8a-f) is effected by treatment of thf solutions with stoichiometric KO'Bu. It is noteworthy that this step has proven sensitive to the nature of the counter-ion, 7OTf on occasion affording greater purity than the respective 7PF₆. Moreover, the persistence of any trace silver often results in the contamination of 8 with a phosphacarbon-free complex; while the identity of this species remains elusive, it would appear to result from an oxidative process. This issue is, however, obviated by preparing 7OTf from TiOTf (cf. AgOTf).

The formation of 8a-f proceeds rapidly, being complete within 1 hour under ambient conditions, as we have previously described. This contrasts starkly Grüttmacher’s report 11 of a 14-hour reaction time, during which the reversibly-formed [RuH(dppe)₂(C(SiPh₃)=P(OPh))] (A) was observed, resulting from attack of phenoxine base at phosphorus (Scheme 2). We do not observe any comparable species, even when operating at low temperature (~78 °C) or when using NaOPh in place of KO'Bu; moreover, we have resynthesized 1 using our methodology, thus excluding the influence of the ancillary ligands in respect of this disparity. We thus reason the enhanced susceptibility of the Me₃Si fragment (cf. the more encumbered Ph₅Si) toward the attack of base (and thus desilylation) allows this pathway to dominate, precluding formation of a ‘dead-end’ reservoir species analogous to A.

The conversions to cyaphide are clearly apparent from spectroscopic changes, which include: i) loss of NMR resonances for the silyl moiety and counter-ion; ii) increased resonant frequency (ΔδP ~ 50) for the unsaturated P-centres; with reduced magnitude of the P=O=O coupling; iii) increased frequency (ΔδP ~ 90) of the cyaphide carbon resonances, to a region comparable to that for metal carbonyls and cyanides (ΔδP ~ 280); and iv) reduction in frequency of the C=O stretch (ΔνC=O ~ 12 cm⁻¹). Retention of the co-ligands follows from the associated spectroscopic signatures, with the bulk molecular composition confirmed by high-resolution mass spectra. Additionally, both 8c and 8d ceded to the growth of single crystals, enabling structural confirmation (vide infra).

Scheme 1. Synthesis of cyaphide complexes 8a-f. Reagents and conditions: (i) MX (AgOTf, AgPF₆, TiOTf), CH₂Cl₂; (ii) Ph₅Me, CH₂Cl₂/CH₃OH; (iii) KO'Bu, thf.

Scheme 2. Reversible formation of a ‘dead-end’ reservoir species (A) upon reaction of 2 with NaOPh, intervening in desilylative rearrangement to cyaphide complex 1.
Table 1: Selected bond distances (Å) and angles (°) for complexes 7a, 7c, 8c and 8d (2 molecules in asymmetric unit) with estimated standard uncertainties in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>7a</th>
<th>7c</th>
<th>3</th>
<th>1.222(13)</th>
<th>175.5(7)</th>
<th>2.051(11)</th>
<th>176.0(5)</th>
<th>179.1(5)</th>
<th>7a</th>
<th>7c</th>
<th>3</th>
<th>1.222(13)</th>
<th>175.5(7)</th>
<th>2.051(11)</th>
<th>176.0(5)</th>
<th>179.1(5)</th>
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<tr>
<td>Ru-Pc</td>
<td>2.264(3)</td>
<td>2.262(1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.070(6)</td>
<td>2.118(3)</td>
<td>2.076(9)</td>
<td>2.051(11)</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Ru-CP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.043(4)</td>
<td>2.053(5)</td>
<td>2.054(20)</td>
<td>2.072(8)</td>
<td>2.072(10)</td>
<td>-</td>
<td>1.515(14)</td>
<td>1.520(5)</td>
<td>1.563(7)</td>
<td>1.493(3)</td>
<td>1.549(10)</td>
<td>1.566(11)</td>
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<td>C-P</td>
<td>1.197(16)</td>
<td>1.182(6)</td>
<td>1.272(9)</td>
<td>1.216(4)</td>
<td>1.216(12)</td>
<td>1.222(13)</td>
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<td>-</td>
<td>-</td>
<td>1.295(14)</td>
<td>1.835(5)</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>C-Si</td>
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<td>-</td>
<td>169.6(4)</td>
<td>177.8(2)</td>
<td>172.6(5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>175.3(10)</td>
<td>176.2(4)</td>
<td>179.6(6)</td>
<td>175.1(8)</td>
<td>175.5(7)</td>
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<tr>
<td>C-Cl</td>
<td>1.718(10)</td>
<td>1.710(4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>174.0(13)</td>
<td>178.6(5)</td>
<td>176.3(3)</td>
<td>178.0(10)</td>
<td>176.7(9)</td>
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<tr>
<td>C-Cr</td>
<td>1.758(3)</td>
<td>1.756(1)</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>173.8(2)</td>
<td>174.2(2)</td>
<td>174.5(1)</td>
<td>172.4(4)</td>
<td>173.0(3)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C-Ru-P</td>
<td>-</td>
<td>-</td>
<td>173.8(2)</td>
<td>174.5(1)</td>
<td>172.4(4)</td>
<td>173.0(3)</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

*a*PF$_2$ salt, *b*crystals of the CH$_2$Cl$_2$ solvate, *c*crystals of the benzene solvate, *d*bond distances and angles for 8d warrant caution, the structure being subject to imperfectly modelled disorder around the dppe backbone. Connectivity can be confidently assigned, with specific geometric parameters subject to significant uncertainty.\(^{19}\)

**Structural Features**

The molecular geometries of the phosphaalkyne-containing complex cations 7a$^+$ and 7c$^+$, and cyaphide complexes 3, 8c and 8d are illustrated in Figures 2–6 respectively, with selected parameters summarised in Table 1.

Both 7a$^+$ and 7c$^+$ exhibit perfectly linear coordination of the phosphaalkyne moieties, with the trans-alkynyls marginally distorted from linearity. In this respect, both are similar to trans-[Ru(dppe)$_2$][η$^1$-P=CSiMe$_2$]C=CCO$_2$Me] (\(\angle_{\text{RuPC}} 175.7(4)^\circ\), \(\angle_{\text{CUP}} 177.0(3)^\circ\), \(\angle_{\text{CUC}} 178(1)^\circ\)) and \(\text{[P}(\mu\text{-CMe})(\mu\text{-CP})\text{CMe}]\) (\(\angle_{\text{RuPC}} 179.3(2)^\circ\), \(\angle_{\text{CUP}} 175.2(2)^\circ\), \(\angle_{\text{CUC}} 173.4(2)^\circ\)).

It is noted that greater deviation from linear coordination was described by Jones for \(\text{[RuH(dppe)$_2$][η$^1$-P=CMe]}\) (\(\langle\angle_{\text{RuPC}} 153.7(2)^\circ\)). Therefore, there is no evidence for concomitantly enhanced interaction of the trans-alkynyl, both Ru–CC and C=C being statistically comparable to those of 1, 4 and 8d.\(^{19}\)

Indeed, solution-phase infrared data for 8c (\(\nu_{\text{CP}} 1245 \text{ cm}^{-1}\), \(\nu_{\text{CC}} 2066 \text{ cm}^{-1}\)) are in line with the rest of the series and indicate the weaker C=P linkages, features that are also

\(\text{P} \leftrightarrow \text{C}\) linkage (2.118(3) Å). Though this may be attributed trivially to a reduced \(\pi\text{Ru-P} \leftrightarrow \pi\text{Cup}\) contribution to ligand binding, there is no evidence for concomitantly enhanced interaction of the trans-alkynyl, both Ru–CC and C=C being statistically comparable to those of 1, 4 and 8d.\(^{19}\)

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mirrored by computational data (see ESI). We thus conclude this to be a crystallographic artefact, warranting caution in discussion of the P=C moiety within 8c.

Despite the dearth of structural comparators, there appears to be a general trend toward elongation of the P=C linkage upon conversion of the $\eta^1$-phosphaalkyne ligand into cyaphide, as is also apparent from reduction in $\nu_{CP}$, which would seem consistent with an appreciable $\pi_{Ru-C-P}$ contribution to the bonding of cyaphide, being most pronounced for Grützmacher’s 1, in which competition for back-bonding from ruthenium is obviated by the $\text{trans}$-hydride ligand.

The central $\pi$-chains of 3, 8c and 8d each exhibit some distortion from linearity, in-line with classical bis(alkynyl) complexes, and indeed 4. Most pronounced for 3 and 8d, this is manifest in contraction of $\angle \text{Ru-C-P}$ and $\angle \text{C-C-Ru-C}$, which are similar to those in 4 ($\angle \text{Ru-C-P} 172.3(3)^\circ$; $\angle \text{C-Ru-C} 171.9(2)^\circ$); in contrast, 8c shows minimal distortion. Notably, 3 appears to exhibit further deviation at the alkynyl terminus ($\angle \text{C-C-C} \sim 169.5(9)^\circ$; C–C, 1.34(2) Å); while possibly attributable to noted disorder within the ester moiety, DFT studies indicate its retention in the gas-phase, and suggest its origin to lie with partial delocalisation between the ester and alkynyl moieties. Computation data do, indeed, more generally the structural parameters (see ESI), showing good agreement with experimental data for 8c and 8d, and suggesting largely comparable features across the series of complexes. Exception lies with the previously described 4, for which more linear P–C–Ru, C–Ru–C and Ru–C–C angles are favoured in the gas phase, as is also apparent for 3, suggesting a prevalence of packing effects in the solid state.

Spectroscopic Features

Selected NMR spectroscopic signatures for $\eta^1$-phosphaalkyne and cyaphide complexes are summarised in Table 2. For both types of complex, perusal of the data for the $\text{trans}$-alkynyl systems reveals general trends in chemical shifts within the phosphacarbon moiety that correlate with the donor/acceptor character of the terminal alkynyl substituent. Thus, for the $\eta^1$-P=CSiMe$_3$ complexes a slight decrease in $\delta_{CP}$ is noted in line with increasing electron-withdrawing capacity of the remote substituent, while $\delta_{C}$ exhibits the opposite, far more modest, trend. This is consistent with increasing acceptor character of the “[Ru(dppe)CCR]” fragment inducing polarisation of the phosphaalkynic moiety, manifest as deshielding of the remote carbon centre, with concomitant shielding at phosphorus.

The cyaphidic systems exhibit the reverse trend (increasing

Table 2: Selected NMR spectroscopic data for [Ru(dppe)(C$^\equiv$CR)) complexes.

<table>
<thead>
<tr>
<th>R</th>
<th>$\delta_{C}$</th>
<th>$\delta_{CP}$</th>
<th>$\delta_{CPR}$</th>
<th>$\delta_{CP}$</th>
<th>$\delta_{CPR}$</th>
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<tbody>
<tr>
<td>$\text{Me}_2\text{Si}^+\cdot[C\equiv\text{C}]^-$</td>
<td>113.5$^a$</td>
<td>42.4$^b$</td>
<td>188.2$^a$</td>
<td>4</td>
<td>159.5$^a$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_5\text{OMe}^+$</td>
<td>112.3$^a$</td>
<td>42.4$^a$</td>
<td>188.4$^a$</td>
<td>4</td>
<td>159.8$^b$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_5\text{Me}^+$</td>
<td>111.9$^a$</td>
<td>42.3$^a$</td>
<td>186.8$^b$</td>
<td>4</td>
<td>160.6$^a$</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_5\text{Bu}^+$</td>
<td>111.0$^a$</td>
<td>41.8$^a$</td>
<td>190.2$^b$</td>
<td>4</td>
<td>165.3$^a$</td>
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<tr>
<td>$\text{C}_3\text{H}_5\text{Et}^+$</td>
<td>109.1$^a$</td>
<td>41.5$^a$</td>
<td>193.8$^a$</td>
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<td>$\text{C}_3\text{H}_5\text{Ph}^+$</td>
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<td>41.3$^a$</td>
<td>193.5$^a$</td>
<td>8</td>
<td>163.3$^a$</td>
</tr>
</tbody>
</table>

*as solutions in CDCl$_3$; $^a$as solutions in CO$_2$; $^b$as reported in ref 14; $^c$redetermined in the present work; $^d$as reported in ref 15; $^e$[Ru(dppe)(C$^\equiv$CR)]$^{[\eta^1-P=\text{SiMe}_3]}$; $^f$as reported in ref 11 (d$_8$-THF);
The δ_p, decreasing δ_C, which is also appreciably more pronounced values of δ_p in particular spanning over 10 ppm. These effects are clearly illustrated in considering the aromatic alkynyl derivatives (4 and 8a-e), Hammett plots (Figures 7 and 8) showing good correlation (R^2 = 0.96) with the α parameter.

Taken together these data suggest a significant long-range influence of the terminal substituent upon the cyaphide moiety, rather than mere modification of acceptor character in the metal-fragment. Indeed, were the latter effect dominant one would anticipate this to be least pronounced for the hydridic 1 (as reflected in data for 2^*), whereas data for 1 actually lie intermediate to the alkynyl systems. This underlines the interplay between cyaphide and the trans-ligand, a long-range communicative regime being consistent with an appreciable level of metal-mediated through-conjugation, as we have previously noted. This defines these complexes as analogues of classical trans-bis(acetylidy)nes, a notion supported by computational data that demonstrate extensive out-of-phase mixing of the Ru (d_{dpr}, d_{pp}) C=C (π) and C=P (π) in HOMO and HOMO-1 across the series (Figure 9 and ESI), with significant contributions from the cyaphide moiety.

In common with the precedent systems 3 – 5,14,15 the low-lying virtual orbitals of 8a-c are dominated by the Ru(dppe)₂ scaffold, while the π* orbitals of the C≡P, C≡C and arene moieties contribute significantly only at higher-energy. Thus, the arene fragments feature prominently in orbitals ca 4.5 eV above the HOMO (LUMO+11/12 and LUMO+16/17) with modest (ca 10%) contributions from the alkynyl π*CC. The cyaphide π* system contributes heavily (>40%) to LUMO+18/19, ca 5 – 5.2 eV above the HOMO. In contrast, the more electron-withdrawing termini of 8d and 8e lead to the C₅H₅R moieties dominating LUMO+1 (8d) and LUMO (8e), which are appreciably stabilised, lying only 3.73 eV and 2.81 eV above the respective HOMOs. Further contributions from the aryl rings are apparent at LUMO+16/19 (8d) or LUMO+13/14 (8e) at energies comparable to those of 8a-c. Similarly, π*CP in each case feature prominently (ca 50% or above) around 5 eV above the HOMO (LUMO+17 to LUMO+19).

Unsurprisingly, the electronic spectra of 8a-c are dominated by LLCT and MLCT transitions from HOMO/HOMO-1 to the supporting dppe ligands (ca 300 nm), with similar features noted for both 8d and 8e, albeit at slightly lower energy (ca 350 nm). Additionally, 8e exhibits a prominent feature around 460 nm (22000 cm⁻¹) attributable to the HOMO→LUMO excitation and composed of LLCT and MLCT into the nitroarene fragment; higher-energy LLCT/MLCT into the arene fragment are also apparent around 350 nm (28572 cm⁻¹). Similar events associated with MLCT/LLCT into arene-based orbitals are noted across the series around 300 nm (33333 cm⁻¹). Additionally, for the less withdrawing termini (8a-c) notable contribution from ILCT within both arene and alkynyl fragments is apparent, as is the π=C→π*CP transition.
TD-DFT studies indicate the latter contributes more prominently to higher energy features from 250 nm (40000 cm\(^{-1}\)) to 230 nm (43478 cm\(^{-1}\)) and is also present within 8d and 8e, albeit far less prominent. These features are largely reminiscent of our previous observations for 3 and 4 and suggest diminished contribution from ILCT within the cyaphide fragment in line with increasing electron-withdrawing capacity of the remote substituent, presumably a corollary of associated stabilisation of the HOMO/HOMO-1.

**Electrochemistry**

In order to probe the redox chemistry of the cyaphide complexes, cyclic voltammetry was undertaken for 4 and 8a-e as CH\(_2\)Cl\(_2\) solutions at a platinum disk working electrode (1mm), with NBu\(_4\)PF\(_6\) supporting electrolyte. The data are summarised in Table 3 (see also ESI).

In all cases, an irreversible oxidation event is observed, at potentials that become increasingly anodic in line with the electron-withdrawing character of the arene substituent and, broadly, stabilisation of the HOMO. This is illustrated in the Hammett plot (Figure 10) for 4 and 8a-e, which is broadly consistent with a positive-gradient linear free energy relation, similar to that previously documented for the respective [Ru(dppe)]\(_2\)(C=CC\(_6\)H\(_5\)R)Cl\(_2\)]. We note that the correlation is significantly improved on removal of the datum for 8e (\(R^2 = 0.94\), vs 0.84); indeed, this compound has proven particularly precocious, resisting isolation above 90 % purity and being prone to contamination with electro-active impurities (including the parent 7 PF\(_6\)). Our confidence in this datum is thus somewhat limited and warrants caution. Nonetheless, the comparison as a whole does demonstrate a net electron-withdrawing character for the cyaphide moiety, \(E_{pa}\) generally lying to more anodic potential than for the respective trans-alkynyl chlorides. The situation for 8b and 8c is, however, less clear, \(E_{pa}\) appearing essentially unchanged from the chloride congeners. In the latter case, this is consistent with a previous report of the complexes [Ru(dppe)]\(_2\)(X(C=C\(_6\)H\(_5\)F\(_2\)-p)) \((X = \text{Cl}, \text{C=CH}, \text{C=CCl}\(_2\)H\(_4\)NO\(_2\)) which also showed near invariance of \(E_{pa}\) across the series and presumably reflects the synergic \(-\pi^*+\pi\) character of the p-fluoro substituent, perhaps implying its response to the character of the trans ligand. Certainly the present data would seem to suggest some level of cooperativity between the two disposed ligands across the entire series, further exemplifying their through-conjugate nature. Notwithstanding, the loss of reversibility upon incorporation of cyaphide (cf. Cl) suggests destabilisation of the oxidation product, consistent with a net acceptor character for the C=P moiety. This is consistent with our observation for the homobimetallic 5, in which this effect was manifest in both reduced stability of the mixed-valence state and a marginally more anodic potential for the initial oxidation event.

The reverse scans reveal a greater variation in behaviour, with 8c devoid of notable reductive events within the solvent window, while 8e undergoes a single reduction, close to the solvent break-down potential (ca –1.89 V), which is assignable to reduction of the nitro group (cf. [Ru(dppe)]\(_2\)(C=CC\(_6\)H\(_5\)NO\(_2\))Cl\(_2\), \(E_{pc} = –1.26 \text{ V vs SCE}^{26} –1.72 \text{ V vs Fc/Fc}^{12}\)). In contrast, the remaining systems (4, 8a, 8b and 8d) each exhibit an irreversible reductive event at appreciably cathodic potential (vs \(E_{pa}\)), which are only observable after the initial oxidative sweep, and are thus assigned to the electrogenerated species. In the case of 8d a second irreversible reduction is observed around –1.70 V, which is similarly attributed, though the lack of consistency across the series precludes any meaningful interpretation in lieu of further data. Unfortunately, efforts to isolate and characterise the oxidation products have thus far proven unsuccessful, chemical oxidation with [Fc]X \((X = \text{PF}_6, B(C_6F_5)_4)\) thus far yielding no isolable species. In situ NMR studies remain inconclusive but would seem to suggest the loss of the cyaphide moiety.

**Conclusions**

We have described the synthesis of a library of homologous cyaphide-alkynyl complexes based around the “Ru(dppe)\(_2\)” core, demonstrating the breath of both the synthetic protocol and intrinsic stability of the cyaphide ligand within this motif. Spectroscopic data demonstrate a strong and systematic variation in electronic properties upon variation of the...
terminal substituent, in line with the $\sigma_p$ Hammett parameter and indicative of long-range interplay between the terminal sites of the central conjugated scaffold. This aligns with our expectations for the cyaphide-alkynyls to be bis(alkynyl) analogues, as we have previously illustrated, and is supported by DFT data that illustrate comparable distribution of the frontier orbitals to that of their carbocentric congeners. Notwithstanding, the cyaphide-alkynyls obtained to date consistently exhibit non-ideal electrochemical behaviour, undergoing irreversible oxidation to give, currently uncharacterised, cyaphide-free species. However, the data do suggest an appreciable linear free energy relation and demonstrate cooperativity between cyaphide and the terminal aromatic substituent. Indeed, comparison with the precedent trans-[Ru(dppe)$_2$(C$_{6}$H$_{4}$R)Cl] demonstrates that replacing Cl$^-$ with C$^-$ leads generally to more anodic oxidation potentials; however, where R is only marginally electron releasing a negligible effect is apparent. This may hint at a degree of ambivalent behaviour for the cyaphide ligand, making it a potentially valuable addition to the organometallic ‘tool-kit’, a potential we continue to explore and develop.

**Experimental**

**General methods**

All manipulations were performed under anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or catalytically purified dinitrogen, respectively. Solvents were distilled from appropriate drying agents and stored over either potassium mirrors. General reagents were obtained from appropriate methodology prior to use. Compounds [Ru(dppe)$_2$(C$_{6}$H$_{4}$R)Cl]$_2$, [Ru(dppe)$_2$(C$_{6}$H$_{4}$R)Cl]Cl and NaOPh$_2$ were obtained indirectly (HMBC). Elemental analyses were obtained for samples taken from the bulk following final refluxing or by the departmental service. In lieu of microanalytical data, serving to confirm the identity of the molecular species.

We note that a number of systems have defied acquisition of acceptable EA data, despite all other data being indicative of purity. The ESI includes full spectra for all compounds, demonstrating consistent and comparable purity, with HRMS, in lieu of microanalytical data, serving to confirm the identity of the molecular species.

**X-ray Diffraction Studies.** Single-crystal X-ray diffraction data were recorded on either an Agilent Xcalibur Eos Gemini Ultra or Rigaku XtaLAB AFC11 diffractometer with CCD plate detectors using Cu-K$_\alpha$ ($\lambda = 1.54184$ Å) or Mo-K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. Structure solution and refinement were performed using SHELXS$^{31}$ and SHELXL$^{31}$ respectively, running under Olex2.$^{32}$

**Crystal Data for 3 (CCDC 1902215).** For C$_9$H$_{14}$O$_2$P$_2$Ru$_3$.3.5C$_{6}$H$_{4}$ (M = 1359.06 g/mol): triclinic, P-1 (no. 2), $a = 10.3386(5)$ Å, $b = 13.4558(6)$ Å, $c = 26.1086(13)$ Å, $\alpha = 82.979(4)^\circ$, $\beta = 81.807(4)^\circ$, $\gamma = 67.587(5)^\circ$, $V = 3309.1(3)$ Å$^3$, $Z = 2$, $T = 173(2)$ K, $\mu$(CuK) = 3.419 mm$^{-1}$, $D_i = 1.302$ Mg m$^{-3}$, 11729 independent reflections, Full matrix R$_1$ refinement $R_1 = 0.0558$ on 9839 independent absorption-corrected reflections, $|I > 2\sigma(I); 2\sigma_{\text{max}} = 134.2^\circ|$, 821 parameters, $wR_2 = 0.1495$ (all data).

**Crystal Data for 7a-PF$_6$ (CCDC 1902212).** For C$_9$H$_{14}$O$_2$P$_2$RuSi.CH$_{C_6}$H$_{4}$ (M = 1359.06 g/mol): orthorhombic, P2$_1$2$_1$2$_1$ (no. 19), $a = 13.5338(4)$ Å, $b = 16.2852(4)$ Å, $c = 28.7574(8)$ Å, $V = 6338.1(4)$ Å$^3$, $Z = 4$, $T = 173(2)$ K, $\mu$(CuK) = 4.872 mm$^{-1}$, $D_i = 1.424$ Mg m$^{-3}$, 10598 independent reflections, Full matrix R$_1$ refinement $R_1 = 0.0575$ on 8576 independent absorption-corrected reflections, $|I > 2\sigma(I); 2\sigma_{\text{max}} = 142.5^\circ|$, 743 parameters, $wR_2 = 0.1763$ (all data).

**Crystal Data for 7c-PF$_6$ (CCDC 1902216).** For C$_9$H$_{14}$O$_2$P$_2$RuSi.CH$_{C_6}$H$_{4}$ (M = 1363.03 g/mol): orthorhombic, P2$_1$2$_1$2$_1$ (no. 19), $a = 13.4662(3)$ Å, $b = 16.1621(4)$ Å, $c = 28.4939(7)$ Å, $V = 6201.4(3)$ Å$^3$, $Z = 4$, $T = 173(2)$ K, $\mu$(MoK) = 0.570 mm$^{-1}$, $D_i = 1.460$ Mg m$^{-3}$, 13451 independent reflections, Full matrix R$_1$ refinement $R_1 = 0.0344$ on 12533 independent absorption-corrected reflections, $|I > 2\sigma(I); 2\sigma_{\text{max}} = 54.2^\circ|$, 742 parameters, $wR_2 = 0.0818$ (all data).

**Crystal Data for 8c (CCDC 202214).** For C$_{4}$H$_{18}$O$_2$P$_2$Ru$_2$.2C$_6$H$_{4}$ (M = 1216.16 g/mol): triclinic, P-1 (no. 2), $a = 11.1652(5)$ Å, $b = 15.8226(6)$ Å, $c = 17.5577(5)$ Å, $\alpha = 98.356(3)^\circ$, $\beta = 93.032(3)^\circ$, $\gamma = 104.248(3)^\circ$, $V = 2961.7(2)$ Å$^3$, $Z = 2$, $T = 173(2)$ K, $\mu$(CuK) = 3.782 mm$^{-1}$, $D_i = 1.364$ Mg m$^{-3}$, 10532 independent reflections, Full matrix R$_1$ refinement, $R_1 = 0.0360$ on 8756 independent absorption-corrected reflections, $|I > 2\sigma(I); 2\sigma_{\text{max}} = 134.0^\circ|$, 721 parameters, $wR_2 = 0.0817$ (all data).

**Crystal Data for 8d (CCDC 202213).** For 2(C$_9$H$_{14}$O$_2$P$_2$Ru$_3$.2C$_6$H$_{4}$ (M = 2356.19 g/mol): triclinic, P-1 (no. 2), $a = 9.2841(4)$ Å, $b = 24.8606(11)$ Å, $c = 26.8008(12)$ Å, $\alpha = 110.850(4)^\circ$, $\beta = 90.296(4)^\circ$, $\gamma = 93.812(4)^\circ$, $V = 5765.2(5)$ Å$^3$, $Z = 2$, $T = 100(2)$ K, $\mu$(CuK) = 3.868 mm$^{-1}$, $D_i = 1.357$ Mg m$^{-3}$, 19809 independent reflections, full matrix R$_1$ refinement, $R_1 = 0.1020$ on 12314 independent absorption corrected reflections, $|I > 2\sigma(I); 2\sigma_{\text{max}} = 134.2^\circ|$, 1365 parameters, $wR_2 = 0.3048$ (all data).

**DFT Calculations.** Calculations were performed using Gaussian 09W, Revision C.01,$^{33}$ running on an intel i5-2500 (Quad, 3.3 GHz) with 8 GB RAM, or Gaussian 09 Revision D.01,$^{34}$ running on the Sussex high Performance Cluster. Results were visualised using Gaussview 5.0; orbital contributions and UV/Vis spectra were obtained using GaussSum.$^{35}$ Geometries were optimised with the hybrid density functional B3LYP, using the RECP basis set Lanl2dz for
Ru and 6-31G** for all other atoms. Stationary points were characterised using frequency calculations and confirmed as minima on the basis of no imaginary frequencies. Excited states were calculated using TD-DFT with the B3LYP functional, using Lanl2dz for Ru and 3-21G* on other atoms. Influence of a solvent model was assessed but found to not be significant for the present discussion.

**Electrochemistry.** Cyclic Voltammograms were obtained under anaerobic conditions, (MBraun glovebox, under catalytically purified dinitrogen) at 298 K, for CH₂Cl₂ solutions (0.1 nM) with 0.1 M [Bu₄N]PF₆ supporting electrolyte, using a three-electrode set-up, comprising platinum disk working electrode (1 mm diameter), platinum wire counter electrode and silver wire pseudoreference. Data were recorded using a PalmSens EmStat3+ Blue potentiostat and the PSTrace software package. Potentials are reported relative to the ferrocene/ferrocinium (FcH/FcH⁺) couple, referenced to the FcH⁺/FcH²⁺ couple of a doped sample (−0.56 V relative to FcH/FcH⁺).

**[Ru(dppe)₂Cl₂CC≡C(CH₂)₃Cl] (6f).** To a stirred solution of [Ru(dppe)₂Cl₂]OTf (2.00 g, 2.06 mmol) in CH₂Cl₂ was added ethyl propiolate (0.210 cm³) and the mixture left to stir for 16 h. Removal of the solvent under reduced pressure afforded a brown powder, which was washed with hexanes (3 x 20 cm³) to yield the intermediate vinylidene salt [Ru(dppe)₂(C≡CH₂Cl)Cl₂OTf] in adequate purity for further use. ³¹P(¹H) (CDCl₃): δ 41 (s, 4H). ¹H (CDCl₃): δ 6.75 (t, J = 7.6, 4H), δ 7.4 (t, J = 7.4, 4H), δ 7.3 (m, br, 8H), δ 7.2 (m, br, 8H), δ 7.1 (t, J = 7.6, 8H), δ 6.3 (br, 8H), δ 3.4 (m, br, 1 H), δ 2.9 (m, br, 8H), δ 1.0 (t, J = 7.1 Hz, 3H). ¹³C(¹H)-NMR (CDCl₃, 100.5 MHz, 303 K): δ 134.3 (qnt. (¹J₁₂ = 12.68 Hz, Ru=C)), 163.3 (s, C=O), 134.3 (qnt. (J = 78.48, 2.54 Hz, C₃H₅), 131.9 (d (J = 57.04), C₄H₅), 130.7 (qnt. (J = 84.34, 11.95 Hz, ipso-C₃H₅), 129.0 (qnt. (J = 58.84, 24.40 Hz, CH₃), 106.1 (s, Ru=C=C), 162.1 (s, OCH₃), 29.6 (qnt. (¹J₂₃ = 11.33 Hz, CH₃)), 14.60 (s, CH₃).

The vinylidene salt (0.239 g, 1.91 mmol) was redissolved in CH₂Cl₂ (ca 20 cm³) followed by the addition of DBU (0.63 cm³, 4.01 mmol) and the mixture stirred for 3 h at ambient temperature. The solvent was removed under reduced pressure and the residue washed with degassed methanol (3 x 20 cm³) to yield 6f as a cream solid. Yield: 1.27 g, 65 %. ³¹P(¹H) (CDCl₃): δ 48 (s, 4H). ¹H (CDCl₃): δ 7.4 (m, 8H), δ 7.3 (m, 8H), δ 7.2 (t, J = 7.4, 5.3 Hz, 8H), δ 7.0 (q, J = 17.17 Hz, 16H), δ 4.0 (q, J = 7.1 Hz, 2H), δ 2.7 (m, br, 8H), δ 1.2 (t, J = 7.1 Hz, 3H).

¹³C(¹H)-NMR (CDCl₃, 100.5 MHz, 303 K): δ 152.2 (s, C=O), 141.3 (qnt. (¹J₂₃ = 14.70 Hz), Ru=C=C), 135.5 (m, ipso-C₃H₅), 134.7 (m, br, C₃H₅), 134.2 (m, br, C₃H₅), 129.1 (d (J = 19.09 Hz), C₃H₅), 127.4 (m, br, C₃H₅), 127.2 (m, br, C₃H₅), 107.1 (s, Ru=C=C), 59.3 (s, OCH₃), 30.6 (qnt. (¹J₂₃ = 11.80 Hz, CH₃), 15.0 (s, CH₃). νmax/cm⁻¹ 2049 (CC). Anal. Found: C, 66.35 %; H, 5.01 %; Calcd for C₃₃H₂₆P₂O₂Cl₂Ru: C, 66.44 %; H, 5.14 %.

[Ru(dppe)₂(C≡C(CH₂)₃Me)(¹⁻P=SC(SiMe₃)) (7a)]. To a stirred solution of [Ru(dppe)₂(C≡C(CH₂)₃Me)Cl] (517 mg, 493 μmol) and Me₂SiCl=P (0.088 M in toluene, 7 cm³, 616 μmol) in dichloromethane (ca 20 cm³) was added either AgPF₆ (125 mg, 493 μmol) or Ti(OTf)₃ (174 mg, 493 μmol) as suspension in dichloromethane (ca 10 cm³). The mixture was allowed to stir for 1 h at ambient temperature, the resulting precipitate being removed by filtration (canna). Removal of the volatiles as reduced pressure afforded a brown solid, which was recrystallized from dichloromethane/pentane to afford the pure salt. Characterized as 7a PF₆⁺ yield: 540 mg, 86 %. M.p. 179 °C (dec. uncorrected). ¹H NMR: (399.5 MHz, CDCl₃) δ 7.73 – 7.66 (m, 8H, C(H₃)₅), 7.38 (m, 4H, C(H₃)₅), 7.16 (m, 8H, C(H₃)₅), 7.11 – 7.01 (m, 18H, C(H₃)₅ and Cδ(H₃)), 6.74 (d, J₂₃ = 7.9 Hz, 2H, C(δ(H₃))), 2.83 (br m, 8H, P(≡C≡C(CH₂)₃)), 2.36 (s, 3H, p-CH₃), -0.12 (s, 9H, Si(CH₃)₃). ³¹P(¹H) NMR (162 MHz, CDCl₃): δ 112.3 (quint., J₂,p = 33.3 Hz, 1P, P≡C-Si(CH₃)₃), 42.3 (d, J₂,p = 33.3 Hz, 4P, P(≡C≡C(CH₂)₃)), -144.5 (sept., J₂,p = 710 Hz, PF₆⁻). ¹³C(¹H) NMR (100 MHz, CDCl₃): δ 188.4 (P≡C-Si(CH₃)₃), indirect observation). 136.2 (C₃H₅), 134.2 (m, C₃H₅), 132.6 (m, C₃H₅), 130.9 (C₃H₅), 129.9 (C₃H₅), 129.1 (C₃H₅), 128.5 (dt, J₂,p = 17.8, 2.5 Hz, C₃H₅), 124.2 (C₃H₅), 116.8 (Ru=C=C, indirect observation), 30.8 (m, P(≡C≡C(CH₂)₃)), 21.5 (p-CH₃), 0.31 (br s, Si(δ(CH₃))), 31P(¹H) NMR (376 MHz, CDCl₃): δ -73.8 (d, J₂,p = 710 Hz, PF₆⁻). ²⁴Si NMR (79 MHz, CDCl₃): δ -13.2 (P≡C-Si(CH₃)₃, indirect observation). IR ν/cm⁻¹: 1269 (C≡P)P, 2112 (C≡P). Elem. Anal. Calc. for C₆₃H₄₅F₆₅P₄RuSi:C: 61.27 %; H: 5.06 %; Found: C: 61.07 %; H: 5.00 %.

[Ru(dppe)₂(C≡C(CH₂)₃Me)(¹⁻P=SC(SiMe₃))]⁺ (7a⁺). In analogous fashion to 7a⁺, the crude material was obtained as a pale yellow solid, which was washed with benzene, then recrystallized from dichloromethane / pentane. Characterized as 7a PF₆⁺ yield: 412 mg, 65 %. M.p. 208 °C (dec. uncorrected). ¹H NMR: (399 MHz, CDCl₃) δ 7.65 – 7.53 (m, 8H, C(H₃)₅), 7.34 (m, 9H, C(H₃)₅), 7.14 (m, 8H, C(H₃)₅), 6.96 (m, 15H, C₃H₅), 6.90 (m, 2H, o-CH₃), 6.70 (m, 2H, m-CH₃), 2.84 (br m, 8H, P(≡C≡C(CH₂)₃)), -0.13 (br s, P≡C-S(δ(CH₃))₃). ³¹P(¹H) NMR: (162 MHz, CDCl₃) δ 111.9 (quint., J₂,p = 33.7 Hz, 1P, P≡C-Si(CH₃)₃), 42.0 (d, J₂,p = 33.0 Hz, P(≡C≡C(CH₂)₃))
1H NMR: (399 MHz, CDCl3) δ 7.88 (d, JH-H = 8.4 Hz, 2H, m-C6H5); 7.56 (m, 8H, C6H5); 7.39 (m, 4H, C6H5); 7.31 (m, 4H, C6H5); 7.17 (m, 8H, C6H5); 7.04 (m, 16H, C6H5); 6.74 (d, JH-H = 8.4 Hz, 2H, m-C6H5); 3.92 (s, 3H), 2.86 (br m, 8H, P=CH2CH2P), -0.11 (s, 9H, P=Si-CH(SiH3)). 13P(1H) NMR: (162 MHz, CDCl3) δ 110.9 (m, 1P, P=Si-CH(SiH3)); 41.8 (d, Jp-H = 33.5 Hz, 4P, P=CH2CH2P).

13C(NMR: (162 MHz, CDCl3) δ 134.2 (m, C6H5); 134.2 (m, C6H5); 134.2 (m, C6H5); 134.2 (m, C6H5); 131.1 (m, C6H5); 131.0 (d, J = 7.2 Hz, C6H5); 129.9 (C6H5); 129.7 (C6H5); 128.3 (dt, J = 18.5, 2.0 Hz, C6H5); 127.5 (C6H5); 127.5 (C6H5); 122.8 (C6H5); 119.6 (Ru-C=C); 115.9 (Ru-C=C), indirect observation. 3F(NMR: (736 MHz, CDCl3) δ -78.0 (s, -CF3). 25Si NMR (79 HZ, CDCl3): δ 16.5 (P=Si-CH(SiH3)), indirect observation. IR ν/cm-1: 1265 (C=O), 1714 (C=O), 2090 (C=C). MS (HR-ESI+): [C6H4F2O3P=SiR3]+. Calc. 1173.2402; Found 1173.2271.

In analogous fashion to previous examples, the crude material was obtained as a pale brown solid, which was washed with benzene. Characterized as 7e.ν/10 min, Me4Si=CH3 (0.0723 M in toluene, 9 cm3, 651 µmol) was added and the resulting mixture stirred for 1 h at ambient temperature. The mixture was filtered and the solvent removed under reduced pressure to afford the crude product, which was washed with benzene (3 x 5 cm3) and dried in vacuo, then recrystallized from dichloromethane. Yield 577 mg, 77 %.

1H NMR (CDCl3): δ 7.15 (1H, t, J = 7.5 Hz, dppe), 7.23 (8H, t, J = 7.6 Hz, dppe), 7.15 (16H, t, J = 7.5 Hz, dppe) 4.12 (2H, q, J = 7.1 Hz, OCH2), 2.82 (8H, m, (br, PC6H5P), 1.30 (3H, t, J = 7.1 Hz, CH3), -0.1 (9H, s, SiCH3).

13P(1H) NMR (CDCl3, 298 K): δ 108 (1H, quint, J = 35 Hz, C6H5P=SiMe3) 41.3 (4P, J = 35 Hz, dppe).

13C(1H)-NMR (CDCl3): δC 193.5 (d, J = 86 Hz, C6H5), 153.1 (s, C-O), 134.1 (d, J = 85, 2.4 Hz, CH3); 131.9 (d, J = 32 Hz, C6H5); 132.5 (d, J = 714, 11.6 Hz, ipso-C6H5), 129.3 (d, J = 22, 2.2 Hz, C6H5); 123.7 (d, J = 321 Hz, Ru=C=C), 110 (d, J = 22 Hz, Ru=C=C), 61.3 (s, OCH3), 30.2 (q, J = 11.7 Hz, CH3), 15.2 (s, CH3). After allowing to stir for 1 h at ambient temperature. The volatiles were removed under reduced pressure and the residue extracted into benzene (15 cm3) and filtered (cannula). The benzene was removed under reduced pressure and the resulting solid washed with hexane, affording 8a as a yellow solid. Isolated yield 65 mg, 50 %. M.p. 188 °C (dec. uncorrected).

1H NMR: (399 MHz, CDCl3) δ 7.60 (br, m, 6H), 7.51 (br, m, 7H), 7.34 - 6.80 (m, 29H), 6.65 (d, JH-H = 7.8 Hz, 2H), 2.88 (br m, 4H, P=CH2CH2P), 2.65 (br m, 4H, P=CH2CH2P), 2.29 (s, 3H, P=CH). 13P(1H) NMR: (162 MHz, CDCl3) δ 159.6 (br s, 1P, C=O), 50.8 (d, Jp-H = 5.2 Hz, 4P, P=CH2CH2P).

13C(1H) NMR: (100 MHz, CDCl3) δ 281.8 (br, s, C=O), 170.0 (quin, J = 172.2 Hz, 11.1 Hz, C6H5), 134.9 - 135.4 (m, C6H5), 133.5 (s, C6H5), 130.2 (br s, C6H5), 129.5 (d, J = 18.4 Hz, C6H5), 128.9 (s, C6H5) 128.8 (C6H5); 127.7 (br, m, C6H5); 127.5 (dt, J = 22.5, 2.2 Hz, C6H5); 119.6 (br, Ru=C=C), 31.7 (quin, J = 12.0 Hz, P=CH2CH2P), 21.5 (s, P=CH).


In a mixture of 7b.ν/10 min, Me4Si=CH3 (0.0723 M in toluene, 9 cm3, 651 µmol) was added and the resulting mixture stirred for 1 h at ambient temperature. The mixture was filtered and the solvent removed under reduced pressure to afford a pale orange solid. Isolated yield 63 mg, 60 %. 1H NMR (399 MHz, CDCl3) δ 7.60 (br, m, 8H, o-C6H5); 7.53 (br m, 8H, o-C6H5); 7.45 (br m, 2H, Ph-M); 7.27 (t, 4H, JH-H = 7.5 Hz, p-C6H5); 7.20 (4H, JH-H = 7.5 Hz, o-C6H5); 7.12 (s, 1H, s-P-H); 7.08 (t, 8H, JH-H = 6.9 Hz, m-C6H5); 6.97 (t, 8H, JH-H = 6.9 Hz, p-C6H5), 6.75 (d, 2H, JH-H = 7.5 Hz, o-P-H), 2.78 (br m, 8H, JH-H = 9.45 Hz, C6H5). 13P(1H) NMR (162 MHz, CDCl3) δ 160.4 (br m, 1P, C=O), 50.8 (d, Jp-H = 3.5 Hz, P=CH2CH2P).

13C(1H) NMR (100 MHz, CDCl3) δ 281.5 (br, m, C=O), 137.8 (m, Jp-H = 10 Hz, ipso-C6H5), 136.1 (m, Jp-H = 10 Hz, ipso-C6H5), 135.4, (m, o-C6H5), 135.2 (br
In comparable fashion to 8a isolated yield 97 mg, 73 %.

[**Rudppe**(C≡CCH₂CO,Me)(C≡P)](8d). In comparable fashion to 8a isolated yield 55 mg, 70 %.

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Notes and references


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34 Gaussian 09, Revision D.01, authors as above, Gaussian, Inc., Wallingford CT, 2013.


36 Compound 8e has proven difficult to obtain in purity, rarely exceeding 90 % and often contaminated by the persistence of 7eOTf. Though impure, the data available are appropriate to the discussion and do not compromise the conclusions.
A homologous series of cyaphide-alkynyl complexes is prepared and their structural, spectroscopic and electrochemical features probed, revealing significant cooperativity between the -C≡P and remote substituents on the trans-alkynyl ligand, indicative of long-range communication; analogy to classical alkynyls is apparent, with cyaphide exhibiting appreciable acceptor character, moderated by the remote substituent.