Controlled reactivity of terminal cyaphide complexes: Isolation of the 5-coordinate $[\text{Ru}(\text{dppe})_2(\text{CP})]^+$

Article (Accepted Version)

Levis, Madeleine C, Pearce, Kyle G and Crossley, Ian R (2019) Controlled reactivity of terminal cyaphide complexes: Isolation of the 5-coordinate $[\text{Ru}(\text{dppe})_2(\text{CP})]^+$. Inorganic Chemistry. ISSN 0020-1669

This version is available from Sussex Research Online: <http://sro.sussex.ac.uk/id/eprint/87428/>

This document is made available in accordance with publisher policies and may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher's version. Please see the URL above for details on accessing the published version.

Copyright and reuse:

Sussex Research Online is a digital repository of the research output of the University.

Copyright and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable, the material made available in SRO has been checked for eligibility before being made available.

Copies of full text items generally can be reproduced, displayed or performed and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Controlled Reactivity of Terminal Cyaphide Complexes: Isolation of the 5-coordinate $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})]^+$.

Madeleine C. Levis, Kyle G. Pearce and Ian R. Crossley*

Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ, UK.

Supporting Information Placeholder

ABSTRACT: The novel cyaphide complex *trans*- $[\text{Ru}(\text{dppe})_2\text{Me}(\text{C}\equiv\text{P})]$ is obtained in excellent yields and exhibits the first instance of controlled reactivity of any terminal-cyaphide complex. Its treatment with $\text{ZnX}_2/\text{PPh}_3$ effects selective metathesis of the methyl moiety to afford the unprecedented halo-cyaphide complexes *trans*- $[\text{Ru}(\text{dppe})_2(\text{X})(\text{C}\equiv\text{P})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), which are structurally characterized ($\text{X} = \text{Cl}, \text{Br}$). Exemplified with the *trans*-bromide, these compounds are susceptible to substitution of the halides by nucleophilic reagents – illustrated with Me_2Mg – and also readily undergo halide abstraction by TiOTf to afford the first hypocoordinate cyaphide complex, *viz.* $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})]\text{OTf}$, which is isolable in bulk and exhibits good stability. NMR spectroscopic and crystallographic data reveal the latter to adopt a square pyramidal geometry with an accessible coordinate vacancy, which is susceptible to the addition of nucleophiles. This is illustrated analytically by reactions with Me_2Mg and $\text{LiC}\equiv\text{CPh}$, and with its facile bulk carbonylation to afford *trans*- $[\text{Ru}(\text{dppe})_2(\text{CO})(\text{C}\equiv\text{P})]^+$.

INTRODUCTION

Cyaphide ($-\text{C}\equiv\text{P}$), a notional analogue of cyanide or acetylide, is the very simplest, yet has been among the most elusive of the phosphacarbons. Despite the relatively extensive study of phosphalkynes ($\text{RC}\equiv\text{P}$) over the past five decades^{1,2} the discrete cyaphide anion remains unknown, due to an apparently intrinsic instability,³ while its engagement as a ligand for transition metals dates only from 1992, with Angelici's report of the transient *trans*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}(\text{C}\equiv\text{P})$,^{4a} trapped as the $\eta^1, \eta^2\text{-C}, P$ -bridged $[(\text{Et}_3\text{P})_2\text{Pt}(\text{Cl})(\mu\text{:}\eta^1\text{:}\eta^2\text{-C}\equiv\text{P})\text{Pt}(\text{PEt}_3)_2]$.⁴ The discrete *C*-terminal coordination of cyaphide was finally unequivocally demonstrated only in 2006, with Grützmacher's seminal report of $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$ (**1**),⁵ the first such complex to be isolated and structurally characterized. Subsequent activity was initially slow to develop and sparse, being limited to Russell's *in situ* observation of $[\text{Mo}(\text{dppe})_2(\eta^1\text{-P}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{P})]^-$.⁶ More recently, however, we have developed a range of complexes comprising *trans*-disposed cyaphide and alkynyl ligands that exhibit through-conjugation, *viz.* $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\text{C}\equiv\text{P})]$ (**2**, $\text{R} = \text{CO}_2\text{Me}$ **a**; $\text{C}_6\text{H}_4\text{R}'$, $\text{R}' = \text{Me}$ **b**, H **c**, F **d**, CO_2Me **e**, OMe **f**, NO_2 **g**, $\text{C}\equiv\text{CRu}(\text{dppe})_2(\text{C}\equiv\text{P})$ **h**),^{7a-c} accessed via a modification of the Grützmacher methodology (Scheme 1). Meanwhile, Meyer has reported a single uranium species obtained via the unexpected fragmentation of the phosphaehtynolate ion (^-OCP).⁸

Despite these advances the reactivity of cyaphide complexes remains an unknown, most examples either appearing inert, or exhibiting a propensity for decomposition with loss of the terminal cyaphide ligand.^{5,7a} This has necessarily precluded the post-synthetic modification of such complexes, requiring that the cyaphide ligand is installed as a final synthetic step. Scope has thus been essentially limited to the availability of precursors of the type *trans*- $[\text{Ru}(\text{dppe})_2\text{R}]^+$ and a reliance on

these then being amenable to installation of an $\eta^1\text{-P}\equiv\text{CSiR}_3$ ligand; this cannot be assured, given the low basicity of phosphalkyne lone pairs.² Indeed, the reluctance of this step bears significant responsibility for the dearth of such compounds reported to date.

Scheme 1. General synthetic route to precedent cyaphide complexes.⁵⁻⁷

Reagents conditions: i) MOTf ($\text{M} = \text{Ag}, \text{Ti}$) or AgPF_6 , CH_2Cl_2 ; ii) $\text{P}\equiv\text{CSiMe}_3$ (in toluene); iii) NaOPh or KO^tBu , THF .

In seeking to develop and exploit the coordination and organometallic chemistry of cyaphide, it is thus essential to establish access to complexes of this ligand that are amenable to post-synthetic ligand exchange, while leaving the terminal ' $\text{C}\equiv\text{P}$ ' moiety intact. Herein, we report the first such examples, achieved by controlled exchange of the *trans*-ligand within a *trans*- $[\text{Ru}(\text{dppe})_2\text{R}(\text{C}\equiv\text{P})]$ scaffold, and leading ultimately to the isolation of an unprecedented 5-coordinate cyaphide-containing cation. We further illustrate the convenience

of this complex as a synthetic precursor through ligand addition at the vacant site.

RESULTS AND DISCUSSION

The ruthenium-methyl fragment $[\text{Ru}(\text{dppe})_2\text{Me}]^+$, prepared by methide abstraction from $[\text{Ru}(\text{dppe})_2\text{Me}_2]$, itself obtained via modification of literature protocols,⁹ reacts with $\text{P}\equiv\text{CSiMe}_3$ to afford $\text{trans-}[\text{Ru}(\text{dppe})_2(\text{Me})(\eta^1\text{-P}\equiv\text{CSiMe}_3)]^+$ (**3**⁺), subsequent treatment with stoichiometric NaOPh effecting its conversion to $\text{trans-}[\text{Ru}(\text{dppe})_2(\text{Me})(\text{C}\equiv\text{P})]$ (**4**). Characteristic spectroscopic signatures for the phosphacarbon and dppe moieties confirm the formation of **3**⁺ (δ_{P} 121.3, 46.7 $^2J_{\text{PP}}$ 28 Hz) and **4** (δ_{P} 177.9, 58.9 $^3J_{\text{PP}}$ 4 Hz), with retention of the Ru-Me fragment in each case apparent from the ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra (δ_{H} -0.34 , δ_{C} 2.7 **3**⁺; δ_{H} -2.31 , δ_{C} -9.8 **4**). The conversion of **3**⁺ to **4** is accompanied by loss of signals associated with the silyl and triflate moieties and a significant decrease in the $\text{C}\equiv\text{P}$ stretching frequency (ν_{CP} = 1217 cm^{-1} **4**, vs 1269 cm^{-1} **3**⁺), as we have previously noted,⁷ with the identity of **4** ultimately confirmed from crystallographic data (Figure 1). While the connectivity is unequivocal, disorder about the cyaphidic carbon center precludes meaningful discussion of the $\text{C}\equiv\text{P}$ distance, which consequently appears truncated with respect to prior examples,^{5,7} while the $\text{Ru}-\text{C}_{\text{CP}}$ linkage is notably longer, albeit still within the range seen for $\text{Ru}-\text{C}_{\text{CC}}$ systems recorded in the CCDC.¹⁰ The *trans* methyl ligand and remaining core geometry are similarly comparable to respective precedents.

Figure 1: Molecular structure of **4** (ellipsoids set at 50 %, hydrogen atoms omitted and supporting ligands simplified for clarity). C1 is disordered across two sites (90%/10%), but not readily modelled, distorting the $\text{C}\equiv\text{P}$ distance. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P1–C1 1.392(8), Ru1–C1 2.186(8), Ru1–C2 2.238(6), Ru1–P2 2.370(2), Ru1–P3 2.364(2), Ru1–P4 2.341(2), Ru1–P5 2.338(2); P1–C1–Ru1 165.5(5), C1–Ru1–C2 171.2(3), C1–Ru1–P2 98.4(2), C1–Ru1–P3 102.13(15), C1–Ru1–P4 85.94(15), C1–Ru1–P5 82.8(2).

In seeking to coordinatively engage the cyaphide moiety of **4** its interaction with $\text{ZnBr}_2(\text{PPh}_3)_2$ was explored, resulting in the exclusive formation of a new complex (**5a**, Scheme 2). Unexpectedly, **5a** retains the characteristic spectroscopic sig-

nature of a terminal cyaphide (δ_{P} 135), albeit shifted to lower frequency, but with no evidence for further coordination. It is, however, devoid of signals associated with the σ -methyl ligand, the exchange of methyl for bromide being ultimately confirmed by crystallographic data (Figure 2 and SI (**5b**, *vide infra*)). These clearly illustrate the *trans*-arrangement of halide and $\text{C}\equiv\text{P}$ (which are both refined equally across two sites), the $\text{C}\equiv\text{P}$ distances being in line with both **1**^{5a} and the alkynyl systems **2a,c-e**^{7a,c} and exhibiting near perfect linear coordination, as observed in **1**, **2c** and **2d**. In contrast, the $\text{Ru}-\text{C}_{\text{CP}}$ distances appear appreciably truncated, while the $\text{Ru}-\text{X}$ linkages lie toward the upper bounds recorded in the CCDC ($\text{X} = \text{Cl}$ 2.30–2.60 $\text{\AA}$; Br 2.45–2.75 $\text{\AA}$).¹⁰

Scheme 2. Syntheses for **5a** – **c**.

Reagents conditions: i) $\text{ZnX}_2(\text{PPh}_3)_2$, THF, 18 h.; ii) ZnX_2 , PPh_3 (5 mol%), THF, 18 h.

Figure 2: Molecular structure of **5a** (ellipsoids set at 50 %, hydrogen atoms omitted and supporting ligands simplified for clarity). The bromide and cyaphide ligands are refined across two equal positions (50 % occupancy) such that the ruthenium atom sits on an inversion center; equivalent atoms are generated by symmetry transformation. The structure for **5b** is similar and depicted in SI. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for **5a**: P1–C1 1.544(10), Ru1–C1 1.901(9), Ru1–Br1 2.690(2); P1–C1–Ru1 175.8(5), C1–Ru1–Br1 177.1(2), C1–Ru1–P2 97.0(2), C1–Ru1–P3 95.2(2), C1–Ru1–P2' 83.0(2), C1–Ru1–P3' 84.8(2).

Optimal formation of **5a** is achieved by replacing the zinc complex with ZnBr_2 and sub-stoichiometric PPh_3 (5 mol%), the analogous reactions with ZnX_2 ($\text{X} = \text{Cl}$, I , Scheme 2) affording respectively **5b** and **5c**, albeit that these are less amenable to bulk isolation in analytical purity. This appears, to the best of our knowledge, to be the first example of zinc-halide mediated halogen/methyl exchange at a transition metal,¹¹ and apparently requires the presence of at least catalytic

PPh_3 , implying that $\text{ZnX}_2(\text{PPh}_3)_2$, formed *in situ*, is the active species. While we have not probed the mechanism of this conversion in detail, we can reasonably dismiss adventitious water giving rise to HX *in situ*. This follows in part from stoichiometric considerations, given both the scrupulous drying of reagents and stringent observation of anaerobic conditions; moreover, we observe that the addition of stoichiometric HCl to **4** is uncontrolled, yielding only small amounts of **5b** alongside numerous unidentified species, while excess of HCl also cleaves the cyaphide moiety, giving $\text{Ru}(\text{dppe})_2\text{Cl}_2$ as the sole identifiable product. We have also observed the reaction of **4** with $\text{ZnBr}_2 / \text{PPh}_3$ by NMR, the characteristic Ru-Me resonance of **4** (δ_{H} -2.3 , *qnt*, J_{PH} 5.6 Hz) being replaced by a broadened ($w_{1/2} = 8$ Hz) signal to higher frequency (δ_{H} -0.83). Though we have not definitively identified the species responsible, it does lie in a region consistent with Zn-Me derivatives,^{12,13} which might suggest Me/X metathesis. Significantly, we observe no evidence for the liberation of CH_4 ,¹⁴ discounting protonation of the methyl, and thus involvement of adventitious acid.

The formation of **5a-c** is notable, given that they have proven inaccessible by more ‘traditional’ routes, the trigonal pyramidal $[\text{Ru}(\text{dppe})_2\text{Cl}]^+$ being apparently inert toward $\text{P}\equiv\text{CSiMe}_3$. Indeed, only by generating the cation *in situ* in the presence of a large excess of $\text{P}\equiv\text{CSiMe}_3$ (enabling trapping prior to relaxation to a trigonal bipyramidal geometry), could a species consistent with $[\text{Ru}(\text{dppe})_2\text{Cl}(\text{P}\equiv\text{CSiMe}_3)]^+$ be observed, and then only at trace levels.¹⁵ This has previously impeded access to this synthetically versatile series of compounds, which present obvious targets for further metathesis. Indeed, this is illustrated by treating THF solutions of **5a** with Me_2Mg , which affords some evidence for the slow regeneration of **4**. In contrast, reaction with $\text{LiC}\equiv\text{CPh}$ requires the presence of TiOTf , presumably to facilitate abstraction of the halide. The latter may suggest the intermediacy of a discrete 5-coordinate species, and thus at least transient stability for the cyaphide ligand within a less encumbered coordination sphere. This possibility was probed by treating a dichloromethane solution of **5a** with stoichiometric thallium triflate, resulting in an immediate color change from yellow to deep purple, with concomitant deposition of a white precipitate. Filtration and removal of the volatiles afforded **6.OTf**, its formulation as $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})]\text{OTf}$, being ultimately confirmed crystallographically (*vide infra*).

Spectroscopically, the cyaphidic (δ_{P} 154 ; *q*, J_{PP} 7 Hz) and supporting dppe (δ_{P} 52.1 ; *d*, J_{PP} 7 Hz) resonances of **6⁺** are clearly observed, their respective multiplicities implying a square-pyramidal geometry. The triflate counterion is confirmed by ^{19}F -NMR data and appears uncoordinated, which was further supported by using AgPF_6 in place of TiOTf , resulting in directly comparable data for the cation. We note that while one might envisage accessing **6⁺** more directly by treating the *trans*-methyl complex **4** with Brookhart’s acid, $[\text{H}(\text{OEt}_2)][\text{BAR}^*_4]$, this reaction is unsuccessful, leading instead to decomposition, albeit ultimately with complete demethylation and the apparent formation of trace levels of methane. While the bulk phosphorus-containing products of this reaction have not been identified, they appear devoid of cyaphide. We have also attempted to abstract methide from **4** with TiOTf (*cf.* formation of $[\text{Ru}(\text{dppe})_2\text{Cl}]^+$), and of hydride from samples of **1** using Ph_3CBF_4 ; in neither instance did a reaction occur.

Figure 3: Orthogonal projections of the molecular structure of **6⁺** in crystals of the triflate salt (ellipsoids set at 50 %, hydrogen atoms and triflate counter ion omitted and supporting ligands simplified for clarity). Within the lower projection (illustrating π -stacking between the dppe ligands) C2/C5 appear superimposed onto the Ru1-C1 bond. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: P1-C1 $1.573(4)$, C1-Ru1 $1.904(4)$, Ru1-P2 $2.363(1)$, Ru1-P3 $2.380(1)$, Ru1-P4 $2.379(1)$, Ru1-P5 $2.351(1)$; P1-C1-Ru1 $178.9(2)$, P2-Ru1-P3 $81.31(3)$, P2-Ru1-P4 $99.16(4)$, P3-Ru1-P5 $99.91(4)$, P4-Ru1-P5 $80.86(3)$, C1-Ru1-P2 $86.48(13)$, C1-Ru1-P3 $94.26(12)$, C1-Ru1-P4 $94.88(12)$, C1-Ru1-P5 $85.84(13)$.

The crystallographic data for **6⁺** (Figure 3) confirm the discrete square-pyramidal complex cation, which exhibits a flattened basal plane, from which the mutually *trans* phosphines are displaced by $\pm 5.5^\circ$; this is consistent with precedent square-pyramidal ruthenium complexes bearing similarly bulky ancillary ligand sets, as recorded in the CCDC.¹⁰ It is, however, notable that there are no direct comparators incorporating either ethynyl or cyanide ligands in the apical site, whether at ruthenium or any other group 8 or 9 metal. Indeed, though the intermediacy of 5-coordinate ruthenium alkynyl complexes is invoked¹⁶ in the synthesis of bis(alkynyl)¹⁷ – and, indeed, cyaphide-alkynyl⁷ – complexes, relatively few discrete examples are known, while in those that are the alkynyl¹⁸ (or cyano¹⁹) ligand adopts a basal, rather than apical, coordination site.

The most closely related comparator to **6⁺** is thus Grützmacher’s archetypal **1**, the hydride ligand of which im-

parts minimal steric perturbation. It is, however, notable that while the C≡P linkages of **1** and **6**⁺ are near identical, the cyaphide ligand is significantly more tightly held in the cation (Ru–C 1.904(4) Å, vs 2.057(2) Å in **1**), presumably in part due to loss of the hydridic *trans* influence; indeed, a comparable scenario is apparent in bromide **5a** (Ru–C 1.901(9) Å), while our previously reported alkynyl derivatives (**2a,d-f**) are more in line with **1**. The geometries of **1** and **6**⁺ are otherwise largely comparable, with **6**⁺ exhibiting only marginal widening of the cleft formed by the flanking dppe scaffold. This appears to be a corollary of constraints imposed by π - π interactions between the dppe ligands, facilitated by the reduced sterics providing more flexibility in the coordination environment. Such minimal geometric perturbation leaves the vacant *trans* coordination site readily accessible, as illustrated by reactions with Me₂Mg and LiC≡CPh, which respectively generate **4** and **2c**.^{7c}

These reactions hint at the synthetic potential of **6**⁺, which should offer an unrivalled starting point from which to access a range of cyaphide complexes, including hitherto inaccessible variants. Indeed, a case in point is the installation of a *trans* carbonyl ligand, which we have long sought (to aid investigation of the electronic character of cyaphide) without success. Bubbling of CO through a dichloromethane solution of **6.OTf**, effects a near instantaneous color change (from purple to yellow), the subsequent removal of the volatiles yielding exclusively **7.OTf**, formulated as [Ru(dppe)₂(CO)(C≡P)].OTf, on the basis of spectroscopic and crystallographic data (Figure 4).

Figure 4: Molecular structure of **7**⁺ in crystals of the triflate salt (ellipsoids set at 50 %, hydrogen atoms omitted and supporting ligands simplified for clarity). The asymmetric unit comprises two half-cations with the C≡O and C≡P ligands modelled across two positions (50 %) occupancy, this disorder requires that the respective carbon atoms be modelled isotropically.²⁰ The second molecule is depicted in the SI file. Selected bond lengths [Å] and angles [°]: *molecule 1 (shown)*: P1–C2 1.53(2), Ru1–C2 2.06(2), Ru1–C1 1.888(19), C1–O1 1.14(2), Ru1–P2 2.417(1), Ru1–P3 2.418(1), P1–C2–Ru1 176.0(13), C2–Ru1–C1 178.3(7), Ru1–C1–O1 177.8(17). *molecule 2 (SI)*: P≡C 1.53(2), Ru–C_{CP} 2.141(11), Ru–C_{CO} 1.815(11), C≡O 1.216(16), Ru–P5 2.399(1), Ru–P6 2.383(2), P–C–Ru 173.6(7), C_{CP}–Ru1–C_{CO} 170.0(5), Ru–C–O 175.6(10).

NMR spectroscopic data demonstrate retention of the cyaphide (δ_P 181, q , J_{PP} 10 Hz) and supporting dppe ligands (δ_P 43.6, d , J 10 Hz), while both cyaphide (ν_{CP} 1261 cm⁻¹) and carbonyl (ν_{CO} 1980 cm⁻¹) are apparent in the infrared spectrum. The latter is comparable to those reported for the very limited range of *trans*-[Ru(dppe)₂(CO)(C≡CR)] (ν_{CO} 1977 – 1984 cm⁻¹)²¹ and in line with more general examples of ruthenium(II) alkynyl carbonyl complexes, with electronically similar ancillary scaffolds,²² consistent with an alkynyl-like character for the C≡P moiety. The C≡P stretching frequency is among the highest recorded for cyaphide complexes, reflecting its *trans*-disposition from a more potent π -acid. The structural data are less conclusive due to uncertainty imparted by disorder of the C≡P and C≡O units, which also differ between two independent molecules within the cell; however, they would in general appear to reflect a truncated C≡P moiety and relatively long Ru–C_{CP} distance,²³ with the opposing trend for the C≡O ligand. Taken together, these data indicate the previously noted acceptor character of the ‘C≡P’ ligand,⁷ though appreciable in respect of alkynyls, is weak in comparison to that of C≡O. This firmly supports assignment of the C≡P ligand as an alkynyl analogue, but with a moderately enhanced acceptor character.

CONCLUSIONS

We have described the first examples of controlled reactivity within the coordination sphere of a transition metal cyaphide complex, resulting in facile exchange of the *trans* ligand, while retaining the cyaphide moiety. This has afforded access – *via* an apparently novel zinc-induced demethylation – to a range of *trans*-halo cyaphides that are susceptible to further metathesis and halide abstraction, the latter affording a discrete 5-coordinate complex cation, *viz.* [Ru(dppe)₂(C≡P)]⁺ (**6**⁺). Isolable in bulk as the triflate salt, the latter is the first complex to feature terminally ligated cyaphide within a flexible coordination sphere, albeit that a square-pyramidal geometry is adopted, thus the C≡P moiety is only marginally less screened than in precedent examples. The geometry is apparently enforced by ligand-ligand interactions and results in a readily accessible coordinate vacancy, which is susceptible to the addition of nucleophiles. This is illustrated by treatment with Me₂Mg, which regenerates the parent complex [Ru(dppe)₂Me(C≡P)] (**4**), while the reaction with LiCCPh offers access to a previously reported alkynyl derivative (**2c**).^{7c} More significantly, treatment with CO affords facile access to the previously elusive [Ru(dppe)₂(CO)(C≡P)]OTf (**7.OTf**), data for which concur with the assignment of cyaphide as an alkynyl analogue.

The facility of ligand addition to **6**⁺ renders it a convenient starting point from which to further develop the range of cyaphide complexes, circumventing difficulties associated with installing the C≡P ligand to a pre-formed scaffold. This both increases the accessibility of cyaphide complexes, allowing more extensive exploitation of this rare ligand, and offers potential for variation of the supporting ligands, the breadth and scope of which we are currently exploring.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or dinitrogen. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å, for CH₂Cl₂, CHCl₃, Et₂O, THF) or potassium mirrors. Reagents were obtained from Sigma-Aldrich, Fisher or Fluorochem and purified by appropriate methods before use; Anhydrous ZnX₂ were further purified and extended heating at >200 °C under high vacuum (10⁻⁷ mbar) and subliming (>250 °C, 10⁻⁷ mbar). Me₂Mg,²⁴ Me₃SiC≡P,^{7,25} [Ru(dppe)₂Cl]OTf²⁶ and NaOPh²⁷ were prepared by literature methods. Unless otherwise stated NMR spectra were recorded at 303 K on a Varian VNMRs 400 (¹H 399.50 MHz, ¹³C 100.46 MHz, ¹⁹F 375.87 MHz, ³¹P 161.71 MHz, ²⁹Si 79.37 MHz) spectrometer. All spectra are referenced to external Me₄Si, 85 % H₃PO₄ and CFCl₃ as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBC) spectra, while silicon shifts were determined indirectly (HMBC). IR spectra were recorded on a Perkin Elmer Spectrum One instrument. Mass spectra were recorded by Dr A. Abdul-Sada of the departmental service and elemental analyses were obtained either by Mr S. Boyer, London Metropolitan University Analytical Service (**3.OTf**), or Pascher Labs, Germany. **CAUTION! Thallium(I) salts have acute toxicity through ingestion and inhalation, with potential long-term health impact. Ensure proper containment and PPE are used when handling these materials and all residues are collected, labelled and disposed of as containing thallium.**

X-ray diffraction studies. Single crystal X-ray diffraction data were recorded on an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector using Cu-Kα (λ = 1.54184 Å) radiation. Structure solution and refinement were performed using SHELXT²⁸ and SHELXL²⁹ respectively, running under Olex-2.³⁰

Synthesis of [Ru(dppe)₂Me₂]. In a modification of the procedure for [Ru(dppe)₂Me₂],⁹ a mixture of [RuCl(dppe)₂]OTf (2.260 g, 2.09 mmol) and Me₂Mg (0.185 g, 3.41 mmol) was suspended in Et₂O (ca 50 cm³) at ambient temperature, resulting in an immediate colour change from red to yellow-brown; the resulting solution was stirred for 18 hours. Filtration afforded a yellow/brown solid, which was washed with Et₂O (3 x 20 cm³) and dried *in vacuo*. The compound was confirmed by reference to related literature data,⁹ then used directly in the subsequent step. Yield: 2.00 g, 89 %. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=6.55–7.49 (*m* (*br*), dppe), 2.41 (8H, *m* (*br*), C₂H₄), -1.18 (6H, *qnt*, *J* = 4.36 Hz, CH₃). ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=59.2 (4H, *s*, PPh₃). The bulk has *cis/trans* ratio of ca 5:95 and is used in crude form for the next step.

Synthesis of [Ru(dppe)₂Me]OTf. A mixture of [Ru(dppe)₂Me₂] DCM (1.689 g, 1.57 mmol) and TiOTf (0.569 g, 1.61 mmol) was suspended in CH₂Cl₂ (30 cm³) and allowed to stir for 1 hour, resulting in a gradual color change from yellow-brown to red-purple. The mixture was filtered via cannula and volatiles removed from the filtrate under reduced pressure, to afford a red-purple solid that was dried *in vacuo*. Compound identity was confirmed by reference to literature data.³¹ Yield: 0.980 g, 59%. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=7.38 (8H, *m* (*br*), dppe), 7.22 (8H, *t*, *J* = 7.6 Hz, dppe), 7.14 (8H, *t*, *J*_{HH} = 7.6 Hz, dppe), 6.78 (16H, *d*, *J*_{PH} = 6.5 Hz, dppe), 2.51 (8H, *m* (*br*), C₂H₄), -0.9 (3H, *m* (*br*), CH₃). ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=55.7 (4H, *s*, PPh₃). Compound is used without further purification in the next step.

Synthesis of *trans*-[Ru(dppe)₂Me(η¹-P≡CSiMe₃)]OTf (3.OTf**).** To a stirred suspension of [Ru(dppe)₂(Me)]OTf (1.36 g, 12.1 mmol) in 1,4-dioxane (ca 20 cm³) was added Me₃SiC≡P (25 cm³, 0.05 mol dm⁻³, 12.5 mmol), then the mixture left to stir for 1 hour. The resulting precipitate was isolated by filtration (cannula) and dried *in vacuo* to afford **3.OTf** as a cream solid. The bulk sample retains an equivalent of dioxane and trace levels of apparently the *cis* isomer. Yield: 1.068 g, 71%. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=7.51 (8H, *m* (*br*), *meta*-C₆H₅), 7.5 (4H, *t*, *J* = 7.3 Hz, *para*-C₆H₅), 7.4 (4H, *t*, *J* = 7.5 Hz, *para*'-C₆H₅), 7.3 (8H, *t*, *J* = 7.3 Hz, *ortho*-C₆H₅), 7.1 (8H, *t*, *J* = 7.3 Hz, *ortho*-C₆H₅), 6.8 (8H, *m* (*br*), *meta*-C₆H₅), 2.7 (8H, *m* (*br*), C₂H₄), -0.01 (9H, *s*, SiMe₃), -0.35 (3H, *m* (*br*), CH₃). ¹³C{¹H}-NMR (100.45 MHz, CD₂Cl₂): δ_C=184.8 (*d*, *J* = 69 Hz, C≡P), 134.7 (*qnt*, *J* =

10.01 Hz, *ipso*-C₆H₅), 133.4 (*qnt*, *J* = 2.56 Hz, *meta*-C₆H₅), 132.8 (*qnt*, *J* = 2.10 Hz, *meta*-C₆H₅), 131.1 (*s*, *para*-C₆H₅), 130.5 (*s*, *para*-C₆H₅), 128.6 (*qnt*, *J* = 2.34 Hz, *ortho*-C₆H₅), 128.4 (*qnt*, *J* = 2.36 Hz, *ortho*-C₆H₅), 28.9 (*qnt*, *J* = 11.7 Hz, CH₂CH₂), 2.12 (*m*, CH₃), 0.35 (*d*, *J* = 5.11 Hz, SiMe₃); ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P 121.3 (1P, *qnt*, *J* = 28 Hz, C≡P), 46.7 (4P, *d*, *J* = 28 Hz, PPh₂); ¹⁹F NMR (375.86 MHz, CD₂Cl₂): δ_F -78.9 (*s*, OTf); ²⁹Si NMR (79.37 MHz, CD₂Cl₂): δ_{Si} 15.4 (Ru-PCSiMe₃). IR (solid, ATR) ν/cm⁻¹: 1269 (C≡P). Calcd for C₆₀H₆₀P₃F₃O₃SSiRu.C₄H₈O₂: C, 59.57 %, H, 5.31 %. Found: C, 59.89 %, H, 5.18 %.

Synthesis of *trans*-[Ru(dppe)₂Me(C≡P)] (4**).** A solution of **3.OTf** (1.068 g, 0.91 mmol) in THF (ca 20 cm³) was cooled to -30 °C, prior to drop-wise addition of a solution of NaOPh (0.138 g, 1.2 mmol) in THF (ca 5 cm³) over the course of 10 minutes. Upon complete addition the mixture was stirred for ca 2 min, removed from cold bath and the volatiles immediately removed under reduced pressure to afford a yellow-brown solid, which was washed with acetonitrile (ca 3 x 15 cm³) and dried *in vacuo*, yielding a yellow solid. Yield: 0.543 g, 63%. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=8.4 (8H, *m* (*br*), *meta*-C₆H₅), 7.3 (4H, *t*, *J*=7.3 Hz, *para*-C₆H₅), 7.2 (8H, *t*, *J*=7.5 Hz, *ortho*-C₆H₅), 7.1 (4H, *t*, *J*=7.4 Hz, *para*-C₆H₅), 6.9 (8H, *t*, *J*=7.6 Hz, *ortho*-C₆H₅), 6.5 (8H, *d*, *J*=7.5 Hz, *meta*-C₆H₅), 2.6 (8H, *m* (*br*), C₂H₄), -2.3 (3H, *qnt*, *J*=5.6, CH₃); ¹³C{¹H} NMR (100.46 MHz, CD₂Cl₂): δ_C=294 (*m* (*br*), C≡P),³² 139.1 (*qnt*, *J*_{CP}=9.77 Hz, *ipso*-C₆H₅), 135.9 (*qnt*, *J*_{CP}=9.90 Hz, *ipso*-C₆H₅), 136.1 (*m*(*br*), *meta*-C₆H₅), 134.7 (*qnt*, *J*_{CP} = 2.02 Hz, *meta*-C₆H₅), 129.8 (*s*, *para*-C₆H₅), 128.5 (*s*, *para*-C₆H₅), 127.4 (*qnt*, *J*_{CP}=1.99 Hz, *ortho*-C₆H₅), 127.2 (*qnt*, *J*_{CP}=2.33 Hz, *ortho*-C₆H₅), 30.9 (*s*, CH₂CH₂), -10.0 (*m* (*br*), CH₃); ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=177.9 (1P, *m* (*br*), C≡P), 58.9 (4P, *d*, *J*_{PP}=4.3 Hz, PPh₂). IR (solid, ATR) ν/cm⁻¹: 1217 (C≡P), 3046 (CH₃). Anal. Calcd for C₅₄H₅₁P₃Ru: C, 67.85 %, H, 5.38 %. Found: C, 68.13 %, H, 5.43 %. **Crystal data for 4 (CCDC 1938745):** Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. C₅₄H₅₁P₃Ru (*M*_w = 955.83 g mol⁻¹), *monoclinic*, *P* 21/*c* (No. 14), *a*=23.6755(12), *b*=11.5267(6), *c*=17.2942(8) Å, β=104.670(5), *V*=4565.7(5) Å³, *Z*=4, *T*=173(2) K, μ(*Cu-Kα*)=4.712 mm⁻¹, *D*_c=1.391 Mg m⁻³, 8676 independent reflections, full matrix *F*² refinement *R*_i=0.0614 on 6218 independent absorption corrected reflections, [*I* > 2σ(*I*); 2θ_{max}= 142.45 °], 543 parameters, *wR*₂= 0.1573 (all data).

Synthesis of *trans*-[Ru(dppe)₂Br(C≡P)] (5a**).** Anhydrous ZnBr₂ (0.305 g, 1.35 mmol), 5mol% PPh₃ (0.017 g, 0.065 mmol) and **4** (1.289 g, 1.35 mmol), were combined in a Schlenk prior to the addition of THF (ca 20 cm³). The resulting solution was stirred for 18 hours, leading to the precipitation of a yellow solid, which was isolated by filtration (cannula) and dried *in vacuo*. Yield: 1.027 g, 75%. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=7.6 (8H, *m* (*br*), *meta*-C₆H₅), 7.32 (4H, *m* (*br*), *meta*-C₆H₅), 7.26 (8H, *dt*, *J*=7.5, 20.0 Hz, *para*-C₆H₅), 7.10 (16H, *dt*, *J*=7.6, 21.7 Hz, *ortho*-C₆H₅), 2.9 (8H, *m* (*br*), C₂H₄); ¹³C{¹H} NMR (100.46 MHz, CD₂Cl₂): δ_C=136.7 (*m* (*br*), *ipso*-C₆H₅), 136.2 (*m* (*br*), *meta*-C₆H₅), 135.8 (*qnt*, *J*_{CP}=2.3 Hz, *meta*-C₆H₅), 130.5 (*s*, *para*-C₆H₅), 130.3 (*s*, *para*-C₆H₅), 128.1 (*m*, *ortho*-C₆H₅), 31.4 (*qnt*, *J*_{CP}=11.6 Hz, CH₂CH₂) the cyaphide carbon could not be resolved;³² ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=135.4 (1P, *m* (*br*), C≡P), 44.8 (4P, *d*, *J*_{PP}=4.3 Hz, PPh₂). IR (solid, ATR) ν/cm⁻¹: 1249 (C≡P). HRMS (ESI): *m/z* calcd. for [C₅₃H₄₈P₃BrRu]⁺: 1020.0659; Found: 1020.0577 [RMS Err 8 ppm]. Anal. Calcd for C₅₃H₄₈P₃BrRu: C, 62.36 %, H, 4.74 %. Found: C, 61.6 %, H, 4.73 %. **Crystal data for 5 (CCDC 1938746):** Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. C₅₃H₄₈BrP₃Ru (*M*_w = 1020.73 g mol⁻¹), *triclinic*, *P*-1 (No. 2), *a*=10.155(1), *b*=10.5071(12), *c*=12.593(1) Å, α=71.169(9), β=85.317(7), γ=62.172(12), *V*=1120.8(2) Å³, *Z*=1, *T*=173(2) K, μ(*Cu-Kα*)=5.844 mm⁻¹, *D*_c=1.512 Mg m⁻³, 4334 independent reflections, full matrix *F*² refinement *R*_i=0.0340 on 3412 independent absorption corrected reflections, [*I* > 2σ(*I*); 2θ_{max}= 145.78 °], 286 parameters, *wR*₂= 0.0747 (all data).

Synthesis of *trans*-[Ru(dppe)₂Cl(C≡P)] (5b). Anhydrous ZnCl₂ (0.007 g, 0.052 mmol), PPh₃ (0.001 g, 0.003 mmol) and **4** (0.050 g, 0.052 mmol), were combined in a Schlenk prior to the addition of THF (*ca* 5 cm³). The resulting solution was stirred for 18 hours, leading to the precipitation of a yellow solid, which was isolated by filtration (cannula) and dried *in vacuo*. Yield: 0.035 g, 80%. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H 7.8 (8H, m (br), *meta*-C₆H₅), 7.3 (8H, m (br), *meta*-C₆H₅), 7.26 (8H, dt, *J*=7.4, 16.00 Hz, *para*-C₆H₅), 7.06 (16H, dt, *J*=7.6, 15.86 Hz, *ortho*-C₆H₅), 2.9 (8H, m (br), C₂H₄); ¹³C{¹H} NMR (100.46 MHz, CD₂Cl₂): δ_C 265.4 (m (br), C≡P),³² 136.6 (qnt, *J*_{CP}=10.3 Hz, *ipso*-C₆H₅), 135.7 (m (br), *meta*-C₆H₅), 135.6 (qnt, *J*_{CP}=2.5 Hz, *meta*-C₆H₅), 135.4 (qnt, *J*_{CP}=10.4 Hz, *ipso*-C₆H₅), 130.1 (s, *para*-C₆H₅), 130.0 (s, *para*-C₆H₅), 127.4 (dnt, *J*_{CP}=2.6, 2.31, 4.6 Hz, *ortho*-C₆H₅), 31.0 (s, CH₂CH₂). ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P 132 (1P, m (br),³² C≡P), 46.2 (4P, d, *J*_{PP}=4.2 Hz, PPh₂). IR (solid, ATR) ν/cm⁻¹: 1250 (C≡P). HRMS (ESI): *m/z* calcd. for [C₅₃H₄₈P₅ClRu]⁺: 976.1169; Found: 976.1240 [RMS Err 7 ppm]. This compound routinely analyses > 10 % low on carbon; presumably reflecting a trace level of high-mass contaminant, which we have been unable to identify. Crystal data for **5b** (CCDC 1938747): Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. C₅₃H₄₈ClP₅Ru (*M_w*=976.28 g mol⁻¹), monoclinic, *P* 21/c (No. 14), *a*=23.6006(6), *b*=11.4193(3), *c*=17.2737(4) Å, β=103.781(3), *V*=4521.3(2) Å³, *Z*=4, *T*=173(2) K, μ(*Cu-Kα*)=5.303 mm⁻¹, *D_c*=1.434 Mg m⁻³, 6901 independent reflections, full matrix *F*² refinement *R_I*=0.0438 on 5275 independent absorption corrected reflections, [*I* > 2σ(*I*); 2θ_{max}=122.32 °], 569 parameters, *wR*₂=0.1123 (all data).

Synthesis of *trans*-[Ru(dppe)₂I(C≡P)] (5c). Anhydrous ZnI₂ (0.008 g, 0.025 mmol), PPh₃ (0.001 g, 0.003 mmol) and **4** (0.023 g, 0.024 mmol), were combined in a Schlenk prior to the addition of THF (*ca* 5 cm³). The resulting solution was stirred for 18 hours, leading to the precipitation of a yellow solid, which was isolated by filtration (cannula) and dried *in vacuo*. Yield: 0.020 g, 75%. Poor solubility has proven limiting for the acquisition of spectroscopic data, and the material has not been obtained in analytical purity. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H 7.5 (8H, m (br), C₆H₅), 7.4 (8H, m (br), C₆H₅), 7.3 (8H, dt, *J*=7.4, 15.5 Hz, C₆H₅), 7.1 (16H, dt, *J*=7.6, 15.9 Hz, C₆H₅), 2.9 (8H, m (br), C₂H₄); ¹³C{¹H} NMR (100.46 MHz, CD₂Cl₂): δ_C=137.0 (unres., *ipso*-C₆H₅), 136.0 (br, *meta*'-C₆H₅), 135.4 (br, *ipso*'-C₆H₅), 135.2 (br, *meta*-C₆H₅), 130.2 (br, *para*'-C₆H₅), 129.8 (br, *para*-C₆H₅), 127.6 (br, *ortho*-C₆H₅), 127.5 (br, *ortho*'-C₆H₅), 30.5 (unres., CH₂CH₂) (cyaphide carbon not resolved);³² ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P 140 (1P, m (br), C≡P), 42.1 (4P, d (br), PPh₂). ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P 140 (1P, m (br), C≡P), 42.1 (4P, d (br), PPh₂).

Synthesis of [Ru(dppe)₂(C≡P)]₂OTf (6.OTf). Compound **5a** (0.400 g, 0.39 mmol) was combined with TfOTf (0.140 g, 0.39 mmol) prior to the addition of CH₂Cl₂ (*ca* 20 cm³). The resulting solution was stirred for *ca.* 2 hours, before separating from the TIBr by filtration (cannula). The volatiles were removed from the filtrate under reduced pressure to afford a purple solid, which was dried *in vacuo*. The sample can be further purified by recrystallization from benzene, yielding the benzene solvate. Yield: 0.365 g, 87%. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=7.7 (8H, m (br), *meta*-C₆H₅), 7.4 (4H, t, *J*=7.5 Hz, *para*-C₆H₅), 7.3 (4H, t, *J*=7.5 Hz, *para*-C₆H₅), 7.1 (16H, t, *J*=7.6 Hz, *ortho*-C₆H₅), 6.5 (8H, m (br), *meta*-C₆H₅), 3.0 (4H, qnt, *J*=8.0 Hz C₂H₄), 2.6 (4H, qnt, *J*=8.0 Hz C₂H₄); ¹³C{¹H} NMR (100.46 MHz, CD₂Cl₂): δ_C=265 (m (br), C≡P),³² 134.1 (m (br), *meta*-C₆H₅), 133.4 (qnt, *J*_{CP}=2.9 Hz *meta*-C₆H₅), 132.3 (m, *ipso*-C₆H₅), 131.9 (s, *para*-C₆H₅), 131.2 (s, *para*-C₆H₅), 129.7 (qnt, *J*_{CP}=2.1 Hz, *ortho*-C₆H₅), 128.7 (qnt, *J*_{CP}=2.5 Hz, *ortho*-C₆H₅), 121.5 (q, *J*_{CF}=320 Hz, CF₃), 29.4 (qnt, *J*_{CP}=11.7 Hz, CH₂CH₂); ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=154 (1P, qnt, *J*_{PP}=7.2 Hz, C≡P), 52.1 (4P, d, *J*_{PP}=7.2 Hz, PPh₂); ¹⁹F NMR (375.86 MHz, CD₂Cl₂): δ_F=-78.9 (s, OTf). IR (solid, ATR) ν/cm⁻¹: 1242 (C≡P). Anal. Calcd for C₅₄H₄₈P₅F₃O₃SRu·0.66(C₆H₆): C; 61.00 %, H; 4.59 %. Found: C; 61.70 %, H; 4.66 % (recrystallized sample as benzene solvate). Cryst-

tal data for **6.OTf** (CCDC 1938748): Crystals were obtained by slow recrystallization from benzene at ambient temperature. C₅₃H₄₈P₅Ru·SO₂CF₂·(1.5C₆H₆) (*M_w*=1207.07 g mol⁻¹), triclinic, *P* -1 (No. 2), *a*=10.8285(2), *b*=13.5818(3), *c*=19.4936(4) Å, α=99.007(2), β=102.137(2), γ=91.643(2), *V*=2762.65(10) Å³, *Z*=2, *T*=100(2) K, μ(*Cu-Kα*)=4.487 mm⁻¹, *D_c*=1.451 Mg m⁻³, 10477 independent reflections, full matrix *F*² refinement *R_I*=0.0506 on 9214 independent absorption corrected reflections, [*I* > 2σ(*I*); 2θ_{max}=143.20 °], 685 parameters, *wR*₂=0.1265 (all data).

Synthesis of [Ru(dppe)₂(CO)(C≡P)]₂OTf (7.OTf). CO gas was bubbled through a dichloromethane solution of **6.OTf** (0.094 g, 0.086 mmol) for 2 min, resulting in a color change of the solution from purple to pale yellow. Removal of the volatiles under reduced pressure afforded **7.OTf** as an off-white solid as a mono-CH₂Cl₂ solvate. ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H=7.57 (8H, m (br), *meta*-C₆H₅), 7.45 (4H, t, *J*=7.3 Hz, *para*'-C₆H₅), 7.42 (4H, t, *J*=7.4 Hz, *para*-C₆H₅), 7.23 (8H, t, *J*=7.5 Hz, *ortho*'-C₆H₅), 7.19 (8H, t, *J*=7.3 Hz, *ortho*-C₆H₅), 7.01 (8H, m (br), *meta*'-C₆H₅), 3.08 (4H, qnt, *J*=8 Hz C₂H₄), 2.65 (4H, qnt, *J*=8 Hz C₂H₄); ¹³C{¹H} NMR (100.46 MHz, CD₂Cl₂): δ_C=249 (m (br), C≡P),³² 200.5 (qnt, *J*_{CP} 10 Hz, 4 Hz, C≡O), 134.8 (qnt, *J*_{CP} 2 Hz, *meta*-C₆H₅), 133.4 (qnt, *J*_{CP}=11 Hz *ipso*'-C₆H₅), 132.9 (qnt, *J*_{CP} 2.7 Hz, *meta*'-C₆H₅), 131.9 (s, *para*'-C₆H₅), 131.7 (s, *para*-C₆H₅), 131.0 (qnt, *J*_{CP}=12 Hz, *ipso*-C₆H₅), 129.5 (qnt, *J*_{CP}=2 Hz, *ortho*'-C₆H₅), (qnt, *J*_{CP}=2.5 Hz, *ortho*-C₆H₅), 121.5 (q, *J*_{CF}=322 Hz, CF₃), 30.0 (qnt, *J*_{CP}=11.7 Hz, CH₂CH₂); ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=181.3 (1P, qnt, *J*_{PP}=10 Hz, C≡P), 52.1 (4P, d, *J*_{PP}=10 Hz, PPh₂); ¹⁹F NMR (375.86 MHz, CD₂Cl₂): δ_F=-78.9 (s, OTf). IR (solid, ATR) ν/cm⁻¹: 1980 (CO), 1261 (C≡P). Anal. Calcd for C₅₅H₄₈F₃O₃P₅SRu·(CH₂Cl₂): C; 55.91 %, H; 4.19 %. Found: C; 55.61 %, H; 4.08 %. Crystal data for **7.OTf** (CCDC 1947211): Crystals were obtained by slow recrystallization from benzene at ambient temperature. C₅₅H₄₈F₃O₃P₅SRu·(C₆H₆) (*M_w*=1196.02 g mol⁻¹), monoclinic, *C*2/c (No. 15), *a*=23.3771(4), *b*=12.6192(3), *c*=37.6417(9) Å, β=101.416(2), *V*=10884.6(4) Å³, *Z*=8, *T*=100(2) K, μ(*Cu-Kα*)=4.564 mm⁻¹, *D_c*=1.460 Mg m⁻³, 10225 independent reflections, full matrix *F*² refinement *R_I*=0.0546 on 8252 independent absorption corrected reflections, [*I* > 2σ(*I*); 2θ_{max}=143.40 °], 830 parameters, *wR*₂=0.1257 (all data).

Treatment of **4 with HCl.** To an NMR sample of **4** in CD₂Cl₂ was added 1 equivalent, or an excess, of HCl in Et₂O (1 M). The sample were sealed and repeatedly inverted (rotor) overnight then analyzed by ³¹P{¹H} NMR.

Treatment of **4 with [H(OEt)₂][BAR^f₄].** To an NMR sample of **4** in CD₂Cl₂ was added 1 equiv. Brookhart's acid. The sample was sealed and agitated, then monitored by NMR after 5 min. and upon completion.

NMR scale reaction of **4 with ZnBr₂ / PPh₃ (*in situ*).** To a solution of **4** in THF (with C₆D₆ capillary) was added 1 equiv. ZnBr₂ and *ca* 10 mol% PPh₃. The sample was sealed and agitated until completion then observed by ³¹P{¹H} NMR.

Reaction of **5a with Me₂Mg.** Samples of **5a** (31 mg, 0.03 mmol) and Me₂Mg (3 mg, 0.04 mmol) were combined in THF (*ca* 10 cm³) and stirred overnight. The mixture was filtered to remove magnesium salts, then free volatiles removed under reduced pressure and the crude product analyzed by ¹H and ³¹P{¹H} NMR in CD₂Cl₂. Key signatures for **4**: ¹H NMR (399.5 MHz, CD₂Cl₂): δ_H -2.1 (3H, qnt, *J*=5.6 Hz, CH₃), 2.6 (14H, m (br), C₂H₄, **4+** unknown). ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=179.8 (1P, m (br), C≡P), 60.7 (4P, d, *J*_{PP}=4.3 Hz, PPh₂). Solvent shift effects (cf. pure **4**) result from appreciable residual THF in the solvent mixture – we have noted, but not probed, significant shift changes between CH₂Cl₂ and THF.

Reaction of **6+ with LiCCPh.** To a sample of **6+**, generated *in situ* from **5a** (50 mg, 0.05 mmol) and TfOTf (2 mg, 0.05 mmol) in THF (5 cm³) was added one equivalent of LiCCPh in THF (5 cm³) and the mixture stirred overnight. The volatiles were removed and the crude material analyzed by ³¹P{¹H} NMR in CD₂Cl₂, indicating >80 % conversion: **2c**: ³¹P{¹H} NMR (161.71 MHz, CD₂Cl₂): δ_P=161.7 (1P, br, C≡P), 51.0 (4P, d, *J*_{PP}=3.6 Hz, PPh₂) (> 80 %). **6+**: ³¹P{¹H} NMR

(161.71 MHz, CD₂Cl₂): δ_P =154 (1P, *qnt*, J_{PP} =7.2 Hz, C≡P), 52.5 (4P, *d*, J_{PP} =7.2 Hz, PPh₂) (< 20 %).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

¹H, ¹³C{¹H}, ³¹P{¹H}, ¹⁹F-NMR, 2D (¹H-¹³C HSQC, HMBC; ¹H-²⁹Si HMBC) spectra for all compounds as appropriate; high-resolution mass spectra (HRMS) for **5a** and **5b**; ORTEP plot and selected distances / angles for **5b** and second molecule of **7**⁺ (PDF)

Accession Codes

CCDC 1938745-1938748 and 1947211 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax:+44 1223 336033

AUTHOR INFORMATION

Corresponding Author

* Email for I.R.C.: i.crossley@sussex.ac.uk.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Royal Society, Engineering and Physical Sciences Research Council (EP/N016785/1 and EP/N509784 [DTP studentship 1805157, MCL]) and University of Sussex (KGP). We thank Dr J.F.C. Turner and Prof. A.F. Hill for useful discussion and Drs N. Tsoureas and S. M. Roe for assistance with structural refinement.

REFERENCES

- (1) For reviews of the general fields of phosphacarbon and phosphalkyne chemistry see: (a) Mathey, F. Phospha-organic chemistry: Panorama and perspectives. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578-1604. (b) Nixon, J.F. Phospha-alkynes, RC≡P: New building blocks in inorganic and organometallic chemistry. *Chem. Soc. Rev.* **1995**, *24*, 319-328. (c) Appel, R. in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, (Eds.: Regitz, M.; Scherer, O. J.), Thieme, Stuttgart, **1990**. (d) Markovski, L. N.; Romaneko, V. D. Phosphaalkynes and phosphaalkenes. *Tetrahedron* **1989**, *45*, 6019-6090. (e) Appel, R.; Knoll, F.; Ruppert, I. Phospha-alkenes and phosphaalkynes. Genesis and Properties of the (p-p)π-Multiple Bond. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731-744. (f) *Phosphorus: The Carbon Copy* (Eds.: Dillon, K. B.; Mathey, F.; Nixon, J.F.), Wiley, Chichester, **1998**.
- (2) (a) Nixon, J. F. Recent developments in the organometallic chemistry of phospha-alkynes, RCP. *Coord. Chem. Rev.* **1995**, *145*, 201-258. (b) Nixon, J. F. The Coordination Chemistry of Compounds Containing Phosphorus-Carbon Multiple Bonds. *Chem. Rev.* **1988**, *1327*-1362.
- (3) (a) M^ó, O.; Yáñez, M.; Guillemin, J.-C.; Riague, E. H.; Gal, J.-F.; Maria, P.-C.; Poliat, C. D. The Gas-Phase Acidity of HCP, CH₂CP, HCAs, and CH₃Cas: An Unexpected Enhanced Acidity of the Methyl Group. *Chem. Eur. J.* **2002**, *8*, 4919-4924. (b) Pascoli, G.;

Lavendy, H. Theoretical Study of C_nP, C_nP⁺, C_nP⁻ (*n* = 1 – 7) Clusters. *J. Phys. Chem. A* **1999**, *103*, 3518-3524.

(4) (a) Jun, H.; Young Jr., V. G.; Angelici, R. J. Phosphorus Analogue (C≡P⁻) of a Bridging Cyanide (C≡N⁻) Ligand: Synthesis and Structure of (Cl)(PEt₃)₂Pt(μ-C≡P)Pt(PEt₃)₂. *J. Am. Chem. Soc.* **1992**, *114*, 10064-10065. (b) Jun, H.; Angelici, R. J. Bridging Cyaphide (C≡P⁻) and Bridging Aryl Isocyaphide (C≡P-R) Ligands: Synthesis and Characterization of (X)(PEt₃)₂Pt(μ-C≡P)Pt(PEt₃)₂ and (X)(PEt₃)Pt(μ-C≡P-R)Pt(PEt₃)₂(X) (X = Cl, Br; R = 2,46-Tri-tert-butylphenyl). *Organometallics* **1994**, *13*, 2454-2460. (c) Konze, W. V.; Young Jr., V. G.; Angelici, R. J. Functionalization of η¹η²-Bridging Cyaphide (C≡P⁻) Ligands: Trinuclear η¹η²η²-Bridging Cyaphide and Dinuclear bridging Isocyaphide (C≡PR) Complexes of Platinum. *Organometallics* **1999**, *18*, 258-267.

(5) (a) Cordaro, J. G.; Stein, D.; Rüggeger, H.; Grützmacher, H. Making the true "CP" ligand. *Angew. Chem.* **2006**, *118*, 6305-6308. (b) Ehlers, A.; Cordaro, J. G.; Stein, D.; Grützmacher, H. Mechanism of cyaphide (C≡P⁻) formation. *Angew. Chem.* **2007**, *119*, 8024-8027.

(6) Mansell, S.M.; Green, M.; Russell, C. A. Coordination chemistry of trimethylsilylphosphaalkyne: A phosphaalkyne bearing a reactive substituent. *Dalton Trans.* **2012**, *41*, 14360-14368.

(7) (a) Trathen, N.; Leech, M. C.; Crossley, I. R.; Greenacre, V. K.; Roe, S.M. Synthesis and electronic structure of the first cyaphide-alkynyl complexes. *Dalton Trans.* **2014**, *43*, 9004-9007. (b) Leech, M. C.; Crossley, I. R. Through-conjugation of two phosphaalkyne (C≡P) moieties mediated by a bimetallic scaffold. *Dalton Trans.* **2018**, *47*, 4428-4432. (c) Furfari, S. K.; Leech, M. C.; Trathen, N.; Levis, M. C.; Crossley, I. R. Cyaphide-alkynyl complexes: metal-ligand conjugation and the influence of remote substituents. *Dalton Trans.* **2019**, *48*, 8131-8143.

(8) Hoerger, C. J.; Heinemann, F. W.; Louyriac, E.; Maron, L.; Grützmacher, H.; Meyer, K. Formation of a Uranium-Bound η¹-Cyaphide (CP⁻) Ligand via Activation and C-O Bond Cleavage of Phosphaethynolate (OCP⁻). *Organometallics* **2017**, *36*, 4351-4354.

(9) (a) Field, L. D.; Magill, A. M.; Shearer, T. K.; Dalgarno, S. J.; Turner, P. Mono- and bis-acetylidoruthenium(II) complexes by controlled metathesis of methylruthenium complexes with acetylenes. *Organometallics* **2007**, *26*, 4776-4780. (b) Field, L. D.; Magill, A. M.; Bhadbhade, M. M.; Dalgarno, S. J. Formation of ruthenaindenes by cyclometallation of ruthenium(II) diarylbutenyne complexes. *Organometallics* **2009**, *28*, 5514-5521.

(10) Search of CCDC: Groom, C. R.; Bruno, I.; Lightfoot, M. P.; Ward, S. C. The Cambridge structural database. *Acta Crystallogr., Sect. B: Struct. Sci.*, **2016**, *72*, 171-179.

(11) While we cannot absolutely discount precedent for ZnX₂ effecting halogenative demethylation of transition metals, we have been unable to locate any such examples. Rather, alkylation of transition metals by zinc-alkyls is common, in line with expected reactivity and relative electronegativity arguments.

(12) While no data have been reported for MeZnBr or MeZnBr(L)₂, data are known for, *inter alia*, MeZn(OAc) (δ -0.68),^{12a} MeZnCl(L)₂ (δ_H -0.13)^{12b} and [(MeZn)₂{(μ-OR)(μ-Cl)}]₂ (δ_H -0.3),^{12c} which constitute reasonable comparators.

(13) (a) Hermann, W. A.; Rost, A. M. J.; Mitterpleininger, J. K. M.; Szesni, N.; Sturm, S.; Fischer, R. W.; Kühn, F. E. A Cheap, Efficient, and Environmentally Benign Synthesis of the Versatile Catalyst Methyltrioxorhenium (MTO). *Angew. Chem. Int. Ed.* **2007**, *46*, 7301-7303. (b) Schultz, S.; Münch, M.; Flörke, U. Reactions of Carbodiimides with ZnEt₂ and MeZnCl. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2221-2225. (c) Lewinski, J.; Marciniak, W.; Ochal, Z.; Lipkowski, J.; Justyniak, I. A Novel Tetranuclear [MeZn(μ₃-OCH₂CH₂SMc)Zn(μ-Cl)Me]₂ Adduct Derived from the Interaction of CH₂Cl₂ with an Alkylzinc Complex. *Eur. J. Inorg. Chem.* **2003**, 2753-2755.

(14) The resonance for CH₄ is typically observed around 0.2 ppm in thf and in the general region 0.16 – 0.20 ppm across the range of common solvents. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176-2179.

- (15) Winrow, P.; Crossley, I. R. unpublished observations
- (16) See for example: (a) De Lós Rios, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. Unexpected formation of a tetranuclear heterobimetallic complex by reaction of a ruthenium alkynyl with AgCF_3SO_3 . *Organometallics* **1998**, *17*, 3356-3363. (b) Lynam, J. M.; Nixon, T. D.; Whitwood, A. C. Solvent and phosphine dependency in the reaction of $\text{cis-RuCl}_2(\text{P-P})_2$ (P-P = dppe or dppe) with terminal alkynes. *J. Organomet. Chem.* **2008**, *693*, 3103-3110.
- (17) For more general examples of bis(alkynyl) synthesis: (a) Touchard, D.; Haquetter, P.; Daridor, A.; Romero, A.; Dixneuf, P. H. Novel ruthenium allenylidene and mixed alkynyl allenylidene complexes: Crystal structure of $\text{trans}[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Ru}(\text{C}\equiv\text{CPh})(=\text{C}=\text{C}=\text{CPh}_2)\text{PF}_6]$. *Organometallics* **1998**, *17*, 3844-3852. (b) Marqués-González, S.; Parthey, M.; Yufit, D. S.; Howard, J. A. K.; Kaupp, M.; Low, P. J. Combined spectroscopic and quantum chemical study of $[\text{trans-Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^1-4)_2(\text{dppe})_2]^{n+}$ and $[\text{trans-Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^1-4)(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^2-4)(\text{dppe})_2]^{n+}$ ($n = 0, 1$) Complexes: Interpretations beyond the Lowest Energy Conformer Paradigm. *Organometallics* **2014**, *33*, 4947-4963. (c) Schauer, P. A.; Skelton, B. W.; Koutsantonis, G. A. Coordinating Tectons 4: Coordination Chemistry of the 4,5-Diazafluoren-9-yl Moiety as a Metallo-Ligand for Allenylidene Complexes. *Organometallics* **2015**, *34*, 4975-4988 and references therein.
- (18) (a) Liu, P. N.; Li, J.; Su, F. H.; Ju, K. D.; Zhang, L.; Shi, C.; Sung, H. H. Y.; Williams, I. D.; Fokin, V. V.; Lin, Z.; Jia, G. Selective formation of 1,4-disubstituted triazoles from ruthenium-catalyzed cycloaddition of terminal alkynes and organic azides: Scope and reaction mechanism. *Organometallics* **2012**, *31*, 4904-4915. (b) Wieder, N. L.; Carroll, P. J.; Berry, D. H. Structure and reactivity of acetylene complexes of bis(imino)pyridine ruthenium(0). *Organometallics* **2011**, *30*, 2125-2136. (c) Chatwin, S. L.; Mahon, M. F.; Prior, T. J.; Whittlesey, M. K. Reactivity of the N-heterocyclic carbene complexes $[\text{Ru}(\text{IMes})_2(\text{CO})\text{HX}]$ (X = Oh, Cl) with alkynes. *Inorg. Chim. Acta* **2010**, *363*, 625-632. (d) Zhang, Q. -F.; Lai, C. -Y.; Qong, W. -Y.; Leung, W. -H. σ -Acetylide complexes of ruthenium(IV) and osmium(IV) thiolates. *Organometallics* **2002**, *21*, 4017-4020. (e) Tsuda, T.; Shiro, M. Preparation reaction and catalysis of the new ruthenium carbamate complex $\text{Et}_2\text{NCO}_2\text{RuH}(\text{CO})(\text{PCy}_3)_2$. *Organometallics* **1999**, *18*, 2741-2743. (f) Huang, D.; Heyn, R. H.; Bollinger, J. C.; Caulton, K. G. Oxidative addition of a Si-C(sp) bond to ruthenium: Synthesis and reactivity of $\text{Ru}(\text{SiMe}_3)(\text{C}\equiv\text{CSiMe}_3)(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$. *Organometallics* **1997**, *16*, 292-293. (g) Pedersen, A.; Tilsted, M.; Følting, K.; Caulton, K. G. Oxidatively Induced Reductive Elimination from $\text{Ru}(\text{C}_2\text{Ph})_2(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$ and $\text{Ru}(\text{CHCHPh})(\text{C}_2\text{Ph})(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$. *Organometallics* **1995**, *14*, 875-888. (h) Kruger, G. J.; Ashworth, T. V.; Singleton, E. The crystal structure of a five-coordinate acetylido-phosphine complex of ruthenium(II). *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Crystallogr.* **1981**, *37*, C220.
- (19) (a) Reinholdt, A.; Vosch, T.; Bendix, J. Modification of σ -Donor Properties of Terminal Carbide Ligands Investigated Through Carbide-Iodine Adduct Formation. *Angew. Chem. Int. Ed.* **2016**, *55*, 12484-12487. (b) Morsing, T. J.; Reinholdt, A.; Sauer, S. P. A.; Bendix, J. Ligand Sphere Conversions in Terminal Carbide Complexes. *Organometallics* **2016**, *35*, 100-105. (c) Stüer, W.; Weberndörfer, B.; Wolf, J.; Wernver, H. Preparation of hydrido(vinylidene)-ruthenium(II) complexes and a one-pot synthesis of Grubbs-type ruthenium carbenes. *Dalton Trans.* **2005**, 1796-1803.
- (20) The triflate anion of **7.OTf** has the C-S bond aligned with a crystallographic glide plane such that when the fragment is grown symmetry translates the second anion outside the cell. One of the cations is bisected by the cell edge and shared with an adjacent cell.
- (21) Touchard, D.; Guesmi, S.; Le Pichon, L.; Daridor, A.; Dixneuf, P. H. Ammonia ruthenium complexes for the access to new hydrido, carbonyl and isocyanide ruthenium-alkynyl derivatives. *Inorg. Chim. Acta* **1998**, *280*, 118-124.
- (22) see for examples: (a) Hill, A. F.; Rae, A. D.; Schultz, M.; Willis, A. C. Bis(alkynyl), Metallocyclopentadiene, and Diphenylbutadiene Complexes of Ruthenium. *Organometallics* **2007**, *26*, 1325-1338. (b) Bohanna, C.; Esteruelas, M. A.; Herrero, J.; López, A. M.; Oro, L. A. Reactions of $[\text{RuH}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\text{P}^t\text{Pr}_3)_2]$ and $[\text{RuH}(\eta^2\text{-C}_2\text{Ph}_2)(\text{CO})(\text{P}^t\text{Pr}_3)_2]$ with terminal alkynes: synthesis and characterization of new five- and six-coordinate bis(alkynyl) and alkynyl(vinyl) derivatives of ruthenium(II). *J. Organomet. Chem.* **1995**, *498*, 199-206. (c) Sun, Y.; Taylor, N. J.; Carty, A. J. Octahedral bis(acetylide) and bis(diacetylide) complexes of ruthenium(II) with linear C_2MC_2 and C_4MC_4 chains: the first X-ray structures of all *trans* bis(acetylides) $\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ and $\text{Ru}(\text{CO})_2(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$. *J. Organomet. Chem.* **1992**, *423*, C43-47.
- (23) A shorter $\text{C}\equiv\text{P}$ (1.493(3) Å) and longer Ru-CP (2.118(3) Å) were apparent for $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})(\text{C}\equiv\text{CC}_6\text{H}_4\text{F}-)]$, but not reflected spectroscopically, IR data suggesting one of the weaker $\text{C}\equiv\text{P}$ distances recorded. The structural data were thus attributed to solid-state effects and thus not representative.^{7c}
- (24) C. Stuchl, R. Anwender, *Dalton Trans.*, **2018**, *47*, 12546-12552 and references therein.
- (25) (a) Greenacre, V. K.; Day, I. J.; Crossley, I. R. Hydrochlorination of Ruthenaphosphaalkenyls: Unexpectedly Facile Access to Alkylchlorohydrophosphane Complexes. *Organometallics* **2017**, *36*, 435-442. (b) Greenacre, V. K.; Trathen, N.; Crossley, I. R. Ruthenaphosphaalkenyls: Synthesis, Structures and Their Conversion of η^2 -Phosphaalkene Complexes. *Organometallics* **2015**, *34*, 2533-2542. (c) Trathen, N.; Greenacre, V. K.; Crossley, I. R.; Roe, S. M. Ambiphilic Reactivity of a Ruthenaphosphaalkenyl: Synthesis of *p*-Pyrazolylphosphaalkene Complexes of Ruthenium(0). *Organometallics* **2013**, *32*, 2501-2504; (d) Averre, C. E.; Coles, M. P.; Crossley, I. R.; Day, I. J. The open-chain triphosphanes $\text{RMe}_2\text{SiCH}_2\text{P}(\text{PR}')_2$ (R = Me, Ph, R' = SiMe₃, Cy, Ph). *Dalton Trans.*, **2011**, *41*, 278-284.
- (26) Fox, M. A.; Harris, J. E.; Heider, S.; Pérez-Gregorio, V.; Zakrzewska, M. E.; Farmer, J. D.; Yufit, D. S.; Howard, J. A. K.; Low, P. J. A simple synthesis of *trans*- $\text{RuCl}(\text{C}\equiv\text{CR})(\text{dppe})_2$ complexes and representative molecular structures. *J. Organomet. Chem.* **2009**, *694*, 2350-2358.
- (27) Junert, M.; Dinjus, E.; Nauck, M.; Sieler, J. Structure and Reactivity of Sodium Phenoxide – Following the Course of the Kolbe-Schmitt Reaction. *Chem. Ber.* **1997**, *130*, 1461-1465.
- (28) Sheldrick, G.M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2015**, *71*, 3-8.
- (29) Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8.
- (30) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.*, **2009**, *42*, 339-341.
- (31) (a) Kumar, R.; Ramakrishnan, S.; Jemmis, E.D.; Jagirdar, B. R. Implication of a σ -Methane Complex en Route to elimination of Methane from a Ruthenium Complex: An Experimental and Theoretical Investigation. *Organometallics* **2015**, *34*, 1245-1254; b) Umezawa-Vizzini, K.; Lee, T. R. Synthesis and Reactivity of $(\text{DPPE})\{(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\}\text{RuCl}$. *Organometallics* **1997**, *16*, 5613-5615.
- (32) Due to the relative magnitudes of the $^1J_{\text{CP}}$ and $^3J_{\text{CP}}$ couplings the resonance associated with the cyaphidic carbon center appears as a complex multiplet, the multiplicity of which is not readily resolved. In some instances, the associated broadening precludes satisfactory resolution of the resonance above the baseline.

Synopsis – For table of contents only

The first example of controlled reactivity in the presence of the cyaphide ligand is achieved by zinc-mediate methyl/halide exchange within $[\text{Ru}(\text{dppe})_2\text{Me}(\text{C}\equiv\text{P})]$ to afford $[\text{Ru}(\text{dppe})_2\text{X}(\text{C}\equiv\text{P})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Halide abstraction from the bromide yields the isolable 5-coordinate cation $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})]^+$, which reacts with nucleophile (R^-) and neutral donors (CO), giving facile access to the respective *trans*-cyaphide complexes.

For table of contents only