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Controlled Reactivity of Terminal Cyaphide Complexes: Isolation of the 5-coordinate [Ru(dppe)2(C≡P)]+.  

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Supporting Information Placeholder

ABSTRACT: The novel cyaphide complex trans-[Ru(dppe)2Me(C≡P)] is obtained in excellent yields and exhibits the first instance of controlled reactivity of any terminal-cyaphide complex. Its treatment with ZnX2/PPh3 effects selective metathesis of the methyl moiety to afford the unprecedented halo-cyaphide complexes trans-[Ru(dppe)2(X=C≡P)] (X = Cl, Br, I), which are structurally characterized (X = Cl, Br). Exemplified with the trans-bromide, these compounds are susceptible to substitution of the halides by nucleophilic reagents – illustrated with Me2Mg – and also readily undergo halide abstraction by TlOTf to afford the first hypo- 
coordinate cyaphide complex, viz. [Ru(dppe)2(C≡P)].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 Me2Mg and LiC≡CPh, and with its facile bulk carbonylation to afford trans-[Ru(dppe)2(CO)(C≡P)]+.  

INTRODUCTION

Cyaphide (‘-C≡P’), a notional analogue of cyanide or acet-
ylide, is the very simplest, yet has been among the most elu-
sive of the phosphacarboxyls. The discrete cyaphide anion remains unknown, due to an apparently intrinsic instability,1 while its engagement as a ligand for transition metals dates only from 1992, with Angelici’s report of the transient trans-Pr[Ph3PAuC≡P][2]. The discrete cyaphide coordination was finally unequivocally demonstrated only in 2006, with Gützlaff’s seminal report of [RuH(dppe)2(C≡P)] (1), the first such complex to be isolated and structurally characterized.  

Recent advances in the coordination chemistry of cyaphide and alkynyl ligands that exhibit through-conjugation, viz. [Ru(dppe)2(C≡R)(C≡P)] (2, R = CO,Me a; C≡R, R = Me b, H c, F d, CO2Me e, OMe f, NO2 g; C≡CRu(dppe)2(C≡P) h),3,4,5 accessed via a modification of the Gützlaff methodology (Scheme 1). Meanwhile, Meyer has reported a single uranium species obtained via the unexpected fragmentation of the phosphoethynolate ion (‘OC≡P’).5

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.3,5 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-[Ru(dppe)2]1+ and a reliance on these then being amenable to installation of an η1-P=CSiR3 ligand; this cannot be assured, given the low basicity of phosphalkyne lone pairs.3 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 (M = Ag, Tl) or AgPF6, CH2Cl2; ii) P=CSiMe3 (in toluene); iii) NaOPh or KO'Bu, 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 ‘C≡P’ moiety intact. Herein, we report the first such examples, achieved by controlled exchange of the trans-ligand within a trans-[Ru(dppe)2(R=C≡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 [Ru(dppe)2Me]+, prepared by methide abstraction from [Ru(dppe)2Me3], itself obtained via modification of literature protocols,7 to afford trans-[Ru(dppe)2(Me)]7+-[P=CSiMe3]([7]+) (3′), subsequent treatment with stoichiometric NaOPh effecting its conversion to trans-[Ru(dppe)2(Me)(C≡P)] (4). Characteristic spectroscopic signatures for the phosphacarbon and dppe moieties confirm the formation of 3′ (δC ≈ 121.3, 46.7 JCP 28 Hz) and 4 (δC ≈ 177.9, 58.9 JCP 4 Hz), with retention of the Ru-Me fragment in each case apparent from the 1H and 13C[1H]NMR spectra (δH ≈ −0.34, δC ≈ 2.7 3′; δH ≈ −2.31, δC ≈ −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 C≡P stretching frequency (νC≡P ≈ 1217 cm−1 4, vs 1269 cm−1 3′), as we have previously noted,7 while the identity of 4 ultimately confirmed from crystallographic data (Figure 1). While the connectivity is unequivocal, disorder about the cyaphide carbon center precludes meaningful discussion of the C≡P distance, which consequently appears truncated with respect to prior examples,8 while the Ru–C≡P linkage is notably longer, albeit still within the range seen for Ru–C≡P systems recorded in the CCDC.9 The trans methyl ligand and remaining core geometry are similarly comparable to respective precursors.

In seeking to coordinatively engage the cyaphide moiety of 4 its interaction with ZnBr2(PPh3)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 (δC 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, and 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 C≡P (which are both refined equally across two sites), the C≡P distances being in line with both 4a and the alkynyl systems 2a,c-e8c and exhibiting near perfect linear coordination, as observed in 1, 2c and 2d. In contrast, the Ru–C≡P distances appear appreciably truncated, while the Ru–X linkages lie toward the upper bounds recorded in the CCDC (X = Cl 2.30 – 2.60 Å; Br 2.45 – 2.75 Å).10

Scheme 2. Syntheses for 5a – c.

Reagents conditions: i) ZnX2(PPh3)2, THF, 18 h.; ii) ZnX2, PPh3 (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 distances being in line with both 1a and the alkynyl systems 2a,c-e8c and exhibiting near perfect linear coordination, as observed in 1, 2c and 2d. In contrast, the Ru–C≡P distances appear appreciably truncated, while the Ru–X linkages lie toward the upper bounds recorded in the CCDC (X = Cl 2.30 – 2.60 Å; Br 2.45 – 2.75 Å).10

Optimal formation of 5a is achieved by replacing the zinc complex with ZnBr2 and sub-stoichiometric PPh3 (5 mol%), the analogous reactions with ZnX2 (X = 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 zine-halide mediated halogen/methyl exchange at a transition metal,11 and apparently requires the presence of at least catalytic
PPh₃, implying that ZnX₃(PPh₃)₂, formed \textit{in situ}, is the active species. While we have not proved the mechanism of this conversion in detail, we can reasonably dismiss adventitious water giving rise to HX \textit{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 Ru(dppe)TeX as the sole identifiable product. We have also observed the reaction of 4 with ZnBr₂/PPh₃ by NMR, the characteristic Ru–Me resonance of 4 (δn = 2.3, qnt, JHH = 5.6 Hz) being replaced by a broadened (w₁₂ ≈ 8 Hz) signal to higher frequency (δn = 0.83). Though we have not definitively identified the species responsible, it does lie in a region consistent with Zn–Me derivatives, which might suggest Me/X metathesis. Significantly, we observe no evidence for the liberation of CH₄, discounting protonation of the methyl, and thus involvement of adventitious acid.

The formation of 5a–e is notable, given that they have proven inaccessible by more ‘traditional’ routes, the trigonal pyramidal [Ru(dppe)TeX]⁺ being apparently inert toward P=CSiMe₃. Indeed, only by generating the cation \textit{in situ} in the presence of a large excess of P=CSiMe₃ (enabling trapping prior to relaxation to a trigonal bipyramidal geometry), could a species consistent with [Ru(dppe)TeX(P=CSiMe₃)]⁺ be observed, and then only at trace levels. 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 Me₂Mg, which affords some evidence for the slow regeneration of 4. In contrast, reaction with LiC≡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 [Ru(dppe)TeX(C≡P)]OTf, being ultimately confirmed crystallographically (vide infra).

Spectroscopically, the cyaphidic (δ 154; q, Jpp 7 Hz) and supporting dppe (δ 52.1; d, Jpp 7 Hz) resonances of 6* are clearly observed, their respective multiplicities implying a square-pyramidal geometry. The triflate counterion is confirmed by ¹⁹F-NMR data and appears uncoordinated, which was further supported by using AgPF₆ 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 \textit{trans}-methyl complex 4 with Brookhart’s acid, [H(OEt)₃][BAR₄], this reaction is unsuccessful, leading instead to decomposition, albeit ultimately with complete demet hyla lation 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 methane from 4 with TiOTf (cf. formation of [Ru(dppe)TeX]⁺), and of hydride from samples of 1 using Ph₃CBF₃; in neither instance did a reaction occur.

The crystallographic data for 6* (Figure 3) confirm the discrete square-pyramidal complex cation, which exhibits a flattened basal plane, from which the mutually \textit{trans} phosphines are displaced by ≈ 5.5 °; 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) – and, indeed, cyaphide-alkynyl – 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 variants. Indeed, a case in point is the installation of a C≡P ligand to a pre-formed scaffold. This both renders it a convenient starting point from which to access the vacant trans coordination site readily accessible, as illustrated by reactions with Me₂Mg and LiC≡CPh, which respectively generate 4 and 2c.⁶

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.¹⁰ The second molecule is depicted in the SI file. Selected bond lengths [Å] and angles [°]: molecule 1 (shown): P1–C2 1.53(2), Ru1–C1 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(9), Ru1–C1–O1 177.8(17). molecule 2 (SI): P=O 1.53(2), Ru=C≡C 2.141(11), Ru=C≡O 1.815(11), C≡O 1.216(16), Ru=P 2.399(1), Ru–P6 2.383(2), P–C–Ru 173.6(7), C≡O–Ru1–C≡O 170.0(5), Ru–C–O 175.6(10).

NMR spectroscopic data demonstrate retention of the cyaphide (δν 181, q, Jα 10 Hz) and supporting dppe ligands (δν 43.6, d, J 10 Hz), while both cyaphide (v_C=O 1261 cm⁻¹) and carbonyl (v_C=O 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)] (v_C=O 1977 – 1984 cm⁻¹)¹¹ 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≡C 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,²⁴ 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 LiC≡CPh offers access to a previously reported alkynyl derivative (2e).²⁵ 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; Anhydroly ZnCl₂ were further purified and extended heating at >200 °C under high vacuum (10⁻² mbar) and subliming (>250 °C, 10⁻² mbar). Me₂Mg,24 Me₂SiCl₂,2,5 [Ru(dppe)Cl₂]OTf⁻ and NaOPh 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 100.64 MHz, 19F 375.87 MHz, 31P 161.71 MHz, 29Si 79.37 MHz) spectrometer. All spectra are referenced to external Me Si, 85 % H₂PO₄ and CF₃COOH as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBCC) spectra, while silicon shifts were determined indirectly (HMBCC). 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 Metropolitan University Analytical Service (MBraun) techniques, working under an atmosphere of dry argon or dried in vacuo, yielding a yellow solid, which was washed with acetonitrile (ca 3 x 15 cm²) and dried. Yield: 0.543 g, 63 %. 1H NMR (399.5 MHz, CDCl₃): δ=8.4 (8H, m, meta-CH₃), 7.3 (4H, t, J=7.3 Hz, para-CH₂), 7.2 (8H, t, J=7.5 Hz, ortho-CH₂), 7.1 (4H, t, J=7.3 Hz, para-CH₂), 2.6 (8H, m, para-CH₂), 1.30 (20H, s, PPh₂). Compound was used without further purification in the next step.

**Synthesis of [Ru(dppe)Me₂](OTf)⁴⁻ (4).** A solution of 3 OTf (1.068 g, 0.91 mmol) in THF (ca 20 cm³) was cooled at 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 dried in vacuo, yielding a yellow solid. Yield: 0.543 g, 63 %. 1H NMR (399.5 MHz, CDCl₃): δ=8.4 (8H, m, meta-CH₃), 7.3 (4H, t, J=7.3 Hz, para-CH₂), 7.2 (8H, t, J=7.5 Hz, ortho-CH₂), 7.1 (4H, t, J=7.3 Hz, para-CH₂), 6.9 (8H, t, J=7.6 Hz, ortho-CH₂), 6.5 (8H, d, J=7.5 Hz, meta-CH₂), 2.6 (8H, m, CH₂), -2.3 (3H, qnt, J=5.6, CH₃), 13C{¹H} NMR (100.46 MHz, CDCl₃): δ=294 (m, br, CP₃), 139.1 (m, J=9.77 Hz, ipso-CH₂), 135.9 (m, J=9.45 Hz, ipso-CH₂), 136.1 (m, br, meta-CH₂), 134.7 (m, qnt, J=2.0 θ, meta-CH₂), 127.4 (qnt, J=1.9 Hz, ortho-CH₂), 127.2 (qnt, J=2.33 Hz, ortho-CH₂), 30.9 (s, CH₂CH₂), -10.0 (m, br, CH₂); 31P{¹H} NMR (161.71 MHz, CDCl₃): δ=-177.9 (1P, m, br, CP₃), 58.9 (4P, d, J=4.3 Hz, PPh₂). IR (solid, ATR) ν/cm⁻¹: 1217 (CP₃), 3046 (CH₂). Anal. Calcd for CaH₁₅P₃Ru: C 62.85 %, H 5.38 %. Found: C 62.83 %, H 5.38 %. Crystal data for 3 (CCDC 1938746). Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. CaH₁₅P₃Ru (M₉ = 955.83 g mol⁻¹), monoclinic, P 2/c (No. 14), a=23.6755(12), b=11.5267(6), c=17.2942(8) Å, β=104.670(5), V=456(5.7) Å³, Z=4, T=173(2) K, µ(Cu Kα)=4.712 mm⁻¹, D=1.391 mg ml⁻¹, 8867 independent reflections, full matrix F refinement R=0.0614 on 6218 independent absorption correction reflected, I > 2σ (I); 2θ=142.45°. 543 parameters, wR=0.1573 (all data).

**Synthesis of trans-[Ru(dppe)Br₂(C≡P)]⁻ (5a).** Anhydrous ZnBr₂ (0.505 g, 3.15 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: 1.055 g, 81 %. 31P{¹H} NMR (199.98 MHz, CDCl₃): δ=-7.3 (8H, m, br, meta-CH₃), 7.2 (8H, m, meta-CH₃), 6.7 (8H, m, ortho-CH₂), 4.8 (16H, m, CH₂), 2.7 (8H, s, PPh₂). Compound was used without further purification in the next step.
The sample can be further purified by recrystallization from benzene, in independent absorption corrected reflections, full matrix F refinement R=0.0506 on 9214 independent absorption corrected reflections, [I > 2σ(I); 2θinc= 143.20°], 685 parameters, wR=0.1265 (all data).

The sample was sealed and agitated until completion then observed by 31P[H] NMR.

Treatment of 4 with [H(OEt)2]2[BAr4]. To an NMR sample of 4 in CDCl3 was added 1 equiv. of Brookhart’s acid. The sample was sealed and agitation then monitored by NMR after 5 min. and upon completion.

4 scale reaction of 4 with ZnBr2 / PPh3 (in situ). To a solution of 4 in THF (CDCl3 capillary) was added 1 equiv. ZnBr2 and ca 10 mol% PPh3. The sample was sealed and agitated until completion then observed by 31P[H] NMR.

Reaction of 5a with MeMg. Samples of 5a (31 mg, 0.03 mol) and MeMg (3 mg, 0.04 mol) 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 analysed by 1H and 31P[H] NMR in CD2Cl2. Key signatures for 4: 1H NMR (399.5 MHz, CD2Cl2): δt=7.8 (8H, br, meta-CH2), 7.4 (4H, t, J=7.5 Hz, para-CH3), 7.3 (4H, J=7.5 Hz, para-CH3), 7.1 (16H, t, J=7.6 Hz, ortho-CH3), 6.5 (8H, t, meta-CH3), 3.0 (4H, q, J=8.0 Hz, para-CH3), 2.6 (4H, q, J=8.0 Hz,ortho-CH3), 1.31 (s, meta-CH), 1.27 (s, ortho-CH). 31P[H] NMR (161.71 MHz, CD2Cl2): δt=57.8 (40.5 ppm, d, J=216 Hz, ortho-CH).
ASSOCIATED CONTENT

Supporting Information

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

Acquisition Codes

CCDC 1938745-1938748 and 1947211 contain the supplementary crystallographic data for this paper. This 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.

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Notes

The authors declare no competing financial interest.

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REFERENCES


(11) While we cannot absolutely discount precedent for ZnX2-ef-fecting halogenative demetallation of transition metals, we have been unable to locate any such examples. Rather, alkylolation 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); data are known for, inter alia, MeZnOAc (δ -0.68),2a MeZnCl(L2) (δt -0.13)2b and [(MeZn)2(μ−OR)(μ−Cl)] (δt -0.3),2c which constitute reasonable comparators.


(14) The resonance for CH4 is typically observed around 0.2 ppm in tff 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.; Bercau, J. E.; Goldberg, K. I. NMR Chemical Shifts of True Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. Organometallics 2010, 29, 2176-2179.
D.; Whitwood, A. C. Solvent and phosphine dependence in the reaction of cis-RuCl$_2$Ru(C$_{2}$H$_4$P$_2$)$_2$ with terminal alkynes. *Organometallics* **2008**, *29*, 693-3103.


(20) The triflate anion of 7.0TF with 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.


(23) A shorter Csp$_2$ (1.493(3) A) and longer Ru-C (2.118(3) A) were apparent for [Ru(dppe)Cp]=C(C$_6$H$_5$H-F)], but not reflected spectroscopically, IR data suggesting one of the weaker Csp$_2$ distances recorded. The structural data were thus attributed to solid-state effects and thus not representative.


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