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ORGANOMETALLICS
Note

Reactions of $[Ru(CO)_2(PPh_3)_3]$ with Alkynylphosphonium Salts: Phosphaallenylidene vs Phosphonioacetylide Coordination

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Summary: $[Ru(CO)_2(PPh_3)_3]$ *reacts with* $[Me_3SiC{\equiv}CPPh_3]$*OTf in the presence of moist* $[^nBu_4N]F$ *to provide the C−H activation product* $[RuH(C{\equiv}CPPh_3)(CO)_2(PPh_3)_2]OTf$*, spectroscopic and structural data for which are used to assess the previously proposed analogy between phosphonioacetylide and phosphaallenylidene (cf. isonitriles) bonding descriptions in an organometallic context.*

In a combined experimental and computational study[1] Bestmann and co-workers considered a possible analogy between the nonisolable molecule "Ph_3PCC" (**1**) and the more familiar isonitrile class of compounds, RNC. The elegant synthetic approach to **1** involved fluorodesilylation of the salt $[Me_3SiC{\equiv}CPPh_3]OTf$ (**2**·OTf)[2] by $[Me_3NCH_2Ph]F$ at −100 °C (Scheme 1), and while the compound decomposes upon warming to room temperature, ^1H, ^{13}C, and ^{31}P NMR data could be obtained at −78 °C which supported the formulation. These data are reproduced in Table S1 (Supporting Information) for reasons that should become apparent (vide infra).

Scheme 1. Synthesis and Reactions of 1[1]

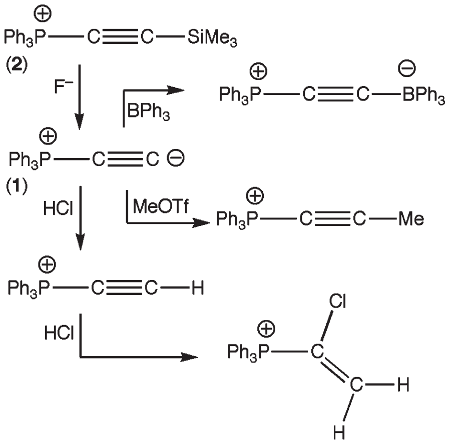
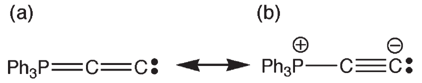


Chart 1. Valence Bond Descriptions of "Ph_3PCC" (2): (a) Phosphaallenylidene (cf. Isonitriles); (b) Phosphonioacetylide



The detailed computational study led, inter alia, to the conclusion that "*it is not possible to formulate a single Lewis structure for Ph_3PCC that correctly reproduces the geometry and charge distribution.*"[1] The same might be said for isonitriles, CNR, and indeed a key theme of the paper was the isoelectronic relationship between **1** and isonitriles: i.e., to what extent do the phosphaallenylidene and phosphonioacetylide descriptions (Chart 1) contribute? In principle, triphenylisocyanosilane, Ph_3SiNC (iso-**3**) would be the most closely related isoelectronic analogue of **1**, though this compound has lain dormant in the literature for the 50 years since its discovery,[3] at which time its formulation (Ph_3SiNC (*iso*-**3**) vs Ph_3SiCN (**3**)) was a matter for unresolved debate (vide infra).

Chemical evidence in support of the **1**:isonitrile analogy was gleaned from reactions with a range of electrophiles (HX, MeOTf, BPh_3), which invariably attacked at the carbon atom β to the phosphorus center ($Ph_3P{-}C_\alpha{-}C_\beta{-}$ ylides are typically nucleophilic at C_α); the computational results suggest C_β contributed substantially to the HOMO in the form of a lone pair. The HOMO-1 and HOMO-2 were found to be an orthogonal set of π orbitals associated with the C−C multiple bond; however, the paper was silent on the nature of unoccupied orbitals. From an organic perspective, the unoccupied orbitals of a demonstrably potent nucleophile would be of little interest. However, in an organometallic context, the invocation of an analogy with isonitriles immediately raises the issue of metal→carbon retrodonation to such orbitals, a question to which we will return.

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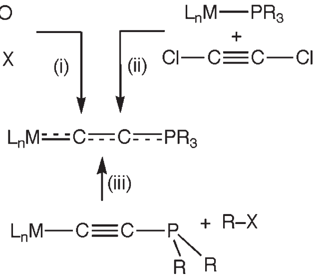
Scheme 2. Previous Synthetic Routes to Phosphonioacetylide Complexes:[4−7] (i) Ylide Route (X = PR$_3$ (H)SiMe$_3$, (H)U(η-C$_5$H$_5$)$_3$); (ii) Haloalkyne/Phosphine Coupling; (iii) Phosphinoalkynyl Alkylation



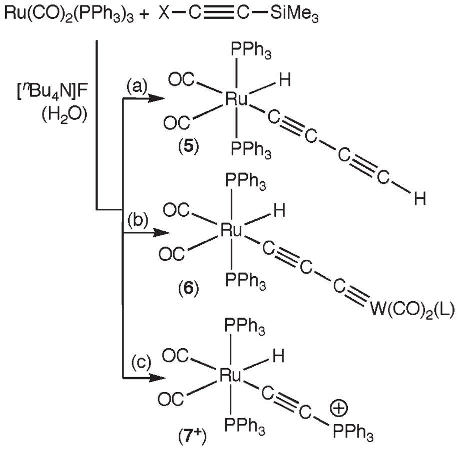
Complexes of **1** (and related CCPR$_3$ derivatives) are known but are rare, and none arise from the intermediacy of free **1**. Rather, they all derive from one of three synthetic approaches. These involve the reactions of the metal carbonyls with various "double" ylides, reminiscent of the Wittig reaction (Scheme 2),[4,5] the reactions of dichloroethyne with labile phosphine complexes,[6] or the alkylation of (somewhat rare) phosphinoalkynyl ligands.[7] Though only briefly explored by Dahlenburg, this last approach perhaps offers the greatest potential for general applicability.

Herein, we wish to address the **1**:CNR analogy from an organo-transition-metal standpoint and have investigated the generation of **1** in the presence of a suitable trapping complex, [Ru(CO)$_2$(PPh$_3$)$_3$] (**4**).[8] The complex **4** is known to react via phosphine substitution with internal alkynes, diynes, and dimetallaoctatetraynes to form simple π adducts,[9] at least in the first instance, though subsequent transformations may ensue. Terminal alkynes and diynes and metalladiynes (propargylidynes), in contrast, undergo oxidative addition (C−H activation),[10] while phosphaalkynes coordinate in the rare, linear η^1-σ(P) manner.[11]

Results and Discussion

It has been previously shown that fluoride-mediated protodesilylation of bis(trimethylsilyl)butadiyne with commercial (i.e., moist) [^{n}Bu$_4$N]F ("TBAF") in the presence of **4** provides the parent butadiynyl hydrido complex [RuH(C≡CC≡CH)(CO)$_2$(PPh$_3$)$_2$] (**5**)[10b] and that a similar strategy employing [W(≡CC≡CSiMe$_3$)(CO)$_2$L] (L = HB(pz)$_3$, HB(pzMe$_2$)$_3$; pz = pyrazol-1-yl) affords the tricarbido complexes [RuH{C≡CC≡W(CO)$_2$L}(CO)$_2$(PPh$_3$)$_2$] (**6**).[10c] We find that treating **2** with TBAF in the presence of **4** affords a salt formulated as [RuH(CCPPh$_3$)(CO)$_2$(PPh$_3$)$_2$]OTf (**7**·OTf) on the basis of spectroscopic and crystallographic data (Scheme 3).

Scheme 3. Fluoride-Mediated Protodesilylation of Alkynylsilanes: (a) X = C≡CSiMe$_3$;[10b] (b) X = C≡W(CO)$_2$L (L = HB(pz)$_3$, HB(pzMe$_2$)$_3$);[10c] (c) X = PPh$_3$(OTf)



We will return to the nature of the RuCCP linkage; however, the gross formulation follows from high- and low-resolution ESI mass spectrometry and elemental microanalytical data. Specifically, in addition to a molecular ion, isotopic clusters attributable to loss of CO and/or phosphine, but not "CCPPh$_3$", are readily identifiable. The stereochemistry at ruthenium, subsequently confirmed crystallographically, follows from spectroscopic data and involves trans phosphine and cis carbonyl ligands: thus, an A$_2$B system is observed in the ^{31}P{^{1}H} NMR spectrum with a barely resolved AB coupling (4 Hz), indicative of remote, very weakly coupled nuclei. The ^{1}H NMR spectrum features a doublet of triplets resonance at −5.80 ppm with $^2J_{\mathrm{PH}}$ coupling (18.3 Hz) typical of the *mer-trans* RuH(PPh$_3$)$_2$ arrangement (e.g., δ_{H} − 5.30, $^2J_{\mathrm{HP}}$ = 20.0 Hz for **5**[10b]). Two chemically distinct carbonyl environments are indicated by triplet resonances in the ^{13}C{^{1}H} NMR spectrum (δ_{C} 197.6, 195.5), while doublet resonances for the two carbon nuclei of the RuC$_\beta$C$_\alpha$P spine appear at 176.7 (C$_\beta$) and 87.31 (C$_\alpha$P), respectively, without coupling to phosphorus nuclei of the ruthenium-bound phosphines being resolved. The infrared spectrum of **7**·OTf in CH$_2$Cl$_2$ is consistent with the formulation in that three intense absorptions are observed (2038, 1988, 1959 cm^{-1}) in addition to one weak, somewhat broad, absorption (1891 cm^{-1}). However, caution should be exercised when assigning these individually to ν_{s}(CO), ν_{as}(CO), ν(C≡C) and ν(RuH) modes, since these oscillations are all likely to be strongly coupled.[4,6,12] Notably, the simple complex [RuH(C≡CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)$_2$] (**8**)[10a] has absorptions in CH$_2$Cl$_2$(Nujol) at 2113 (2112) m, 2031 (2026) vs, 1983 (1981) vs, and 1894 (1902) w cm^{-1}, while the precursor **2**$^+$ has ν_{CC} 2128 cm^{-1} (CH$_2$Cl$_2$). Thus, the bands that appear most common to **5**, **7**$^+$, and **8** would appear to occur at

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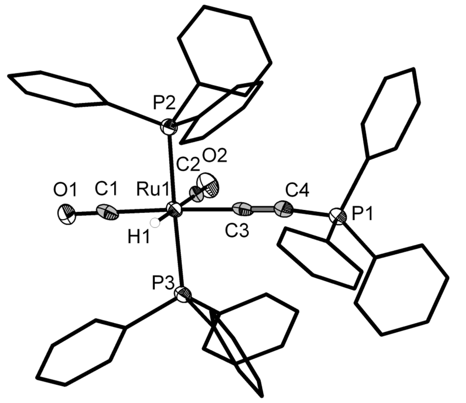

Figure 1. Molecular geometry of the complex $\mathbf{7}^+$ in a crystal of the salt $\mathbf{7}\cdot$OTf$\cdot$CH$_2$Cl$_2$ (60% displacement ellipsoids at 100 K, phenyl groups simplified, solvent and counteranion omitted). Selected bond lengths (Å) and angles (deg): Ru1−C1 = 1.898(7), Ru1−C2 = 1.952(6), Ru1−C3 = 2.041(6), Ru1−P3 = 2.3623(15), Ru1−P2 = 2.3761(15), Ru1−H1 = 1.64(6), P1−C4 = 1.698(6), C3−C4 = 1.235(9); C1−Ru1−C2 = 93.7(2), C2−Ru1−C3 = 94.2(2), C1−Ru1−P3 = 91.51(18), C2−Ru1−P3 = 94.87(17), C3−Ru1−P3 = 87.24(16), P3−Ru1−P2 = 168.10(5), C4−C3−Ru1 = 177.4(5), C3−C4−P1 = 172.4(5).

ca. 2030 and 1990 cm^{-1}; therefore, we would suggest that these are predominantly ν_{CO} in character while the more substituent-dependent band (1959 cm^{-1}) is most likely *primarily* ν_{CC} in character. While this is somewhat lower than the values assigned to most other complexes (2050−2105 cm^{1}), it should be noted that ruthenium(II) is a comparatively π-basic metal center, and in the absence of competing π-acidic ligands values as low as 1932 cm^{-1} have been assigned for the salt [Ru(C≡CP^{t}Bu$_2$Bu)(PPh$_3$)$_2$(η-C$_5$Me$_5$)]-Br.[7] In this respect the response of ν_{CC} to the π-basicity of a metal might well appear to mimic that of isonitriles, though the separation of σ-dative and π-retrodative contributions to ν_{CN} for isonitriles is less straightforward than for ν_{CO} in carbonyl complexes.[13]

The formulation of $\mathbf{7}\cdot$OTf was confirmed by a crystallographic study of the solvate **7**.OTf.CH$_2$Cl$_2$, the results of which are summarized in Figure 1.

The geometric features of the "RuH(CO)$_2$(PPh$_3$)$_2$" unit are generally unremarkable, other than to note the characteristic bending of ligands toward the small hydride, which exerts a trans influence upon the CO to which it is trans coordinated. Although the position of the ruthenium hydride ligand is typically imprecise, the ruthenium−hydride bond length (Ru1−H1 = 1.64(6) Å) is comparable to that observed for **5** (1.57 Å). It is perhaps noteworthy that one ortho C−H group of each trans-disposed phosphine approaches the hydride ligand (Ru−H···H−C = 2.24, 2.44 Å). Such Ru−H···H−C hydrogen-bonding interactions have been noted previously by Junk for the complex [RuH$_2$(CO)(PPh$_3$)$_3$][14] and more recently for the methimazolylborate complexes [RuH(CO)(PPh$_3$){HB(mt)$_3$}] (mt = methimazolyl)[15a] and [RuH(PPh$_3$)$_2${HB(mt)$_3$}][15b] and may well be more widespread than previously appreciated. Equivocal evidence that such interactions may persist to some extent in solution is provided by the observation of an uncharacteristically complex ^{1}H NMR spectrum of $\mathbf{7}^+$ in the phenyl region, suggesting arrested, or at least restricted, rotation about the Ru−P or P−C bonds of the phosphines. The ^{1}H NMR spectrum of the precursor **2** is by comparison quite conventional and unremarkable (δ_H(CDCl$_3$) 7.76, 7.88, m × 2), as is the ^{31}P{^{1}H} spectrum (δ_P 5.74), notwithstanding the ca. 11 ppm shift that occurs upon replacement of the SiMe$_3$ group by ruthenium. These features aside, our interest centers on the RuCCP spine and whether this is best described as the coordination of neutral **1** to cationic "RuH(CO)$_2$(PPh$_3$)$_2^+$", drawing upon the isonitrile analogy, e.g. [RuH(CNR)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ ($\mathbf{9}\cdot$ClO$_4$: R = C$_6$H$_4$Me-4),[15] or if it is more akin to a conventional σ-alkynyl (cf. **5** and **8**) with a remote cationic phosphonium substituent. There is an enormous amount of structural data available for octahedral (or pseudo-octahedral half-sandwich) acetylides of ruthenium(II),[17] and although these have previously been tabulated,[17b] the growth of the field in the interim has been most notable. The question arises as to whether there is anything untoward in the metrical parameters associated with the RuCCPPh$_3$ spine which might point toward a phosphaallenylidene canonical form having a role to play in understanding the bonding. On comparison of the structural data for these previously reported ligands, the CC bond spans the range 1.21−1.23 Å while the C−PPh$_3$ bonds span 1.68−1.71 Å. Thus, $\mathbf{7}^+$ would appear to not show remarkable departure from this albeit limited precedent. There is no obvious correlation between the values of "ν_{CC}" and the geometric parameters of the MCCP spines; however, this may simply reflect the low precision of these structural data and variations in the media used for IR measurements. The Ru1−C3 bond length of 2.041(6) Å falls within the range (1.91−2.10 Å) typical of conventional ruthenium alkynyls, as does the C3−C4 bond length of 1.235(9) Å; i.e., there is no structural evidence for significant contributions from the phosphaallenylidene description. The Ru−C3−C4−P1 spine does not depart significantly from linearity, in contrast to [Fe(CCPPh$_3$)(CO)$_4$] (**10**), which has the phosphine bent off the FeCC axis (162.1°),[4e] most likely a soft response to crystal -packing effects.

An Isonitrile Analogue or a Phosphoniacetylide? We may approach this from two perspectives−empirical or computational. The characterization of L$_n$MCCPPh$_3$ complexes is somewhat patchy (Table S1, Supporting Information), reflecting the historical availability of various spectroscopic techniques such that only two examples, [(OC)$_4$FeCCPPh$_3$] (**10**)[4e] and now $\mathbf{7}^+$, offer both full spectroscopic and structural data. The structural data are somewhat unresponsive to variations in substitution at either the metal or phosphorus, with differences failing to attain statistical significance. Upon coordination, there is a significant upfield shift in the C$_\beta$ resonance from 229 ppm in free **1** to 197.4 ppm (for **10**) or 176.7 ppm (for $\mathbf{7}^+$). Alkylphosphonium derivatives span a wider range (147−223 ppm), and the chemical shift is responsive to variations in phosphorus substituents, e.g., δ(C$_\beta$) values for the series [Ru(CCPR$_3$)(PPh$_3$)$_2$(η-C$_5$H$_5$)]$^+$

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Table 1. Infrared Data for Selected Complexes $[RuH(CO)_2(L)(PPh_3)_2]^n$

L	*n*	ν_{CO} (cm^{-1})	k_{CO}
$C{\equiv}CC_6H_4Me$	0	2031, 1983	16.24
$C{\equiv}CPPh_3$	1+	2038, 1988	16.34
$C{\equiv}NC_6H_4Me$	1+	2085, 2045	17.20
$C{\equiv}O$	1+	2072, 2050, 2010	

Table 2. Infrared Data for Selected Complexes $[Mn(CO)_2(L)(\eta\text{-}C_5H_5)]^n$

L	*n*	ν_{CO} (cm^{-1})	k_{CO}
CMe[19]	1+	2095, 2056	17.37
CPh[20]	1+	2088, 2047	17.24
CSe[21]	0	2015, 1963	15.95
CS[22]	0	2010, 1959	15.88
$C{=}CHPh$[23]	0	2009, 1955	15.84
CBrPh[24]	0	2002 1960	15.83
$C{=}C{=}CPh_2$[25]	0	1995, 1945	15.65
CClPh[24]	0	1995 1935	15.57
$C{=}CH_2$[19]	0	1996, 1932	15.56
CFPh[24]	0	1980, 1918	15.32
CPh_2[26]	0	1977,1919	15.30
CNCy[27]	0	1944, 1890	14.82
$CNNPPh_3$[28]	0	1930, 1860	14.48
P^iPr_3[27]	0	1923, 1855	14.39
$CCPMe_2Ph$[5b]	**0**	**1887, 1852**	**14.09**
$C(NMeCH)_2$[29]	0	1906, 1823	14.02

span the range 191−206 ppm. This range impinges upon those typical of coordinated CO and isonitriles but is far downfield of the region in which metal-bound terminal acetylide carbons resonate (100−120 ppm). There are two spectroscopic parameters which do appear to show some variation within the PPh_3 series of compounds. (i) The first is δ_P for the phosphorus nucleus, which so far appears between −0.44 and −10.4 ppm for metal complexes, cf. −13.85 ppm for free **1** and +5.22 ppm for **2**$^+$, in which the addend may be considered primarily σ-interactive. (ii) There is a dramatic increase in the coupling between phosphorus and both C_α (50−60 Hz) and C_β (10−15 Hz, ca. doubling) upon coordination of **1** to a metal, suggesting an increase in the s character of the orbitals involved (conversely a decrease in the p character). The HOMO for free **1** in addition to having s lone pair character is also C−C bonding in character with some modest C−P σ-antibonding contribution; i.e., coordination of a (σ) Lewis acid to C_β should indeed reduce the C−P bond strength.

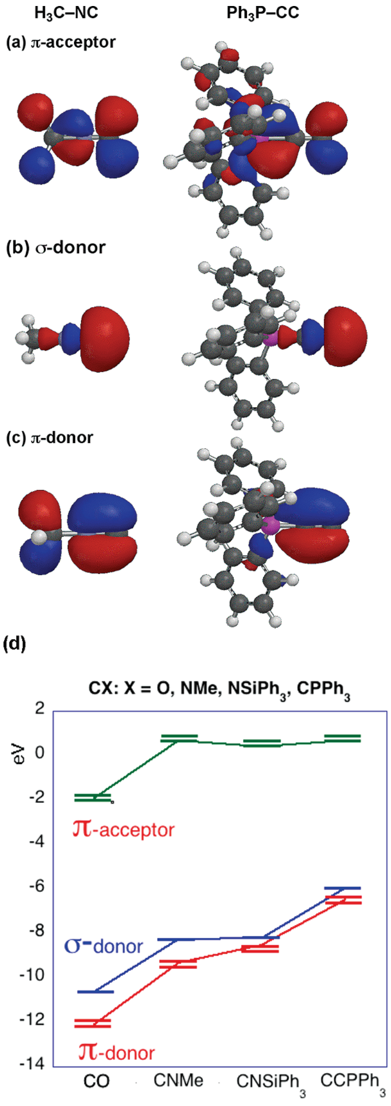

Figure 2. Topologies and relative energies of the frontier orbitals of **1** and relevant compounds.

To further assess the nature of $MCCPR_3$ bonding, we have therefore turned to infrared data associated with ancillary ligands. The complex $[RuH(CNC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2]^+$ (**9**$^+$) is most closely akin to **7**$^+$ (and the alkynyl **8**), having the same stereochemistry at ruthenium. Putting aside the caveats associated with coupled oscillations of coligands, Table 1 collates infrared data for **7**$^+$, **8**, **9**$^+$ and the tricarbonyl salt $[RuH(CO)_3(PPh_3)_2]PF_6$, though the Cotton−Kraihanzel force constant (k_{CO}) is not directly comparable.

Table 1 provides a somewhat brief list of C_1 ligands for comparison, though it does indicate that the net donor strength is comparable to a (formally anionic) alkynyl ligand rather than a neutral isonitrile: i.e., the effect of the positive charge on phosphorus is not strongly felt at the metal center. A more extensive listing is provided by adducts of the familiar "$^RCpMn(CO)_2$" fragment, and although no complex with **1** has been isolated, adducts of $CCPMe_3$ and $CCPMe_2Ph$ are known.[5] Spectroscopic data for these and a range of C_1 ligands are given in Table 2.

These data would appear to suggest that **2** is a poor acceptor ligand, weaker than conventional isonitriles, and far weaker than alkylidenes and cumulenic ligands such as

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vinylidenes and allenylidenes. Among the neutral C_1 ligands (cf. charged alkylidynes), carbon monoselenide is the strongest π acid, while Lappert's N-heterocyclic carbenes are by a considerable margin the most electron releasing. To investigate the individual contributions to the net bonding, the energies of π-donor, σ-donor, and π-acceptor orbitals of **1** are compared with those of CO, $CNCH_3$, and $CNSiPh_3$ (*iso*-**3**, isoelectronic with **1**) at the level of theory previously employed[1] for **1** (B3LYP, 6-311G*). Figure 2a−c demonstrates that, from the perspective of an incoming metal center, the relevant orbitals (π-acceptor, σ-donor, and π-donor) have remarkably similar topology. Figure 2d displays the relative energetics of these orbitals in addition to those for CO and $CNSiPh_3$. The relative energies of the σ-donor and π-acceptor orbitals for CO and CNMe reinforce the accepted wisdom that isonitriles in general are both stronger σ-donors and weaker π-acceptors than CO. The relative energies of these orbitals do not change markedly between CNMe and $CNSiPh_3$, and the π-acceptor orbitals for **1** are essentially identical in energy with those for CNMe and *iso*-**3**. The distinctive feature of **1** in this scheme is that both the σ-donor orbital and the degenerate π-donor orbitals are significantly higher in energy, accounting for **1** being a potent donor ligand with very modest retrodative capacity.

Concluding Remarks. Previous routes to $CCPR_3$ complexes are somewhat substrate specific. The ylide route requires sufficiently electrophilic carbonyl ligands and proceeds via sterically encumbered intermediates, while the haloalkyne route requires sufficiently electron rich metal centers for oxidative addition to be viable. Dahlenburg's phosphinoalkynyl alkylation approach promises some generality, yet to be explored, so long as the precursor complexes can be obtained. At present, isolable mononuclear phosphinoalkynyl complexes remain extremely rare.[30] The route demonstrated herein offers broad applicability, whether the transfer reagent is $[HC{\equiv}CPPh_3]OTf$ or, in this case, its conjugate base, **1**. Furthermore, the potential exists with the current strategy to vary both the electronic and steric properties by employing different phosphines in place of PPh_3.

In terms of the coordination properties of **1**, carbonyl coligand infrared data suggest that **1** is a stronger net donor ligand than are isonitriles. While the use of carbonyls as reporter ligands for the comparative π-basicity of a metal has a long and illustrious history, deconvoluting σ-donor, π-acceptor, and π-donor contributions for a ligand of interest can be problematic. In the case of **1**, the energies of the π-acceptor orbitals are comparable to those of a conventional isonitrile. Thus, the principal features that therefore distinguish **1** from isonitriles relate to both the σ-donor and π-donor orbitals being substantially higher in energy, making **1** a potent net donor. In this respect, the interactions with a metal center assume character more akin to σ-alkynyls (albeit neutral).

Experimental Section

General Considerations. All manipulations involving $[Ru(CO)_2(PPh_3)_3]$ (**1**)[8] were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum-line, and inert-atmosphere drybox techniques, with dried and degassed dichloromethane which was distilled from calcium hydride (CH_2Cl_2) or THF which was distilled from sodium benzophenone ketyl. NMR spectra were obtained at 25 °C on a Varian Gemini 300BB (^1H at 299.944 MHz, ^{13}C at 75.420 MHz, ^{31}P at 121.470 MHz) spectrometer. Chemical shifts (δ) are given relative to residual protio solvents (^1H, ^{13}C) or external 85% D_3PO_4 (^{31}P), with coupling constants given in Hz. Elemental microanalytical data were obtained from the microanalytical service of the Australian National University. The compound $[Ru(CO)_2(PPh_3)_3]$ was prepared by a minor modification[8b] of Roper's original protocol.[8a] The salt $[Ph_3PC{\equiv}CSiMe_3]OTf$ (**2**·OTf) was prepared as described previously.[2]

Synthesis of $[RuH(C{\equiv}CPPh_3)(CO)_2(PPh_3)_2]OTf$ (7·OTf). (a) A solution of $[Me_3SiC{\equiv}CPPh_3]OTf$ (0.109 g, 0.21 mmol) in dichloromethane (10 mL) was cooled (dry ice/propanone), treated with a tetrahydrofuran solution of $[{}^nBu_4N]F$ (Aldrich "TBAF", 1.0 mol L^{-1}, 0.22 mL, 0.22 mmol), and stirred for 30 min. Solid $[Ru(CO)_2(PPh_3)_3]$ (0.200 g, 0.22 mmol) was added, and the mixture was stirred for 15 min and then warmed to 0 °C and stirred for 1 h. The resulting pale yellow solution was filtered through diatomaceous earth and freed of volatiles in vacuo. The residue was crystallized from a mixture of dichloromethane and ethanol. Yield: 0.062 g (26%).

(b) It transpired that commercial grade THF is sufficiently moist that the desilylation may be achieved without fluoride mediation: to an intimate mixture of $[Me_3SiC{\equiv}CPPh_3]OTf$ (0.545 g, 1.06 mmol) and $[Ru(CO)_2(PPh_3)_3]$ (1.00 g, 1.06 mmol) was added thoroughly degassed but otherwise benchtop grade tetrahydrofuran (50 mL) and the resulting mixture stirred for 1 h to provide a pale solid and dark supernatant. Dilution with hexane afforded a precipitate that was isolated by filtration and recrystallized from a mixture of dichloromethane and hexane as a dichloromethane monosolvate. Yield: 0.763 g (64%). Crystals of this dichloromethane solvate suitable for crystallographic and elemental microanalysis were grown by slow diffusion of hexane into a saturated solution of the salt in dichloromethane. IR (CH_2Cl_2): 2038 s, 1988 vs ν_{CO}, 1959 s ν_{CC}, 1891 w br ν_{RuH} cm^{-1}. NMR (CD_2Cl_2): ^1H, δ_H −5.80 (dt, 1 H, $^2J_{PH} = 18.3$, $^4J_{PH} = 1.5$ Hz, RuH), 6.80, 6.85 (dd × 2, 6 H, $^3J_{HH} = 8.4$, $^4J_{HH} = 1.2$, $H^1(C_6H_5)$), 7.17−7.33 (m × 7, 24 H, $H^{3,5}(C_6H_5)$), 7.45−7.52 (m, 12 H, $H^{3,5}(C_6H_5)$), 7.59 (ttd, 3 H, $^3J_{HH} = 7.7$, $^4J_{HH} = 2$, $^5J_{PH} = 4$, $H^4(C_6H_5)$); $^{13}C\{^1H\}$, δ_C 197.6 (t, RuCO, $^2J_{PC} = 16$), 195.5 (t, RuCO, $^2J_{PC} = 12$), 176.7 (d, $^2J_{PC} = 24.6$), 134.0 ($C^{3,5}(P_2C_6H_5)$), 133.8 ($C^{3,5}({}^+PC_6H_5)$), 132.8 ($C^{3,5}({}^+PC_6H_5)$), 129.9 ($C^4({}^+PC_6H_5)$), 128.7 ($C^{2,6}(P_2C_6H_5)$), 131.0 ($C^4(P_2C_6H_5)$), $C^1(PC_6H_5)$ obscured, 87.31 (d, $^1J_{PC} = 183.1$ Hz, $Ru\mathit{C}{\equiv}CP$); $^{31}P\{^1H\}$, −5.87 (t, 1 P, $^4J_{PP} = 5$), 44.20 (d, 2 P, $^4J_{PP} = 4$ Hz). ESI-MS (positive ion, high resolution): found (calcd) *m*/*z* 969.1806 (969.1779). ESI-MS (positive ion, low resolution): *m*/*z*(%) [assignment] 969.5 (7) $[\mathbf{7}]^+$, 939.5 (100) $[\mathbf{7} - H - CO]^+$, 913 (4) $[\mathbf{7} - 2CO]^+$, 677.3 (7) $[\mathbf{7} - PPh_3]^+$, 649.2 (7) $[\mathbf{7} - PPh_3 - CO]^+$. Anal. Found: C, 59.62; H, 3.88. Calcd for $C_{60}H_{48}Cl_2F_3O_5P_3RuS$: C, 59.91; H, 4.02. Crystal data for **4**·OTf·CH_2Cl_2: $C_{60}H_{48}Cl_2F_3O_5P_3RuS$, $M_w = 1202.92$, triclinic, $P\bar{1}$, $a = 10.0272(2)$ Å, $b = 14.6376(4)$ Å, $c = 19.3095(7)$ Å, $\alpha = 86.3740(10)°$, $\beta = 78.064(2)°$, $\gamma = 79.451(2)°$, $V = 2725.05(14)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 1.466$ Mg m^{-3}, μ(Mo Kα) = 0.572 mm^{-1}, colorless plate 0.40 × 0.10 × 0.03 mm, $T = 100(2)$ K, 9482 independent measured reflections ($2\theta \le 50°$), R1 = 0.0619, wR2 = 0.1684 for 8225 independent observed absorption-corrected reflections ($I > 2\sigma(I)$), 696 parameters, 9 restraints, residual electron density between −0.985 and 0.616 e $Å^{-3}$. Data were collected from a twinned crystal and were detwinned by employing an initial structural model using TWINROTMAT as implemented in WinGX PLATON. An HKL5 format data set thus derived was employed for the final refinement. Twin populations were refined to 83% and 17% (CCDC 699397).

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solution and refinement of the structure of **4**·OTf·CH_2Cl_2. We thank the Australian Research Council (ARC) for financial support (Grant No. DP0556236) and the Deustcher Akademischer Austauschdienst for the award of a fellowship (to J.W.).

Supporting Information Available: A table giving selected spectroscopic and structural data for phosphonioacetylide complexes and a CIF file giving details of the crystal structure determination of **7**·OTf·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.