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Chlorophosphino Carbyne Complexes of Tungsten

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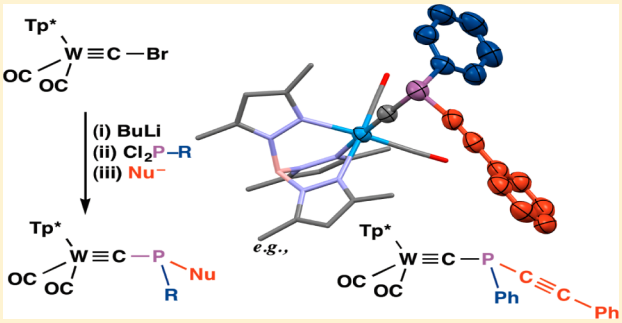
Supporting Information

ABSTRACT: A range of chlorophosphinocarbyne complexes $[W(\equiv CPClR)(CO)_2(Tp^*)]$ (R = Cl, Cy, Ph; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) has been prepared by reaction of chlorophosphines with the lithiocarbyne complex $[W\{\equiv CLi(THF)_n\}(CO)_2(Tp^*)]$. These complexes undergo nucleophilic substitution of chloride to enable the preparation of phosphinocarbynes bearing alkyl, aryl, alkynyl, aryloxy, and secondary phosphino substituents $[W(\equiv CPRR')(CO)_2(Tp^*)]$ (R = Ph, R′ = Me, Ph, C≡CPh, OPh, H; R = Cy, R′ = H).



INTRODUCTION

Carbynes $L_nM{\equiv}CR$, as one of the simplest carbon-based ligands, and phosphines, as ubiquitous (spectator and noninnocent) ligands, both represent in their own way fundamental groups in organometallic chemistry. Despite dating back to Fischer's seminal report in 1973,[1] the appearance of carbyne complexes in the literature remains somewhat sporadic. A notable exception to this involves carbyne complexes serving as catalysts for alkyne metathesis, which continues to receive considerable attention.[2−8] Carbyne complexes bearing heteroatom carbyne substituents have been less studied, and in part this reflects limitations in synthetic methodologies that are typically distinct from classical Fischer or Schrock protocols.[9−16]

We have enjoyed some success employing the "$M(CO)_2(Tp^*)$" fragments (M = Mo, W; Tp* = 3,5-hydrotris(dimethylpyrazolyl)borate)) for the construction of comparatively elaborate carbyne complexes, in particular those that bear heteroatomic carbyne subsitutents.[17−29] The combination of the bulky Tp* ligand (Tolman cone angle = 224°),[30] which affords kinetic stabilization, and the π-acidic CO coligands, which render the metal center relatively inert, allows modifications at the carbyne ligand to proceed, in many cases, without disruption of the M≡C linkage or $M(CO)_2(Tp^*)$ coordination sphere. In contrast to carbyne chemistry, phosphorus chemistry is very mature. Chlorophosphines are the quintessential building blocks for a myriad of phosphorus species due to the high reactivity of the P−Cl linkage and subsequent ease of nucleophilic substitution at this position.

Combining these two principles we have considered the marriage of conventional organophosphorus chemistry with that of carbyne complexes. We have previously demonstrated that tertiary phosphinocarbyne complexes $[M(\equiv CPPh_2)(CO)_2(Tp^*)]$ (M = W **2a**, Mo **2b**))[21,29] and phosphonito carbynes $[Mo\{\equiv CP(O)(OEt)_2\}(CO)_2(Tp^*)]$[21] are readily accessible from the bromocarbyne precursor $[M(\equiv CBr)(CO)_2(Tp^*)]$ (M = W **1a**, Mo **1b**) via lithium/halogen exchange with ^{n}BuLi and nucleophilic substitution of $PClPh_2$ or alternatively via palladium-catalyzed phosphination using $PH(O)(OEt)_2$, respectively. These complexes possess relatively inert phosphorus centers, undergoing conventional "phosphine-type" reactions with electrophiles, oxidants, and metal centers.

In search of more versatile precursors, it has been found that the palladium-mediated protocol is also effective for the preparation of secondary phosphinocarbynes $[W(\equiv CPHR)(CO)_2(Tp^*)]$ (R = Cy, Ph), which undergo deprotonation upon treatment with potassium hydride to provide the first terminal phosphaisocyanide complexes (Scheme 1a).[28]

The synthetic utility offered by chlorophosphines underpinned the first preparation of phosphinocarbynes by Cummins,[31,32] wherein reduction of the P−Cl bond of $[Mo(\equiv CPClPh)\{N^tBu(C_6H_3Me_2\text{-}3,5)\}_3]_2$ with sodium amalgam was targeted as a potential route to phosphaisocyanide complexes. In this case the resulting dimer $[Mo(\equiv CPPhNa)(L)_2\{N^tBu(3,5\text{-}C_6H_3Me_2)\}_3]_2$ (L = Et_2O, THF) was found to more closely adhere to a phosphidocarbyne description rather than the phosphaisocyanide alternative (Scheme 1). Attempts to synthesize a *neutral* phosphaisocyanide complex $[Mo(CPPh)\{N^tBu(3,5\text{-}C_6H_3Me_2)\}_3]$ led instead to the diphosphinocarbyne dimer $[Mo(\mu\text{-}CPPh)_2\{N^tBu(C_6H_3Me_2\text{-}3,5)\}_6]$ (Scheme 1), either via reduction of $[Mo(\equiv CPClPh)\{N^tBu(3,5\text{-}C_6H_3Me_2)\}_3]$ or reaction of $[Mo(\equiv CPClPh)\{N^tBu(3,5\text{-}C_6H_3Me_2)\}_3]$ with the phosphido complex $[Mo(\equiv CPPhNa)(L)_2\{N^tBu(3,5\text{-}C_6H_3Me_2)\}_3]_2$.

Herein we report the preparation of a series of tungsten chlorophosphinocarbyne complexes and studies into their reactivity.

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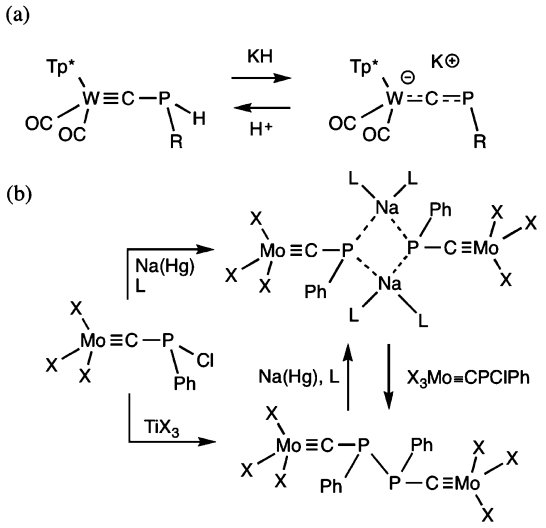
Scheme 1. Phosphinocarbynes as Precursors to Phosphaisocyanide Complexes[a]

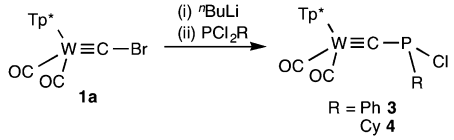


[a]R = Ph, Cy; X = N^{t}BuC$_6$H$_3$Me$_2$-3,5; L = Et$_2$O, THF.

RESULTS AND DISCUSSION

Applying the synthetic protocol used for the preparation of tertiary phosphinocarbynes,[21,29] the bromocarbyne complex **1a** was lithiated using ^{n}BuLi at −78 °C, followed by *in situ* treatment at this temperature with dichlorophenylphosphine to provide [W(≡CPClPh)(CO)$_2$(Tp*)] (**3**) as a peach-colored powder in 71% yield (Scheme 2). The infrared spectrum of **3**

Scheme 2. Synthesis of Chlorophosphinocarbyne Complexes



contains carbonyl absorption bands at higher frequency (THF: 1992, 1905 cm^{-1}) than those of the diphenyl analogue **2a** (1981, 1893 cm^{-1}), indicating an increase in the π-acceptor capacity of the carbyne ligand, perhaps resulting from negative hyperconjugation involving the P−Cl σ^* orbital. In the solid-state (Nujol) infrared spectrum of **3** five absorption bands are seen in the carbonyl region, implicating either solid-state effects or the presence of rotational isomers, as has been noted previously for the complex [W(≡CPPh$_2$)(CO)$_2$(Tp*)] (**3**).[29]

As expected, the ^{31}P{^{1}H} NMR spectrum of **3** (δ_P = 91.2) displays a resonance shifted to significantly higher frequency compared to the tertiary phosphine **2a** (δ_P = 32.0), similar to what was observed for [Mo(≡CPClPh)(X)$_3$] (δ_P = 94.0; X = N^{t}Bu(3,5-C$_6$H$_3$Me$_2$)).[32] Coupling to ^{183}W is observed, with a $^2J_{WP}$ value of 77.9 Hz, this being slightly larger than that for **2a** (69.0 Hz). The chiral phosphorus center in **3** is reflected in the ^{1}H and ^{13}C{^{1}H} NMR spectra, which demonstrates the inequivalence of all three pyrazolyl rings, in addition to two ^{13}C resonances due to the diastereotopic carbonyl ligands. The carbyne carbon resonance appears to higher frequency at δ_C = 285.2 as a doublet straddled by ^{183}W satellites with a large $^1J_{PC}$ coupling constant of 96.0 Hz (cf. **2a** 74.5 Hz) and with $^1J_{WC}$ 189.0 Hz.

Unexpectedly, the ^{31}P{^{1}H} NMR resonance of **3** contained a shoulder to lower frequency of the main resonance, from which the presence of rotational isomers resulting from restricted rotation about the carbyne C−P bond was inferred, consistent with the solid-state IR data. Variable-temperature NMR studies in toluene-d_8 over the temperature range −90 to +90 °C failed to completely resolve signals attributable to the presumed rotamers (Figure 1). Complex **3** is the first phosphinocarbyne

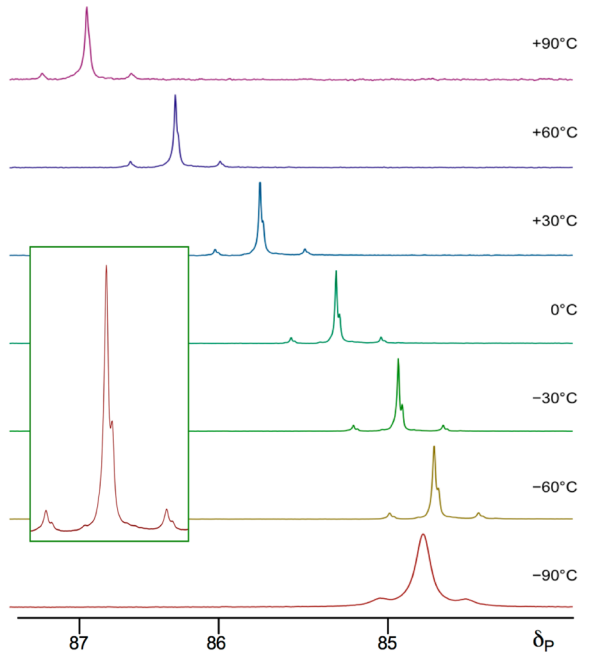


Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra of **3** (−90 to +90 °C, toluene-d_8, 121 MHz) indicating two rotamers δ_P = 84.88 ($^1J_{WP}$ = 76.5 Hz), 84.86 ($^1J_{WP}$ = 75.3 Hz). Inset: Maximum resolution enhancement for the spectrum measured at −30 °C.

for which rotational isomerism about the phosphorus−carbon bond is evident on the ^{31}P NMR time scale (121 MHz), although in a number of cases the coexistence of such isomers was apparent on the infrared time scale.[29]

Interestingly, the binuclear disubstitution product [W$_2$(μ-C$_2$PPh)(CO)$_4$(Tp*)$_2$][28] did not appear to form in significant quantities, indicating that the first P−Cl substitution step proceeds more readily than the second. This complex has however been observed as a side product in the palladium-mediated cross-coupling of **1** with phenylphosphine.

Complex **3** exhibits reasonable thermal stability; no significant decomposition was observed over 8 days at 80 °C in a toluene solution. However, **3** is highly moisture sensitive and decomposes within minutes in solution when exposed to either air or N$_2$-degassed H$_2$O, resulting in ca. five inseparable products, among which the complex [W{≡CPH(O)Ph}-(CO)$_2$(Tp*)] (initially ca. 30%) would appear to correspond to the resonance at δ_P = 13.9 ($^2J_{PW}$ = 156.1 Hz) given that the same resonance is observed, *inter alia*, when [W(≡CPHPh)-(CO)$_2$(Tp*)] is treated with hydrogen peroxide. Over 16 h, this complex decomposes such that the ^{31}P{^{1}H} NMR spectrum comprises ca. 90% of a single species (δ_P = 23.7) without visible ^{183}W satellites, suggesting hydrolysis ultimately results in cleavage of the P−C(carbyne) bond with formation of *P*-phenylphosphinous acid and Templeton's binuclear vinylidene complex [W$_2$(μ-CCH$_2$) (CO)$_4$(Tp*)$_2$].[33]

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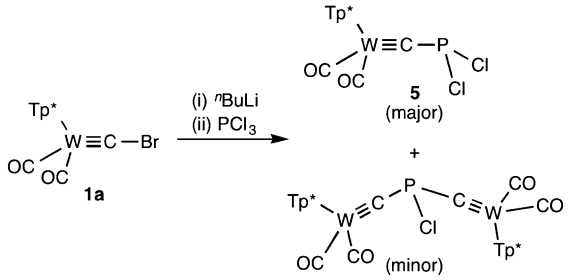
This approach was also extended to an alkyl-substituted phosphine. Thus, the reaction of **1**, ^{n}BuLi, and PCl_2Cy provides $[W(\equiv CPClCy)(CO)_2(Tp^*)]$ (**4**) in 65% yield (Scheme 2). The key spectroscopic features of **4** are similar to those associated with **3**. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ_P = 120.2 ($^2J_{WP}$ 67.9 Hz), to significantly higher frequency of the aryl derivative **3** (δ_P = 91.2), with no evidence of rotational isomerism on the ^{31}P NMR time scale. However, the THF infrared spectrum contains three carbonyl absorption bands at 1989 (s), 1969 (m), and 1901 (s) cm^{-1}, implicating the coexistence of rotamers, as seen previously.

Extending this work to trichlorophosphine proved problematic. When the reaction of the lithiocarbyne $[W(\equiv CLi)(CO)_2(Tp^*)]$ with one equivalent of PCl_3 was examined, a mixture of products was obtained (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum indicated that the desired product $[W(\equiv CPCl_2)(CO)_2(Tp^*)]$ (**5**) (δ_P 136.2, $^2J_{WP}$ 80.5 Hz) constituted *ca.* 90% of the isolated product, but that it was contaminated with *ca.* 10% of the bimetallic complex $[W_2(\mu\text{-}C_2PCl)(CO)_4(Tp^*)_2]$ (δ_P 124.7, $^2J_{WP}$ 70.3 Hz). In the synthesis of **3** and **4**, trace (<5%) quantities of the bimetallic complexes were observed on occasion.

Scheme 3. Synthesis of Chlorophosphinocarbyne Complexes Derived from PCl_3



While purification options beyond this level were somewhat restricted due to the hydrolytic sensitivity of the P−Cl linkage precluding chromatography, the IR and NMR data obtained substantiate the predominant formation of **5**. The phosphorus resonance for **5** appears at δ_P 136.2, close to that of Cummins' $[Mo(\equiv CPCl_2)(X)_3]$ (δ_P 120.1, X = N^{t}Bu(3,5-$C_6H_3Me_2$)),[32] while the $^2J_{WP}$ coupling constant (80.5 Hz) is indicative of the three-coordinate environment at phosphorus.[34]

Although the inability to purify **5** beyond this level restricted the acquisition of microanalytical data, some inferences could be made based on the spectroscopic data available. Table 1 summarizes some of the key spectroscopic data for the series $[W(\equiv CPRR')(CO)_2(Tp^*)]$ (R, R′ = Cl, Ph).

Substitution of phenyl substituents for chloro groups leads to a shift to higher frequency of the resonance in the ^{31}P NMR spectrum, accompanied by a modest increase in the tungsten−phosphorus coupling constant. The infrared frequencies and derived force constants of the carbonyl absorption bands increase upon replacement of phenyl substituents by chloro groups, which might be understood in terms of negative hyperconjugation between the W≡C π system and the empty P−Cl σ^* orbital(s).

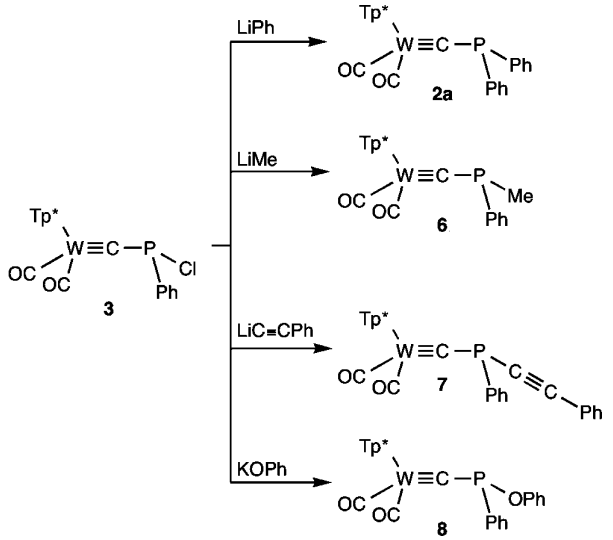
Table 1. Selected Spectroscopic Data for $[W]\equiv CPRR'$[a]

complex	δ_P, ppm	^2J_W, Hz	ν_{CO}, cm^{-1}	k_{CK}, N cm^{-1}
$[W]\equiv CPPh_2$ (**2**)[29]	32.2	66.2	1981, 1893	15.14
$[W]\equiv CPClPh$ (**3**)	91.2	74.9	1992, 1905	15.32
$[W]\equiv CPCl_2$ (**5**)	136.2	80.5	2005, 1920	15.54

[a] $[W] = W(CO)_2(Tp^*)$; R, R′ = Cl, Ph. NMR spectra were recorded in C_6D_6. IR spectra were recorded in THF. k_{CK}, Cotton−Kraihanzel force constant.

Having established a viable synthetic route to halophosphinocarbyne complexes, we next considered the reactivity of the P−Cl with respect to a range of nucleophiles to establish if these complexes might serve as general late intermediates for the synthesis of diversely substituted phosphinocarbynes. The proof of concept was established by treating a THF solution of **3** at −78 °C with a slight excess of phenyllithium, which resulted in exclusive formation of the known complex **2a**, as indicated by ^1H and $^{31}P\{^1H\}$ NMR analysis (Scheme 4).

Scheme 4. Nucleophilic Substitution Reactions of the Chlorophosphinocarbyne Complex $[W(\equiv CPClPh)(CO)_2(Tp^*)]$ (3)



With the viability of this approach demonstrated, the generality of the protocol was explored. A diethyl ether suspension of **3** was cooled to −78 °C and treated with methyllithium, resulting in a brown suspension. Following chromatography on silica gel, $[W(\equiv CPMePh)(CO)_2(Tp^*)]$ (**6**) was obtained as a yellow powder in 49% yield (Scheme 4). This route complements that in which **6** is obtained from the reaction of the anionic phosphaisocyanide $K[W(CPPh)(CO)_2(Tp^*)]$ with iodomethane.[28]

The synthesis of an alkynylphosphinocarbyne was considered attractive, as this would allow for internal comparison of carbyne M≡C and alkyne C≡C linkages bound to a single phosphorus within the one molecule. A THF solution of **3** at −78 °C was treated with a solution of lithium phenylacetylide in THF. The solution turned orange, and after chromatographic workup the alkynylphosphinocarbyne $[W\{\equiv CP(C\equiv CPh)Ph\}(CO)_2(Tp^*)]$ (**7**) was obtained as a spectroscopically and analytically pure yellow powder in excellent yield (90%) (Scheme 4).

A significant shift to lower frequency (95 ppm) in the $^{31}P\{^1H\}$ NMR spectrum of **7** (δ_P = −4.0, $^2J_{WP}$ 82.5 Hz) demonstrates the replacement of chloride from the precursor **3**. The resonance appears to higher frequency of that of the simple alkynylphosphine $P(C\equiv CPh)Ph_2$ (δ_P = −33.5).[35] The

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infrared spectrum (Nujol) contains carbonyl absorption bands at 1981 and 1890 cm^{-1}, similar to those seen for **2a** (1981, 1893 cm^{-1}).[29] Additionally, a weak absorption band at 2162 cm^{-1} is observed, which is attributed to the C≡C stretch of the alkynyl unit, close to that of P(C≡CPh)Ph_2 ($\nu_{C\equiv C}$ = 2161 cm^{-1}).[35] The introduction of the alkynyl moiety leads to a slight shift to lower frequency of the carbyne resonance (δ_C = 281.5) compared to that of **2a** (δ_C = 292.6).[29] The presence of the alkynyl unit is evident in the $^{13}C\{^1H\}$ NMR spectrum from peaks at δ_C = 107.4 (PC≡CPh, $^2J_{PC}$ 3.5 Hz) and δ_C = 82.6 (PC≡CPh, $^1J_{PC}$ 7.5 Hz). Curiously, the magnitude of this $^1J_{PC}$ coupling seems remarkably small compared to the $^1J_{PC}$(carbyne) value of 75.9 Hz. This is, however, not unprecedented; the corresponding resonance of the alkynylphosphine P(C≡CMes)Ph_2 appears as a doublet at δ_C 94.2 with $^1J_{PC}$ 6 Hz.[35]

X-ray quality crystals were obtained from a benzene/hexane solution of **7** at −20 °C, thus allowing for a comparison of the geometric features of the alkyne versus carbyne moieties (Figure 2). The W1−C1 (1.823(6) Å) and P1−C1 (1.790(6) Å) distances do not differ significantly from those of **2a** (W1−C1 1.827(2), P1−C1 1.783(3) Å),[29] despite incorporation of the alkynyl unit. The alkynylphosphino moiety resembles that of P(C≡CMe)Ph_2, with a formal P−C single bond (P1−C4 1.747(8) Å, cf. 1.759(2) Å) and C−C triple bond (C4−C5 1.224(10) Å, cf. 1.206(2) Å).[36] The P(C≡CPh)Ph moiety is oriented such that the phenyl group eclipses one carbonyl ligand, while the C≡CPh group bisects the N31−W1−C2(O) angle (Figure 2 inset). This differs from the PPh_2 conformation in **2a**, in which the two phenyl groups eclipse one carbonyl ligand and one pyrazolyl ring. However, the contrasting conformational preferences of **2a** and **7** are not surprising since calculations have shown that conversion between conformers of **2a** is facile due to the low energy differences involved.[29]

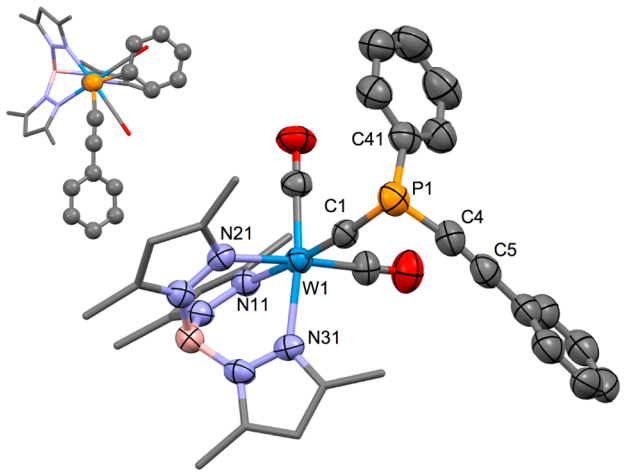


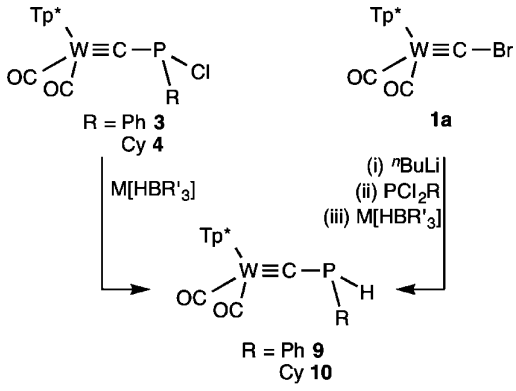
Figure 2. Molecular structure of one enantiomer of **7** in a crystal of *rac*-**7**·C_6H_6 (50% displacement ellipsoids, hydrogen atoms omitted). Inset: View along P1−C1−W1. Selected bond lengths (Å) and angles (deg): W1−C1 1.823(6), C1−P1 1.790(6), P1−C4 1.747(8), C4−C5 1.224(10), C5−C51 1.451(11), W1−C1−P1 169.4(4), C1−P1−C4 97.9(3), P1−C4−C5 172.3(7), $\sum(C_x-P1-C_y)$ = 300.3(11). Alternative enantiomer gerenated by crystallograhic $P\bar{1}$ symmetry.

Given the ease of substitution with carbon-based nucleophiles, attempts to extend this chemistry to an aryloxy reagent were undertaken. The reaction of **3** with phenol in the presence of either Et_3N or potassium hydride gave complex mixtures of products, as evident in the $^{31}P\{^1H\}$ NMR spectrum, with the desired phenoxyphosphine representing less than 10% of the mixture. The use of isolated KOPh[37] was however more fruitful, resulting in a $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture containing one major product at δ_P = 127.1 ($^2J_{WP}$ 74.0 Hz), for which both the chemical shift (cf. P(OPh)Ph_2 δ_P 111.0) and the magnitude of the coupling constant are consistent with the desired product [W{≡CP(OPh)Ph}$(CO)_2$(Tp*)] (**8**) (Scheme 4).

Although the spectroscopic yield for the reaction was respectable (ca. 65% by $^{31}P\{^1H\}$ NMR spectroscopy), attempts to chromatograph the crude reaction mixture led to significant decomposition, with **8** isolated in only 17% yield, presumably due to facile hydrolysis of the P−O bond on the acidic silica gel. Fortunately, spectroscopically and analytically pure **8** could be obtained in 44% yield by filtration through diatomaceous earth and precipitation of the impurities from benzene/hexane.

We have recently described the preparation of the first examples of secondary phosphinocarbyne complexes via a palladium-catalyzed P−C bond forming reaction between **1a** and primary phosphines.[28] However, the use of hydride reagents to convert halophosphines to the corresponding secondary phosphines is well documented.[38] This methodology provided an alternative route for the preparation of secondary phosphinocarbyne complexes, which is particularly attractive in the case of compounds in which the requisite primary phosphine is not readily available. Treatment of a THF solution of **3** with Li[$BHEt_3$] or K[BH^sBu_3] resulted in formation of the secondary phosphinocarbyne [W(≡CPHPh)$(CO)_2$(Tp*)] (**9**) (Scheme 5). Conveniently, the synthesis of **9** can also be achieved in a one-pot reaction from **1a** (Scheme 5), and this approach also allows the preparation of bulk samples of **9** with relative ease, obviating the purification of the intermediate halophosphine. This borohydride reduction route also provides the cyclohexyl derivative [W(≡CPHCy)$(CO)_2$(Tp*)] (**10**).

Scheme 5. Preparation of Secondary Phosphinocarbyne Complexes[a]



[a]M[HBR′$_3$] = Li[$HBEt_3$], K[HB^sBu_3].

CONCLUSIONS

The lithium−halogen exchange/substitution method has been extended to the generation of tungsten chlorophosphinocarbyne complexes bearing alkyl, aryl, and halo substituents. The reactive nature of the P−Cl bond in these complexes can be

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exploited, enabling late-stage functionalization of such species. Halide metathesis with organometallic alkyl, aryl, alkynyl, and aryloxy nucleophiles has provided mixed phosphinocarbynes [W(≡CPRR′)(CO)$_2$(Tp*)], while reduction generates secondary phosphinocarbynes [W(≡CPHR)(CO)$_2$(Tp*)]. This work has demonstrated that, in many cases, conventional organophosphorus chemistry is applicable to organometallic C_1 systems, including late-stage P-functionalization.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air-sensitive compounds were carried out at room temperature under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, and inert atmosphere (argon) glovebox techniques with dried and degassed solvents. NMR spectra were obtained at 25 °C on Varian Mercury 300 (^{1}H at 300.1 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.5 MHz), Varian Inova 300 (^{1}H at 299.9 MHz, ^{13}C at 75.42 MHz, ^{31}P at 121.4 MHz), Varian MR 400 (^{1}H at 399.9 MHz, ^{13}C at 100.5 MHz, ^{31}P at 161.9 MHz), Bruker Avance 400 (^{1}H at 400.1 MHz, ^{31}P at 162.0 MHz), Varian Inova 500 (^{1}H at 500.0 MHz, ^{13}C at 125.7 MHz), Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz), or Bruker Avance 800 (^{1}H at 800.1 MHz, ^{13}C at 201.2 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P) with coupling constants given in Hz. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of ^{183}W satellites. While ^{13}C{^{1}H} signals for carbon nuclei of PPh and PCy groups could be routinely observed, their narrow spectral range and comparable J_{PC} values often precluded unequivocal assignment, in which case they are designated as "C^{2,3,5,6}(PPh)" or "C^{2,3,5,6}(Cy)". In some cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (i.e., 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. Infrared spectra were obtained using a PerkinElmer Spectrum One FT-IR spectrometer. Elemental microanalytical data were obtained from the ANU Research School of Chemistry microanalytical service. Electrospray ionization mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. For compounds containing P−Cl or P−O moieties no interpretable mass spectrometry data were obtained due to the hydrolytic sensitivity of the P−X bond. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer. The compounds [W(≡CBr)(CO)$_2$(Tp*)],[28] KOPh,[37] and LiCCPh[39] were prepared according to published procedures. All other reagents were used as obtained from commercial sources. All new compounds and reagents employed were treated as toxic.

Synthesis of [W(≡CPClPh)(CO)$_2$(Tp*)] (3). A solution of [W(≡CBr)(CO)$_2$(Tp*)] (**1a**: 2.999 g, 4.768 mmol) in THF (100 mL) was cooled to −78 °C (dry ice/acetone) and treated with ^{n}BuLi (3.0 mL, 1.6 M in hexanes, 4.8 mmol). The resulting light brown solution was stirred for 30 min and then treated with PCl_2Ph (0.65 mL, 4.8 mmol). The solution instantly turned dark red and was stirred for a further 70 min, then allowed to warm to room temperature. Volatiles were removed under reduced pressure, and the solid residue was extracted with *n*-pentane (4 × 50 mL). The combined extracts were collected by cannula filtration followed by concentration under reduced pressure and cooling to −15 °C to afford a peach-colored precipitate, which was isolated by filtration. Yield: 2.335 g (3.371 mmol, 71%). IR (Nujol) ν/cm^{-1}: 2550 w, 2524 w (BH), 2006 sh, 1987 s, 1970 sh, 1923 sh, 1898 s (CO). IR (THF) ν/cm^{-1}: 2551 w (BH), 1992 vs, 1905 vs (CO). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.85−7.79 (m, 2 H, C_6H_5), 7.45−7.42 (m, 3 H, C_6H_5), 5.90 (s, 1 H, pzH), 5.89 (s, 1 H, pzH), 5.75 (s, 1 H, pzH), 2.45 (s, 3 H, $pzCH_3$), 2.37 (s, 3 H, $pzCH_3$), 2.36 (s, 6 H, $pzCH_3$, coincident), 2.36 (s, 3 H, $pzCH_3$), 2.30 (s, 3 H, $pzCH_3$). ^{1}H NMR (C_6D_6) δ/ppm: 7.96−7.91 (m, 2 H, C_6H_5), 7.10−6.99 (m, 3 H, C_6H_5), 5.48 (s, 2 H, pzH, coincident), 5.27 (s, 1 H, pzH), 2.55 (s, 3 H, $pzCH_3$), 2.51 (s, 3 H, $pzCH_3$), 2.28 (s, 3 H, $pzCH_3$), 2.02 (s, 3 H, $pzCH_3$), 2.01 (s, 3 H, $pzCH_3$), 1.96 (s, 3 H, $pzCH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ/ppm: 285.2 (d, W≡C, $^1J_{PC}$ = 96.0, $^1J_{WC}$ = 189.0), 224.7 (CO, $^1J_{WC}$ = 165.4), 224.7 (CO, $^1J_{WC}$ = 165.4), 152.6 (1 C), 152.1 (1 C), 152.0 (1 C), 145.6 (1 C), 144.8 (1 C), 144.8 (1 C) [C^{3,5}(pz)], 138.7 [d, C^1(C_6H_5), $^1J_{PC}$ = 33.2], 132.2 [d, C^{2,3,5,6}(C_6H_5), J_{PC} = 27.2], 130.3 [C^4(C_6H_5)], 128.7 [d, C^{2,3,5,6}(C_6H_5), J_{PC} = 7.5], 107.0 (1 C), 106.7 (2 C, coincident) [C^4(pz)], 16.9 (2 C, coincident), 15.2 (1 C), 12.7 (2 C, coincident), 12.7 (1 C) ($pzCH_3$). ^{13}C{^{1}H} NMR (C_6D_6) δ/ppm: 286.6 (d, W≡C, $^1J_{PC}$ = 95.5, $^1J_{WC}$ = 189.3), 225.7 (CO, $^1J_{WC}$ = 164.6), 225.5 (CO, $^1J_{WC}$ = 165.4), 152.8 (1 C), 152.2 (1 C), 152.2 (1 C), 145.3 (1 C), 144.5 (1 C), 144.5 (1 C) [C^{3,5}(pz)], 139.5 [d, C^1(C_6H_5), $^1J_{PC}$ = 33.3], 132.7 [d, C^{2,3,5,6}(C_6H_5), J_{PC} = 26.3], 130.5 [C^4(C_6H_5)], 129.0 [d, C^{2,3,5,6}(C_6H_5), J_{PC} = 8.1], 107.3 (1 C), 107.1 (2 C, coincident) [C^4(pz)], 17.2 (1 C), 17.1 (1 C), 15.1(1 C), 12.4 (3 C, coincident) ($pzCH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ/ppm: 91.2 ($^2J_{WP}$ = 77.9). ^{31}P{^{1}H} NMR (C_6D_6) δ/ppm: 91.2 ($^2J_{WP}$ = 74.9). Anal. Found: C, 41.58; H, 4.11; N, 12.17. Calcd for $C_{24}H_{27}BClN_6O_2PW$: C, 41.62; H, 3.93; N, 12.13.

Synthesis of [W(≡CPClCy)(CO)$_2$(Tp*)] (4). A solution of [W(≡CBr)(CO)$_2$(Tp*)] (**1a**: 2.500 g, 3.975 mmol) in THF (80 mL) was cooled to −78 °C (dry ice/acetone) and treated with ^{n}BuLi (2.35 mL, 1.7 M in hexanes, 4.0 mmol). The resulting light brown solution was stirred for 45 min and then treated with PCl_2Cy (0.61 mL, 4.0 mmol). The solution instantly turned dark red and was stirred for a further 60 min, then allowed to warm to room temperature. Volatiles were removed under reduced pressure, and the solid residue was extracted with *n*-pentane (4 × 30 mL). The combined extracts were collected by cannula filtration. Concentration under reduced pressure then cooling to −15 °C resulted in an orange-colored precipitate, which was isolated by filtration. Yield: 1.814 g (2.596 mmol, 65%). IR (Nujol) ν/cm^{-1}: 2552 w, 2528 w (BH), 2006 s, 1987 s, 1967 m, 1917 s, 1897 s (CO). IR (THF) ν/cm^{-1}: 2550 w (BH), 1989 s, 1969 m, 1901 s (CO). IR (pentane) ν/cm^{-1}: 2551 w (BH), 1989 s, 1969 m, 1901 s, 1888 m (CO). ^{1}H NMR ($CDCl_3$) δ/ppm: 5.97 (s, 2 H, pzH, coincident), 5.80 (s, 1 H, pzH), 2.64 (s, 6 H, $pzCH_3$, coincident), 2.42 (s, 9 H, $pzCH_3$, coincident), 2.36 (s, 3 H, $pzCH_3$), 2.20−1.31 (m, 11 H, Cy). ^{1}H NMR (C_6D_6) δ/ppm: 5.53 (s, 2 H, pzH, coincident), 5.32 (s, 1 H, pzH), 2.74 (s, 3 H, $pzCH_3$), 2.70 (s, 3 H, $pzCH_3$), 2.32 (s, 3 H, $pzCH_3$), 2.28−2.17 (m, 2 H, Cy), 2.05 (s, 6 H, $pzCH_3$, coincident), 2.00 (s, 3 H, $pzCH_3$), 1.68−1.10 (m, 9 H, Cy). ^{13}C{^{1}H} NMR (C_6D_6) δ/ppm: 292.2 (d, W≡C, $^1J_{PC}$ = 99.9, $^1J_{WC}$ = 193.6), 227.2 (CO, $^1J_{WC}$ = 165.7), 225.8 (CO, $^1J_{WC}$ = 166.9), 152.7 (1 C), 152.2 (2 C, coincident), 145.3 (1 C), 144.7 (1 C), 144.5 (1 C) [C^{3,5}(pz)], 107.3 (1 C), 107.1 (2 C, coincident) [C^4(pz)], 46.1 [d, C^1(Cy), $^1J_{PC}$ = 30.2], 29.0 [d, C^{2,3,5,6}(Cy), J_{PC} = 16.7], 28.7 [d, C^{2,3,5,6}(Cy), J_{PC} = 10.4], 27.1 [d, C^{2,3,5,6}(Cy), J_{PC} = 12.6], 27.0 [d, C^{2,3,5,6}(Cy), J_{PC} = 8.8], 26.3 [C^4(Cy)], 17.5 (1 C), 17.4 (1 C), 15.2 (1 C), 12.5 (2 C, coincident), 12.5 (1 C) ($pzCH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ/ppm: 121.1 ($^2J_{WP}$ = 69.0). ^{31}P{^{1}H} NMR (C_6D_6) δ/ppm: 120.2 ($^2J_{WP}$ = 67.9). Anal. Found: C, 41.79; H, 5.12; N, 11.61. Calcd for $C_{24}H_{33}BClN_6O_2PW$: C, 41.26; H, 4.76; N, 12.03.

Synthesis of [W(≡CPCl$_2$) (CO)$_2$(Tp*)] (5). A solution of [W(≡CBr)(CO)$_2$(Tp*)] (**1a**: 0.150 g, 0.238 mmol) in THF (20 mL) was cooled to −78 °C and treated with ^{n}BuLi (0.53 mL, 0.45 M in hexanes, 0.24 mmol). The resulting light brown solution was stirred for 20 min and then treated with PCl_3 (0.79 mL, 0.30 M in hexanes, 0.24 mmol). The solution instantly turned red and was stirred for a further 30 min, then allowed to warm to room temperature. Volatiles were removed under reduced pressure. The product was extracted with benzene, and the solvent was removed under reduced pressure to afford crude **5** as a dark red solid (ca. 90% **5** by ^{31}P{^{1}H} NMR spectroscopy). Yield: 0.121 g (0.186 mmol, 78%). The complex is unstable with respect to chromatography on silica gel or alumina, and attempts to purify the material by fractional recrystallization failed to provide an analytically pure compound. Limited spectroscopic data for the crude product are given here. IR (THF) ν/cm^{-1}: 2552 w (BH), 2005 s, 1920 vs (CO). ^{1}H NMR (C_6D_6) δ/ppm: 5.48 (s, 2 H, pzH), 5.30 (s, 1 H, pzH), 2.58 (s, 6 H, $pzCH_3$), 2.22 (s, 3 H, $pzCH_3$), 2.04 (s, 6 H, $pzCH_3$), 1.96 (s, 3 H, $pzCH_3$). ^{31}P{^{1}H} NMR (C_6D_6) δ/ppm: 136.2 ($^2J_{WP}$ = 80.5). A second product could be identified as a very minor (<10%) side

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product, which was identified as $[W_2(\mu\text{-}C_2PCl)(CO)_4(Tp^*)_2]$: IR (THF) ν/cm^{-1}: 2550 w (BH), 1996 s, 1986 s, 1906 vs (CO). ^{1}H NMR (C_6D_6) δ/ppm: 5.48 (s, 4 H, pzH), 5.32 (s, 2 H, pzH), 2.69 (s, 6 H, pzCH$_3$), 2.54 (s, 6 H, pzCH$_3$), 2.31 (s, 6 H, pzCH$_3$), 2.09 (s, 12 H, pzCH$_3$), 2.02 (s, 6 H, pzCH$_3$). ^{13}C{^{1}H} NMR (C_6D_6) δ/ppm: 280.0 (d, W≡C, $^1J_{PC}$ = 97.9, $^1J_{WC}$ = 194.0), 226.4 (s, WCO, $^1J_{WC}$ = 164.5), 225.0 (s, WCO, $^1J_{WC}$ = 166.0), 152.8 (2 C), 152.6 (2 C), 152.2 (2 C), 145.4 (2 C), 144.4 (2 C), 144.3 (2 C) [C^{3,5}(pz)], 107.4 (2 C), 106.9 (4 C) [C^4(pz)], 17.3 (2 C), 17.0 (2 C), 15.2 (2 C), 12.6 (4 C), 12.5 (2 C) (pzCH$_3$). ^{31}P{^{1}H} NMR (C_6D_6) δ/ppm: 124.9 (s, $^2J_{WP}$ = 66.4).

Synthesis of [W(≡CPMePh)(CO)$_2$(Tp*)] (6). A suspension of [W(≡CPClPh)(CO)$_2$(Tp*)] (**3**: 0.167 g, 0.241 mmol) in Et$_2$O (20 mL) was cooled to −78 °C and treated with MeLi (0.16 mL, 1.6 M in Et$_2$O, 0.26 mmol). The resulting brown suspension was stirred for 1 h, then allowed to warm to room temperature. The reaction mixture was chromatographed on silica gel using 2:1 hexane/THF as the eluent. The first yellow band containing the product was collected, and the solvent removed under reduced pressure to afford **6** as a yellow powder. Yield: 0.080 g (0.12 mmol, 49%). Spectroscopic data conform to those previously reported.[28]

Synthesis of [W{≡CP(C≡CPh)Ph}(CO)$_2$(Tp*)] (7). A solution of [W(≡CPClPh)(CO)$_2$(Tp*)] (**3**: 0.200 g, 0.289 mmol) in THF (10 mL) was cooled to −78 °C and treated with LiC≡CPh (1.6 mL, 0.18 M in THF, 0.29 mmol). The resulting orange solution was stirred for 40 min, then allowed to warm to room temperature and stirred for a further hour. The volatiles were removed under reduced pressure. The residue was chromatographed on silica gel, using hexane as the initial eluent followed by increasing the polarity to 1:1 CH_2Cl_2/hexane. The first orange fraction was collected, and the solvent was removed under reduced pressure to afford **7** as an orange powder. Crystals of a benzene monosolvate suitable for crystallographic analysis were grown from a solution of **7** in benzene/hexane. Yield: 0.196 g (0.258 mmol, 90%). IR (Nujol) ν/cm^{-1}: 2549 w (BH), 2162 w (C≡C), 1981 s, 1890 s, br (CO). IR (THF) ν/cm^{-1}: 2550 w (BH), 2160 w (C≡C), 1983 s, 1896 vs (CO). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.90 (m, 2 H, C_6H_5), 7.60 (m, 2 H, C_6H_5), 7.42 (m, 3 H, C_6H_5), 7.37 (m, 3 H, C_6H_5), 5.92 (s, 1 H, pzH), 5.90 (s, 1 H, pzH), 5.78 (s, 1 H, pzH), 2.54 (s, 3 H, pzCH$_3$), 2.48 (s, 3 H, pzCH$_3$), 2.43 (s, 3 H, pzCH$_3$), 2.39 (s, 6 H, pzCH$_3$), 2.35 (s, 3 H, pzCH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ/ppm: 281.5 (d, W≡C, $^1J_{PC}$ = 75.9, $^1J_{WC}$ = 192.1), 224.4 (CO, $^1J_{WC}$ = 166.9), 224.3 (CO, $^1J_{WC}$ = 167.0), 152.6 (1 C), 152.2 (2 C, coincident), 145.4 (1 C), 144.6 (1 C), 144.6 (1 C) [C^{3,5}(pz)], 133.9 [d, C^1{P(C_6H_5)}, $^1J_{PC}$ = 3.0], 133.2 [d, C^{2,3,5,6}{P(C_6H_5)}, J_{PC} = 22.0], 131.9 [C^{2,3,5,6}{CC(C_6H_5)}], 129.2 [C^4(C_6H_5)], 128.7 [d, C^{2,3,5,6}{P(C_6H_5)}, J_{PC} = 8.0], 128.7 [C^4(C_6H_5)], 128.4 [C^{2,3,5,6}{CC(C_6H_5)}], 123.3 [C^1{CC(C_6H_5)}], 107.4 (d, PC≡*C*Ph, $^2J_{PC}$ = 3.5), 106.9 (1 C), 106.6 (1 C), 106.6 (1 C) [C^4(pz)], 82.6 (d, P*C*≡CPh, $^1J_{PC}$ = 7.5), 16.9 (1 C), 16.8 (1 C), 15.2 (1 C), 12.7 (2 C, coincident), 12.7 (1 C) (pzCH$_3$). N.B. The C^4(C_6H_5) resonances could not be unambiguously assigned. ^{31}P{^{1}H} NMR ($CDCl_3$) δ/ppm: −4.0 ($^2J_{WP}$ = 82.5). MS-ESI(+): *m*/*z* 797.0 [M + K]$^+$, 781.5 [M + Na]$^+$, 759.5 [M + H]$^+$, 731.5 [M − CO + H]$^+$, 701.9 [M − 2 CO]$^+$. Accurate mass: found 797.1568 [M + K]$^+$. Calcd for $C_{32}H_{32}{}^{11}BN_6O_2{}^{39}KP^{184}W$: 797.1564. Found: 759.2010 [M + H]$^+$. Calcd for $C_{32}H_{33}{}^{11}BN_6O_2P^{184}W$: 759.2005. Anal. Found: C, 50.46; H, 4.46; N, 11.14. Calcd for $C_{32}H_{32}BN_6O_2PW$: C, 50.69; H, 4.25; N, 11.08. Crystal data for $C_{32}H_{32}BN_6O_2PW$: M_w = 836.39, triclinic, $P\bar{1}$ (No. 2), a = 12.2295(5) Å, b = 12.8837(5) Å, c = 13.0374(6) Å, α = 66.331(2)°, β = 78.549(3)°, γ = 77.752(3)°, V = 1823.77(14) Å^3, Z = 2, ρ_{calcd} = 1.523 Mg m^{-3}, μ(Mo Kα) = 3.25 mm^{-1}, T = 200(2) K, orange prism, 0.16 × 0.07 × 0.06 mm, 6448 independent reflections. F^2 refinement, R = 0.041, wR = 0.082 for 5307 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 50°), 442 parameters.

Synthesis of [W{≡CP(OPh)Ph}(CO)$_2$(Tp*)] (8). A solution of [W(≡CPClPh)(CO)$_2$(Tp*)] (**3**: 0.099 g, 0.14 mmol) in THF (2 mL) was cooled to 0 °C and treated with KOPh (0.020 g, 0.15 mmol) in THF (1 mL). The resulting orange-brown solution was stirred for 30 min, then allowed to warm to room temperature and stirred for a further 30 min. The solvent was removed under reduced pressure. The residue was dissolved in benzene and filtered through diatomaceous earth, and the filter was washed through with benzene until the washings were colorless. The filtrate was concentrated to ca. 0.5 mL, and hexane (2 mL) was added with stirring. The orange suspension was cooled to −50 °C and filtered to yield a bright orange solution. The solvent was removed under reduced pressure to afford **8** as an orange solid. Yield: 47 mg (0.063 mmol, 44%). IR (Nujol) ν/cm^{-1}: 2551 w (BH), 2004 s, 1984 s, 1915 s, 1893 s (CO). IR (THF) ν/cm^{-1}: 2550 w (BH), 1987 s, 1900 vs (CO). ^{1}H NMR (C_6D_6) δ/ppm: 7.94 (m, 2 H, C_6H_5), 7.33−6.80 (m, 8 H, C_6H_5), 5.51 (s, 1 H, pzH), 5.49 (s, 1 H, pzH), 5.30 (s, 1 H, pzH), 2.62 (s, 3 H, pzCH$_3$), 2.52 (s, 3 H, pzCH$_3$), 2.31 (s, 3 H, pzCH$_3$), 2.04 (s, 3 H, pzCH$_3$), 2.03 (s, 3 H, pzCH$_3$), 1.98 (s, 3 H, pzCH$_3$). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.75−6.81 (m, 10 H, C_6H_5), 5.86 (s, 1 H, pzH), 5.83 (s, 1 H, pzH), 5.71 (s, 1 H, pzH), 2.44 (s, 3 H, pzCH$_3$), 2.35 (s, 3 H, pzCH$_3$), 2.33 (s, 9 H, pzCH$_3$), 2.23 (s, 3 H, pzCH$_3$). ^{13}C{^{1}H} NMR (C_6D_6) δ/ppm:[40] 294.8 (d, W≡C, $^1J_{PC}$ = 42.5, $^1J_{WC}$ = 185.1), 225.8 (CO, $^1J_{WC}$ = 167.0), 225.6 (CO, $^1J_{WC}$ = 167.0), 152.7 (1 C), 152.2 (1 C), 152.1 (1 C), 145.1 (1 C), 144.4 (1 C), 144.3 (1 C) [C^{3,5}(pz)], 158.0 [d, C^1(POC$_6$H$_5$), $^1J_{PC}$ = 10.1], 141.0 [d, C^1(PC$_6$H$_5$), $^1J_{PC}$ = 16.1], 130.9 [d, C^{2,3,5,6}(PC$_6$H$_5$), J_{PC} = 22.1], 129.7 [C^{3,5}(POC$_6$H$_5$)], 129.7 [C^4(PC$_6$H$_5$)], 128.8 [d, C^{2,3,5,6}(C_6H_5), J_{PC} = 8.0], 122.6 [C^4(POC$_6$H$_5$)], 119.3 [d, C^{2,6}(POC$_6$H$_5$), J_{PC} = 10.1], 107.2 (1 C), 106.9 (1 C), 106.9 (1 C) [C^4(pz)], 17.1 (1 C), 16.9 (1 C), 15.1 (1 C), 12.4 (2 C, coincident), 12.4 (1 C) (pzCH$_3$). ^{31}P{^{1}H} NMR (C_6D_6) δ/ppm: 127.3 ($^2J_{WP}$ = 74.0). ^{31}P{^{1}H} NMR ($CDCl_3$) δ/ppm: 126.4 ($^2J_{WP}$ = 76.2). MS-ESI(+): *m*/*z* 807.7 [M + O + MeCN]$^+$, 789.6 [M + O + Na]$^+$, 767.6 [M + O + H]$^+$. Accurate mass: found 789.1725 [M + O + Na]$^+$. Calcd for $C_{30}H_{32}{}^{11}BN_6O_4{}^{23}NaP^{184}W$: 789.1723. Found: 807.2098 [M + O + MeCN]$^+$. Calcd for $C_{32}H_{35}{}^{11}BN_7O_4P^{184}W$: 807.2091. Anal. Found: C, 48.02; H, 4.32; N, 11.24. Calcd for $C_{30}H_{32}BN_6O_3PW$: C, 48.03; H, 4.30; N, 11.20.

Synthesis of [W(≡CPHPh)(CO)$_2$(Tp*)] (9). A solution of [W(≡CBr)(CO)$_2$(Tp*)] (**1a**: 1.000 g, 1.590 mmol) in THF (50 mL) was cooled to −78 °C and treated with ^{n}BuLi (0.64 mL, 2.5 M in hexanes, 1.6 mmol). The resulting light brown solution was stirred for 30 min and then treated with PCl$_2$Ph (1.6 mL, 0.99 M in THF, 1.6 mmol). The solution instantly turned dark red and was stirred for a further 25 min, then allowed to warm to room temperature and stirred for 20 min. The solution was recooled to −78 °C and treated with Li[BHEt$_3$] (1.6 mL, 1.0 M in THF, 1.6 mmol). The resultant orange-brown solution was stirred for 20 min, then allowed to warm to room temperature. Volatiles were removed under reduced pressure. The residue was suspended in toluene and filtered through diatomaceous earth. The filter pad was washed with toluene until the washings were colorless. The solvent was removed from the combined filtrates under reduced pressure to afford crude **9** as a dark red powder. ^{31}P{^{1}H} NMR spectroscopy indicated that the crude product contained ca. 90% **9**. Crude yield: 0.965 g (1.47 mmol, 92%). As previously described,[28] further purification may be achieved by cryostatic chromatography at −20 °C, but significant losses of product are encountered during chromatography. Spectroscopic data obtained conform to those previously reported.[28] The cyclohexyl analogue **10** can also be similarly prepared using this method.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00314.

Crystallographic data for **8** (CCDC 1448556) (CIF)

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Notes

The authors declare no competing financial interest.

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