ARTICLE

Phosphaisonitrile Umpolung – Synthesis and Reactivity of Chloro aminophosphino Carbynes.

Annie L. Colebatch,^a Benjamin J. Frogley^a and Anthony F. Hill^{*a}

Sequential treatment of $[W(\equiv CBr)(CO)_2(Tp^*)]$ (Tp^* = hydrotris(dimethylpyrazolyl)borate) with $nBuLi$ and $Cl_2PN'Pr_2$ provides the aminochlorophosphinocarbyne $[W(\equiv CPClN'Pr_2)(CO)_2(Tp^*)]$. The chloro substituent undergoes substitution with RLi (R = Me, Et, Ph) to afford $[W(\equiv CPRN'Pr_2)(CO)_2(Tp^*)]$ and with $[W(\equiv CLi)(CO)_2(Tp^*)]$ to give the aminobis(alkylidynyl)phosphine $[Pr_2NP\{C\equiv W(CO)_2(Tp^*)\}_2]$. Treatment with $Li[BHET_3]$ gives the primary aminophosphine $[W(\equiv CPHN'Pr_2)(CO)_2(Tp^*)]$, formed in a mixture with the ethyl derivative $[W(\equiv CPEN'Pr_2)(CO)_2(Tp^*)]$. Although they could not be isolated, spectroscopic data indicated that halide abstraction with Al_2Cl_6 forms the phosphaisonitrile salt $[W(CPN'Pr_2)(CO)_2(Tp^*)][AlCl_4]$, which displays electrophilic character at phosphorus, *e.g.*, in the reaction with diphenylacetylene to furnish the phosphirenium salt $[W\{CP(C_6H_5)_2N'Pr_2\}(CO)_2(Tp^*)][AlCl_4]$. Finally, the reaction with $LiNPh_2$ gives the a mixed diaminophosphinocarbyne, $[W(\equiv CP(N'Pr_2)(NPh_2))(CO)_2(Tp^*)]$.

Introduction

Isonitrile ligands (CNR) have been known for 160 years and are prevalent in organotransition metal chemistry. In contrast, complexes of the heavier analogues, phosphaisonitriles (phosphaisocyanides) CPR, are limited to Cummins' $[Mo(CPPhNa(OEt_2))(THF)\{NR_2\}_3]_2$ (NR_2 = $N^tBuC_6H_3Me_2-3,5$), which arises from reduction (Na/Hg) of the chlorophosphinocarbyne complex $[Mo(\equiv CPClPh)(NR_2)_3]$,¹ and $[K(18-crown-6)][W(CPR)(CO)_2(Tp^*)]$ (R = Ph, Cy; Tp^* = hydrotris(3,5-dimethylpyrazol-1-yl)borate, Scheme 1), which are obtained by deprotonation of the primary phosphinocarbynes $[W(\equiv CPHR)(CO)_2(Tp^*)]$.²

Scheme 1. Synthesis of phosphaisonitrile complexes.¹⁻²

Despite their disparate ligand sets, the nucleophilicity of phosphorus is implicit in the former complex through its coordination to sodium and was demonstrated experimentally

in the latter complex *via* protonation or methylation at phosphorus. The phosphorus nucleophilicity is also substantiated by computational interrogation of the hypothetical model $[Mo(CPPh)(NH_2)_3]^-$, the results of which suggest a 'phosphidocarbyne' description (Scheme 2) has some relevance.¹ In the latter tungsten complexes, the short P–C bond is indicative of multiple-bonding character and suggests that the contribution from the phosphidocarbyne canonical form is less significant. In the context of metal-carbon multiple bonding, the two classes might be seen as falling into 'Schrock-type' and 'Fischer-type' regimes. In the case of the related phosphinocarbyne $[W(\equiv CPh_2)(CO)_2(Tp^*)]$ the HOMO–1 is substantially localised on phosphorus (the HOMO corresponds to W–CO π -bonding) and this is manifest in the reactions of this complex with electrophiles.³

Scheme 2. Canonical descriptions of phosphaisonitrile bonding.

To a first approximation, in the absence of any structural reorganisation, the LUMO of a cation is likely to resemble the HOMO of the corresponding anion. We might therefore anticipate that the presently unknown cation $[W(CPPh)(CO)_2(Tp^*)]^+$ might display electrophilic character at phosphorus (or tungsten, *vide infra*). It is worth noting that the site of nucleophilic attack at cationic isonitrile complexes is generally at the isonitrile carbon. Although we have succeeded in preparing the chlorophosphino carbyne $[W(\equiv CPClPh)(CO)_2(Tp^*)]$ and shown that it readily undergoes nucleophilic halide substitution,⁴ attempts to observe or intentionally generate the putative cationic intermediate $[W(CPPh)(CO)_2(Tp^*)]^+$ (implicit in an S_N1 process) have not met with success. We have therefore turned our attention to stacking the odds of observing such a species by deploying a

^a Research School of Chemistry, Australian National University, Canberra, Australia ACT 2601.

*Corresponding author: Email: a.hill@anu.edu.au

CCDC 1908155-1908159 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.

positively mesomeric amino substituent at phosphorus so as to help stabilise the presumed electrophilic phosphorus centre. We report herein the first synthesis of a amino-halo phosphinocarbene complex and its reactivity towards nucleophiles. Tentative results are also presented with respect to its reactivity towards halide abstracting agents.

Results and discussion

As noted above, one might expect that the hypothetical complex $[W(CPPh)(CO)_2(Tp^*)]^+$ might display electrophilic character at phosphorus. This is supported by computational interrogation (DFT: B3LYP-6-31G*/LANL2DZ, Figure 1, Table 1). The geometry was minimised beginning from the experimentally established geometry for the corresponding anion.

Figure 1. Optimised geometries for the hypothetical cationic complexes $[W(CPR)(CO)_2(Tp^*)]^+$ ($R = Ph, NMe_2$) and selected frontier orbitals of interest. Inset = HOMO for $[W(CPPh)(CO)_2(Tp^*)]^-$.

The overall geometry of $[W(CPPh)(CO)_2(Tp^*)]^-$ is similar to that determined experimentally² other than a modest contraction of the $W\equiv C$ and elongation of the $C-P$ bond lengths. On 'oxidation' *in silico* to $[W(CPPh)(CO)_2(Tp^*)]^+$ the $C-P-C$ and $W\equiv C-P$ angles remain essentially invariant, however the $W\equiv C$ bond length contracts further by *ca* 0.01 Å, as does the CP multiple bond (by 0.02 Å). This might seem counter-intuitive given that by analogy with isonitriles, oxidation of the metal centre would be expected to compromise π -retrodonation. However, for the free ligands themselves, there are significant differences to the frontier orbitals of $CPPh$ and the analogous isonitrile $CNPh$. Geometry optimisation for the free molecules $CPPh$ (and $CPNMe_2$, *vide infra*) results in a near linear CPC spine, however with this angle constrained to be 120° (i.e., bent as observed, 104.4°, in the crystal structure of

Table 1. Experimental^a and Calculated^b Geometrical features of the WCPR spine for the complexes $[W(CPR)(CO)_2(Tp^*)]^+$ ($R = Ph, NMe_2$).

R	n	W≡C Å	C-P Å	P-R Å	W≡C-P °	C-P-R °
Ph ^a	-1	1.915	1.693	1.830	167.0	104.4
Ph ^b	-1	1.888	1.715	1.849	170.5	105.7
Ph ^b	+1	1.878	1.693	1.799	168.9	108.8
NMe ₂ ^b	+1	1.858	1.710	1.633	167.7	109.1

^aCrystallographic data taken from ref. 2; ^b DFT:B3LYP/6-31G*(LANL2DZ).

$[W(CPPh)(CO)_2(Tp^*)]^-$ the molecular orbital scheme (Figure 2; See ESI for MOs arising from unconstrained geometry) presents interesting features. Specifically, the σ -donor orbital is no longer the HOMO of the free molecule but instead lies beneath one of the two non-degenerate and occupied π -bonding orbitals associated with the CP multiple bond.

A similar situation was recognised long ago when comparing the frontier orbitals of CO *cf.* CS when the 2π and 7σ orbitals were found to be "practically degenerate."⁵ However, in the interim (to the best of our knowledge) no reported thiocarbonyl complex has possessed a suitably vacant metal d-orbital of metal-ligand π -symmetry to allow the CS ligand to act as a π -donor. The 14-valence electron ' $W(CO)_2(Tp^*)$ ' fragment does indeed possess such a vacant ' t_{2g} -type' orbital to which the $CPPh$ might serve as a π -donor, attended by contraction of the WC bond length. This amphoteric π -character somewhat complicates the unpacking of individual bonding components from a fragment orbital approach but may well play a distinctive role in the development of phosphaisonitrile chemistry.

Figure 2. Optimised geometries for the free hypothetical phosphaisonitriles with the angle at phosphorus constrained to 120°.

The LUMO of $[W(CPPh)(CO)_2(Tp^*)]^+$ does indeed show substantial phosphorus character. Given that this complex remains elusive, the possibility of mesomeric stabilisation of the low-coordinate phosphorus by an amino group was considered. The frontier orbitals of interest for the hypothetical cationic complex $[W(CPNMe_2)(CO)_2(Tp^*)]^+$ are also included in Figure 1. The geometries of both $[W(CPR)(CO)_2(Tp^*)]^+$ ($R = Ph, NMe_2$) were minimised starting from the two possibilities (linear or bent at phosphorus), ending in each case with angles of *ca* 109° (Table 1). In the case of $R = NMe_2$, a starting geometry with pyramidal nitrogen was also used to ensure the resulting

trigonality was a genuine feature. Upon replacing CPPh with CPNMe₂, the notable changes in the geometry include a further (0.02 Å) contraction of the W≡C bond length and elongation (*ca* 0.02 Å) of the C–P bond, whilst retaining near coplanarity of one carbonyl ligand with the CPNC₂ plane. The frontier molecular orbitals show generally similar topology to those for the phenyl derivative. The HOMO, which is of little interest in the current context, is primarily associated with carbonyl binding (*d_{xy}*). As with the phenyl derivative, the LUMO is predominantly associated with phosphorus, with some P–N π-antibonding character and is raised (0.33 eV), thereby deactivating the complex somewhat with respect to frontier orbital controlled nucleophilic attack at this site. Replacing the phenyl substituent with NMe₂ does however result in a slight *increase* (*ca* +0.19) in the positive natural charge at phosphorus and a smaller decrease (*ca* –0.08) in the negative natural charge at the carbyne carbon whilst the charge at tungsten remains essentially unchanged. The C–P bond order (Lowdin) decreases on replacing Ph (1.57) with NMe₂ (1.42) while the W–C bond order increases by a similar amount (0.14) to 2.21. In valence bond terms we might consider these changes in bond orders as reflecting increased contribution from canonical form **C** (Scheme 3).

Scheme 3. Canonical descriptions of a cationic phosphaisonitrile complex stabilised by a positively mesomeric (*M*⁺) substituent 'R'.

In both cationic cases, geometry optimisation results in a bent phosphorus (108.7 for CPPh; 109.2 for CPNMe₂) which is not significantly different from that found for the real anionic CPPh complex (105.7°). In both cases, the C–P vector and one carbonyl ligand are near to co-planar with the mesomeric phenyl or amino substituent. This results in the substituent making a close approach to the carbon of the carbonyl ligand (C–H...C *ca* 2.7 Å) and is attended by a modest bending away of the W–C–P spine. One can consider alternative conformers with considerably less inter-ligand repulsion and we therefore infer that conjugation of the Ph or NMe₂ groups into the PCW spine is favourable and maximised in this orientation. The LUMO is considerably more stabilised than the LUMO+1 which corresponds to W–C π-antibonding, *i.e.*, although an orbital is available for nucleophilic attack at the carbon (common for cationic isonitrile complexes), this is too high in energy to provide a competitive site for attack. Encouraged by these results, the synthesis of hitherto unknown chloroaminophosphinocarbyne complexes was explored to provide potential precursors to aminophosphaisonitrile complexes.

In addition to their capacity to react *via* nucleophilic halide substitution,⁶ Lalor's bromocarbyne complexes [M(≡CBr)(CO)₂(Tp*)] (M = Mo **1a**, W **1b**)⁷ readily undergo lithium/halogen exchange on treatment with ⁿBuLi to afford the lithiocarbynes [M(≡CLi)(CO)₂(Tp*)] (M = Mo, W).⁸ These in turn can react with a range of electrophiles to afford new carbyne

ligands (Scheme 4),⁹ including rare examples of phosphinocarbynes.^{2–4,10}

Scheme 4. Halocarbyne umpolung.

The reaction of [W(≡CLi)(CO)₂(Tp*)], generated *in situ*, with dichloro(diethylamino)phosphine resulted in formation of one major product with carbonyl infrared absorptions at 1993 and 1904 cm^{–1}, which was identified as the desired phosphinocarbyne [W{≡CPCl(NEt₂)}(CO)₂(Tp*)] (**2a**) (Scheme 5).

Scheme 5. Synthesis of halo-aminophosphinocarbynes.

The ³¹P{¹H} NMR spectrum supported this formulation, wherein a singlet resonance at δ_P = 136.7 was identified which displayed ¹⁸³W-coupled satellites (²J_{WP} = 76 Hz). The coupling values are comparable to the corresponding values for [W(≡CPClPh)(CO)₂(Tp*)] (δ_P = 91.2, ²J_{WP} = 75 Hz).⁴ Unfortunately, although ³¹P{¹H} NMR spectroscopy indicated that the desired product had formed in *ca* 80% yield, purification beyond this level was unsuccessful. Extraction with *n*-pentane or toluene (to remove the liberated lithium chloride) followed by concentration and cooling did not yield any precipitate, even at –78°C. Chromatographic purification is not feasible (confirmed by TLC) due to the presence of the hydrolytically sensitive P–Cl bond. The impure nature of the product meant that unambiguous identification of resonances attributed to **2a** in the ¹H NMR spectrum was problematic, particularly in the alkyl region, and because of these difficulties efforts were redirected towards the diisopropylamino analogue as it was hoped that this might have a greater propensity to crystallise whilst also providing informative spectroscopic characteristics in the ¹H NMR spectrum.

The synthesis of $[W\{\equiv CPCI(N^iPr_2)\}(CO)_2(Tp^*)\}]$ (**2b**) was carried out in an analogous manner to **2a** and fortunately in this case concentration of the filtered *n*-hexane extract from the crude reaction mixture residue afforded **2b** as a spectroscopically and analytically pure orange solid in excellent yield (96%). The spectroscopic data for **2b** are as expected and serve to substantiate the formulation of **2a**. The infrared spectrum contains two carbonyl absorption bands (THF: 1992, 1904 cm^{-1}), very close to those observed for $[W\{\equiv CPCI(Ph)\}(CO)_2(Tp^*)\}]$ (THF: 1992, 1905 cm^{-1}) indicating that the incorporation of the positively mesomeric amino group does not result in a marked increase in electron density at the metal centre. The $^{31}P\{^1H\}$ NMR spectrum shows a resonance at $\delta_P = 129.4$ flanked by ^{183}W -coupled satellites ($^2J_{WP} = 83$ Hz), similar to those observed for **2a** and $[W\{\equiv CPCI(Ph)\}(CO)_2(Tp^*)\}]$. The carbyne carbon gives rise to a resonance in the $^{13}C\{^1H\}$ NMR spectrum in the typical downfield region at $\delta_C = 291.5$, displaying phosphorus-carbon (94 Hz) and tungsten-carbon (194 Hz) couplings similar to those of other chlorophosphinocarbynes.^{4,11}

In the 1H and $^{13}C\{^1H\}$ NMR spectra of **2b** the peaks due to the isopropyl groups are broad at room temperature, whilst all remaining resonances are sharp, indicating that rotation about the phosphorus-nitrogen bond is slow on both the 1H and ^{13}C NMR timescales. Four distinct iPr methyl environments and two distinct iPr methine environments are observed as a result of this restricted rotation. Variable temperature NMR spectroscopy demonstrated changes in the 1H NMR spectrum over the temperature range -60 °C to $+100$ °C (see ESI). At -60 °C four iPr methyl environments were observed, although two of these resonances overlap, indicating restricted rotation. At 40 °C this collapses into two broad resonances and at 100 °C two doublets are observed. These two doublets correspond to the two diastereotopic methyl groups of the isopropyl substituents, indicating free rotation about the P–N bond. At high temperatures broad unresolved iPr methine resonances are observed at 3.5 – 5 ppm. Following measurements at 100 °C, the spectrum re-measured under ambient conditions showed no sign of decomposition of the complex, indicative of considerable thermal stability. This is somewhat surprising given the air-sensitivity of the complex — outside of an inert atmosphere, rapid decomposition occurs within hours to give dark-brown complex mixtures of (with one exception) unidentified products.

Unfortunately, X-ray quality crystals of **2b** were not forthcoming. The crystallographically characterised compounds $[PCI(N^iPr_2)\{C(PPh_3)_2\}]AlCl_4$,¹² and $\{PCI(N^iPr_2)\}_2(C_2B_{10}H_{10})$,¹³ however, contain trigonal pyramidal (sp^3) phosphorus coordination and trigonal planar (sp^2) geometry at nitrogen, and it is assumed that the amine moiety in **2b** would similarly adopt a trigonal planar geometry, consistent with the observation that all four iPr methyl groups are chemically inequivalent.

While X-ray quality single crystals of **2b** were not obtained, bright blue crystals formed when a benzene solution was left exposed to air for several days. These proved to be suitable for single crystal X-ray structure determination and found to be the benzene solvate of the remarkable alkyne complex $[WCl\{\eta^2-HOC\equiv CPh(O)(OH)\}(CO)(Tp^*)\}]$ (**3**) (Scheme 5, Figure 3). In this

complex the amine has been lost, the phosphorus has been oxidised to a phosphinic acid and the alkylidyne C has coupled with an adjacent carbonyl to form a π -coordinated acetylene. The coupling of adjacent carbonyl and carbyne ligands¹⁴ has considerable precedent which has been reviewed¹⁵ and in many cases the oxygen-centred nucleophilicity of the resulting η^2 -C,C'-ketenyl ligand has been shown to afford alkoxyalkyne complexes upon alkylation. Whilst common for alkylidyne ligands, such processes are rare for hetero-atom functionalised carbynes, however Angelici has reported one such example whereby initial coupling of methylthiolatocarbyne and carbonyl ligands generated an η^2 -ketenyl complex which can subsequently be methylated on the carbonyl oxygen to give a $MeSC\equiv COMe$ ligand.¹⁶ Presumably **3** is formed similarly with an acidic phosphorus intermediate acting as an internal proton source for the carbonyl oxygen protonation. Disappointingly, **3** proved unreceptive to other characterisation techniques and is thought to be just one intermediate *en route* to other decomposition products — indeed, outside of the benzene solvent the crystals rapidly turn brown, as do $CDCl_3$ or $DMSO-d_6$ solutions, and no products could be identified from the resulting mixtures. This unfortunately precluded the acquisition of useful spectroscopic data and the isolation of crystals of **3** appears to be a simply serendipitous result of their insolubility in benzene. Nevertheless, the structural characterisation (Figure 3) of **3** is included here due to the unprecedented nature of the exotic alkyne ligand which is not independently stable and unlikely to ever be observed free of a metal (hydroxyalkynes, $HOC\equiv CR$, are unstable with respect to the tautomeric ketenes, $O=C=CHR$).

Figure 3. Molecular structure of **3** in a crystal of $3.C_6H_6$ showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and most hydrogen atoms, solvent molecules and a minor disorder component are not shown for clarity. Selected distances [Å] and angles [°]: W–C1 2.052(5), W–C2 2.067(5), W–C3 2.061(5), W–N1 2.231(4), W–N3 2.177(4), W–N5 2.227(4), W–Cl 2.4050(14), O2–C2 1.309(7), C2–C3 1.284(9), C3–P 1.738(6), P–O3 1.550(9), P–O4B 1.479(6), C2–W–C3 36.2(2), O2–C2–C3 142.4(6), C2–C3–P 141.4(5), C3–P–O4B 113.1(3), O3–P–O4B 115.9(4). Location of the remaining hydrogen atom on O3 or O4b was not unambiguously established however with P–O3 being marginally longer than P–O4, the former would seem more likely. The refinement process indicated *ca* 20% hydrolysis of the C3–P bond to $[W(\eta^2-HOCCH)Cl(CO)(Tp^*)]$.

The W–C and C–C distances associated with the acetylenic fragment in **3** (W–C1 2.052(5), W–C2 2.067(5), C2–C3 1.284(9) Å) are consistent with reported tungsten complexes containing acetylene ligands (*ca* 2.00–2.10 and 1.30–1.32 Å, respectively),

although these are highly dependent on (i) whether the alkyne acts as a nominally two, three or four electron donor and (ii) the acetylenic substituents.¹⁷ Structural data are available for a small number of alkyne complexes of the form $[W(\eta^2\text{-RCCR}')Cl(CO)(Tp^*)]$ ($R = R' = \text{Me}, \text{CH}_2\text{OH}, \text{SCH}_2\text{Ph}$; $R = \text{Ph}, R' = \text{Se}^i\text{Pr}$; $R = \text{C}_6\text{H}_4\text{Me-4}, R' = \text{Cl}$) and, as for **3**, in all cases the alkyne aligns to be near co-planar with the carbonyl ligand rather than the chloride.¹⁸ This orientational preference has been extensively investigated by Templeton and Seidel for corresponding and more numerous iodide complexes $[W(\eta^2\text{-RCCR}')I(CO)(Tp^*)]$ (*inter alia* $R = R' = \text{PPh}_2$, $\text{RCCR}' = \text{cyclo-decyne}$ $R = \text{Ph}, R' = \text{Me}, \text{CH}=\text{CHC}_5\text{H}_4\text{FeC}_5\text{H}_5$, $R = \text{H}, R' = \text{PPh}_2$; $R = \text{POPh}_2$, $R' = \text{PPh}_2\text{NH}_2^+$),¹⁹ for which the same arguments apply. Specifically, the two orthogonal retrodonative orbitals presented by tungsten to the alkyne are non-degenerate due to interaction with either the π -donor iodide or π -acidic CO co-ligands. The orbital that interacts with the CO ligand is stabilized and therefore a poorer retrodonor than the orbital which interacts with the iodide such that the alkyne orients to maximise overlap with the latter, *i.e.*, co-planar with the carbonyl ligand. The alkynyl C–O bond in **3** (1.309(7) Å) is somewhat short in length when compared to those found for the few structurally characterized tungsten hydroxyalkyne complexes^{20–22} *viz* $[W(\eta^2\text{-HOCCcC}_6\text{H}_4\text{Me-4})(CO)(PMe_3)(\eta\text{-C}_5\text{H}_5)]^+$ (1.325 Å),²⁰ and $[W(\eta^2\text{-HOCCcC}_6\text{H}_5)(CO)(PMe_3)_2Cl_2]$ (1.355 Å).²¹

We have previously encountered problems in the synthesis of $[W(\equiv\text{CPCl}_2)(CO)_2(Tp^*)]$ (**4**) from $[W(\equiv\text{CLi})(CO)_2(Tp^*)]$ and PCl_3 due to contamination with the disubstitution product $[W_2(\mu\text{-C}_2\text{PCl})(CO)_4(Tp^*)_2]$.^{4,11} Controlling the degree of substitution *via* halide metathesis transmetalation is a common problem in conventional halophosphine synthesis, however aminophosphines can be cleaved with HCl to provide the corresponding chlorophosphines.²³ It was thought this might therefore provide an alternative route to **4**, thus circumventing the problems previously encountered. A d_6 -benzene solution of **2b** was treated with two equivalents of anhydrous HCl (1.0 M in Et_2O) and the reaction progress was monitored by NMR spectroscopy. After 15 minutes, the major product was indeed **4** ($\delta_P = 136.2$, $^2J_{\text{WP}} 80$ Hz),⁴ although the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contained six other peaks and **4** constituted only *ca* 40% of the mixture. After 20 hours, the peak due to **4** had virtually disappeared and the largest peak in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was identified as $\text{PCl}_2\text{N}^i\text{Pr}_2$. The ^1H NMR spectrum comprised one major Tp^* -containing compound which was identified as the methylidyne complex $[W(\equiv\text{CH})(CO)_2(Tp^*)]$, described previously by Templeton.²⁴ These products most likely arise from the reaction of the initially liberated $[\text{H}_2\text{N}^i\text{Pr}_2]\text{Cl}$ with **4** (Scheme 5). Accordingly, although **4** was produced in this reaction, this does not represent an expedient synthetic route but does demonstrate the protolytic sensitivity of the C–P bond. We have previously shown that for the phosphinocarbyne complex $[W(\equiv\text{CPh}_2)(CO)_2(Tp^*)]$, the kinetic and reversible site of protonation is the phosphorus, while carbyne carbon is the irreversible site of thermodynamic protonation.³

Chlorophosphinocarbynes react with organolithium reagents to afford substituted derivatives^{4,10d} and accordingly the same protocol was applied to **2b**. Treatment with methylolithium resulted in the isolation of the methyl-

aminophosphinocarbyne $[W(\equiv\text{CPMe}(\text{N}^i\text{Pr}_2))(CO)_2(Tp^*)]$ (**5a**) (Scheme 6) in good (90%) yield and purity after a simple extraction with *n*-pentane.

Scheme 6. Nucleophilic substitution of halo-aminophosphinocarbynes.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5a** showed a significant upfield shift of the phosphorus resonance compared to that of **2b** ($\delta_P = 53.3$ *cf.* 129.4 for **2b**). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5a** comprise only a single ^iPr -methine resonance and two ^iPr -methyl resonances, in contrast to the two and four resonances, respectively, observed for the precursor **2b**. The appearance of only one isopropyl environment (unless coincidental) in the NMR spectra of **5a** is indicative not only of free rotation about the P–N linkage (*cf.* the restricted rotation inferred for **2b**), but also of trigonal nitrogen since pyramidal geometry would render the two methine protons diastereotopic due to the stereogenic phosphorus. Low temperature ^1H NMR studies of **5a** in d_8 -toluene did not completely resolve the two diastereotopic methyl group resonances into four constituent peaks (see ESI). At -80°C three broad resonances are observed, indicating some degree of fluxionality in the rotation about the P–N bond. Notably, the resonance due to the PCH_3 group was essentially invariant throughout this temperature range and accordingly it seems reasonable to discard the possibility that phosphine inversion accounts for higher time-averaged symmetry. The solid-state infrared spectrum (Nujol) contains six bands in the carbonyl region, but as only two bands are observed in the solution-state spectrum (THF: 1974, 1884 cm^{-1}) this might be attributable to solid state effects (crystal packing, polymorphs *etc.*) rather than rotational isomerism. The greater ease of rotation about the P–N bond in the methyl derivative **5a** compared to **2b** presumably results from the electron-withdrawing ability of the chloro substituent. Negative hyperconjugation from the (trigonal) nitrogen to the P–Cl σ^* orbital has an angular dependence, being maximised when the Cl–P–N–C dihedral angles are 90° , such that the loss of this interaction perhaps contributes to the rotation barrier. In contrast, the energies of P–CH₃ σ^* orbitals are sufficiently high as to make negative hyperconjugation of negligible impact.

The molecular structure of **5a** has been determined and the geometry is shown in Figure 4. The data are reassuringly unremarkable: bond distances and angles are in good agreement with other reported phosphinocarbynes.^{2–4,10} The geometry about phosphorus is approximately pyramidal ($\Sigma^\circ(\text{P})$

Figure 4. Molecular structure of **5a** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and some hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [°]: W–C1 1.840(4), W–N1 2.304(3), W–N3 2.215(3), W–N5 2.230(3), C1–P 1.792(5), P–C4 1.838(4), P–N7 1.694(4), W–C1–P 168.0(3), C1–P–C4 100.4(2), C1–P–N7 105.35(19), N7–P–C4 105.7(2), C5–N7–C8 118.7(4), P–N7–C5 121.7(3), P–N7–C8 118.7(3). Inset: view along the W···C1 vector.

= 311.5°) and approximately trigonal about the amino nitrogen ($\Sigma^\circ(\text{N7}) = 359.1^\circ$).

The reaction of **2b** with organolithium reagents is not limited to methyllithium and treatment with ethyllithium or phenyllithium furnishes the related ethyl and phenyl derivatives, $[\text{W}(\equiv\text{CPRN}^i\text{Pr}_2)(\text{CO})_2(\text{Tp}^*)]$ (**5b** R = Et; **5c** R = Ph) (Scheme 6), respectively. Spectroscopic data for these two compounds are in good agreement with those of **5a**, with a single resonance located in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra ($\delta_{\text{P}} = 68.2$ and 69.1 for **5b** and **5c**, respectively) and one set of resonances (one methine, two methyl) at room temperature corresponding to the isopropyl groups. Complex **5c** was further characterised by X-ray crystallography, the results of which are summarised in Figure 5. The structural parameters call for little comment, being in good agreement with reported phosphinocarbynes^{2–4,10} and. Akin to **5a**, the geometry about the phosphorus in **5c** is pyramidal ($\Sigma^\circ(\text{P}) = 314.8^\circ$) and approximately trigonal about the amino nitrogen ($\Sigma^\circ(\text{N7}) = 357.8^\circ$). The (ground state) orientation of the N^iPr_2 group most likely reflects the minimization of steric pressures.

Figure 5. Molecular structure of **5c** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [°]: W–C1 1.850(9), W–N1 2.293(5), W–N3 2.210(6), W–N5 2.206(6), C1–P 1.786(9), P–C10 1.852(9), P–N7 1.713(7), W–C1–P 162.8(5), C1–P–N7 109.6(4), C1–P–C10 101.8(4), N7–P–C10 103.4(4), C4–N7–C7 119.3(8), C4–N7–P 121.8(6), C7–N7–P 116.7(5). Inset: view along the W···C1 vector.

The aminochlorophosphinocarbyne **2b** also reacts with an equivalent of the lithiocarbyne **1b** to give the aminobis(alkylidynyl)phosphine $[\text{Pr}_2\text{NP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ (**6**) (Scheme 6), although in practice it is simpler to prepare this species directly from the lithiocarbyne **1b** and 0.5 equivalents of $\text{PCl}_2\text{N}^i\text{Pr}_2$. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **6** contains a single resonance at $\delta_{\text{P}} = 112.1$ ($^2J_{\text{WP}} = 76$ Hz) and a single set pyrazolyl resonances (relating to the Tp^* ligands) in both the of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra implying that the two tungsten environments are equivalent on the NMR timescale. The molecular structure of **6** has also been determined, the results of which are shown in Figure 6, and are also consistent with the small number of reported bis(alkylidynyl)phosphines.^{10,11} It might be suspected that the proximity of the bulky Tp^* ligands would lead to a flattening of the pyramidal geometry about phosphorus, although this does not seem to be the case ($\Sigma^\circ(\text{P}) = 311.8^\circ$).

Figure 6. Molecular structure of **6** in a crystal of $6 \cdot \text{CH}_2\text{Cl}_2$ showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms, solvent molecules and a minor disorder component are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.826(4), C1–P 1.825(5), P–C2 1.842(5), C2–W2 1.822(4), P–N13 1.661(3), W1–N7 2.307(3), W1–N9 2.225(3), W1–N11 2.237(3), W2–N1 2.313(3), W2–N3 2.209(3), W2–N5 2.222(3), W1–C1–P 153.3(3), C1–P–C2 97.17(19), P–C2–W2 166.2(3), C1–P–N13 108.19(19), C2–P–N13 106.48(19), C7–N13–C10 118.2(4), C7–N13–P 118.1(3), C10–N13–P 123.6(3). Inset: view along the W···C1 vector.

In the absence of exaggerated steric encumbrance or coordination to a transition metal, acyclic aminophosphines bearing a P–H bond are relatively rare,²⁵ with only a small number having been structurally characterised.²⁶ In most cases they are thermally unstable with respect to amine elimination and formation of *cyclo*-polyphosphines. Reduction of the corresponding chlorophosphine is commonly employed as a preparative route^{25g} although isolated examples from alternative routes have been reported.²⁵ⁱ Given the steric bulk associated with the ' $\text{W}(\text{CO})_2(\text{Tp}^*)$ ' fragment, we suspected that this might impart sufficient kinetic stability to allow isolation of the secondary aminophosphine. Treatment of a THF solution of **2b** with $\text{Li}[\text{BHET}_3]$ resulted in a mixture of compounds, as determined by both IR and NMR spectroscopies. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum included a peak attributable to the desired secondary phosphine $[\text{W}(\equiv\text{CPHN}^i\text{Pr}_2)(\text{CO})_2(\text{Tp}^*)]$ (**7**) (Scheme 7) at $\delta_{\text{P}} = 22.4$ with coupling to tungsten ($^2J_{\text{WP}} = 78$ Hz), consistent with a three-coordinate phosphine. Removal of ^1H -decoupling

gave rise to a doublet of triplets resonance with $^1J_{\text{PH}} = 229.5$ Hz due to the P–H proton and $^2J_{\text{PH}} = 20.8$ Hz due to coupling to the two ^1P -methine protons. The second major species identified from this reaction was the ethyl-substituted derivative **5b**, which was prepared separately from the reaction of **2b** and ethyllithium (*vide supra*). This side product presumably results from competitive transfer of an ethyl group from the $\text{Li}[\text{BHET}_3]$ reductant rather than the desired H-transfer. Unfortunately, separation of **5b** and **7** was not successfully achieved by chromatography on silica or alumina as both species were found to decompose on these supports such that neither eluted from the columns. In an attempt to circumvent these problems, the reaction of **2b** with $\text{K}[\text{BH}^t\text{Bu}_3]$ was carried out but this resulted in a number of broad peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum ($\delta_{\text{P}} = 155.3, 130.2, 86.8, 24.6, 20.9, 13.4$ and 3.2). Phosphorus coordination of liberated B^tBu_3 might account for the broad nature of the peaks. The reactions of **2b** with $\text{Li}[\text{AlH}_4]$, $\text{Li}[\text{BH}_4]$, $\text{K}[\text{BH}_4]$ and KH were all explored but were met with limited success and so while these results indicate that **7** was indeed formed, the isolation of this species remains disappointingly elusive.

Scheme 7. Attempted synthesis of a secondary aminophosphinocarbene.

Phosphenium ions are two-coordinate phosphorus cations in which a large degree of the positive charge density is localised upon the phosphorus.²⁷ Phosphenium cations are highly reactive and are much less stable than phosphide anions, typically requiring at least one substituent to be a positively mesomeric amino group that is capable of stabilising the cation by charge dispersion through resonance. The most common synthetic route involves abstraction of chloride from chlorophosphines, for which a range of reagents are available, *e.g.*, GaCl_3 , SnCl_4 , $\text{Na}[\text{BPh}_4]$, Me_3SiOTf and TiOTf , although aluminium trichloride is by far the most frequently employed and provides the phosphenium as the AlCl_4^- salt. In many cases, the instability and high reactivity of these species preclude their isolation and instead a Lewis base such as an alkene,²⁸ alkyne,^{28,29} phosphine³⁰ or arsine³¹ affords the corresponding Lewis base-stabilised cations.

Chloride abstraction from **2b** was targeted as a potential route to a carbyne-functionalised phosphenium salt that might display possible phosphazide character as the electron-donating amino substituent should act to stabilise the resulting cation. A variety of chloride abstracting agents were trialled, but reactions of **2b** with Me_3SiOTf , AgPF_6 and $\text{Na}[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_3]$ led to a multitude of peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, none of which fell in the expected range for the phosphenium cation $[\text{W}(\equiv\text{CPN}^i\text{Pr}_2)(\text{CO})_2(\text{Tp}^*)]^+ [\text{8}]^+$, which are typically observed *ca* 100 ppm downfield from their halophosphine precursors²⁴ (**2b**: $\delta_{\text{P}} = 129.4$). When a CD_2Cl_2 solution of **2b** was treated with an excess of Al_2Cl_6 a broad signal arose at $\delta_{\text{P}} = 283.5$ without resolvable ^{183}W satellites. With GaCl_3 a similarly broad signal

was observed at $\delta_{\text{P}} = 294.6$. These remarkably low-field chemical shifts are strongly suggestive of reduced coordination at phosphorus and formation of the desired phosphenium salt **[8]⁺** (Scheme 8) and far enough downfield to discount simple $\text{P} \rightarrow \text{Al}$ or $\text{P} \rightarrow \text{Ga}$ Lewis adduct formation. Phosphorus-31 resonances for organophosphenium ions have been reported in the wide range of $\delta_{\text{P}} = 513 - 111$,²⁷ although when one substituent is replaced by a transition metal they may occur beyond $\delta_{\text{P}} = 800$,^{29a} and even as high as $\delta_{\text{P}} = 1007.5$ for $[\text{Mo}(\text{PN}^i\text{Pr}_2)(\text{CO})_3(\eta\text{-C}_5\text{Me}_5)]\text{AlCl}_4$.³² Unfortunately, the reactions did not proceed cleanly (as indicated by the numerous other unidentified signals which arose in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and the complex ^1H NMR spectra) and efforts to isolate any pure product by fractional crystallisation were not met with success. In some test reactions $[\text{W}(\equiv\text{CPCl}_2)(\text{CO})_2(\text{Tp}^*)]^4$ could be identified amongst the products and diisopropylammonium salts were encountered frequently during attempts at crystallisation, indicating that hydrolytic cleavage of the amine group is a significant source of the undesired side products being formed.

Scheme 8. Attempted halide abstraction from **2b**.

It was thought that a Lewis-base stabilised adduct of **[8]⁺** might prove more amenable towards isolation and so the chloride abstraction from **2b** with AlCl_3 or GaCl_3 was conducted in the presence an excess of diphenylacetylene. This procedure was employed effectively by Sterenberg to stabilise reactive phosphinidenes $[\text{M}(\equiv\text{PR})(\text{L})_n]^+$, including examples which lack positively mesomeric substituents.^{28-30,33} When the abstraction of chloride from **2b** was conducted with Al_2Cl_6 in the presence of diphenylacetylene, a new peak arose in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This singlet, at $\delta_{\text{P}} = -77.9$ and straddled by tungsten satellites ($^2J_{\text{WP}} = 221$ Hz), appears to significantly higher frequency consistent with what would be expected from a phosphirenium cation (*ca* -57 to -70 ppm for $[\text{PR}_2(\text{CR}'\text{CR}'')]\text{AlCl}_4$; $\text{R}, \text{R}', \text{R}'' = \text{H}, \text{Me}, \text{Ph}$),³⁴ consistent with the formation of the desired phosphirenium carbyne $[\text{W}(\equiv\text{CP}(\text{CPhCPh})\text{N}^i\text{Pr}_2)(\text{CO})_2(\text{Tp}^*)]\text{AlCl}_4$ (**[9]** AlCl_4) (Scheme 8). An identical $^{31}\text{P}\{^1\text{H}\}$ shift was observed when Ga_2Cl_6 was used, confirming that the Lewis acid is not associated with the phosphorus for the two presumed salts. Disappointingly, this product did not form any more cleanly and was found to be equally intractable. Thus, although isolation of these products was ultimately unsuccessful, the results hint towards the viability of such a species and imply that their synthesis should be achievable under the yet to be identified conditions. An alternative perspective of the nature of the sought phosphirenium complex would be as a phosphirene adduct of

of a cationic carbide (Scheme 9). Such an interpretation takes credence from the isolation of phosphoniocarbynes $[W(\equiv C-PR_3)(CO)_2(Tp^*)]PF_6$ ($PR_3 = PMe_2Ph, PPh_3, PCy_3$) from the reactions of **1b** with phosphines PR_3).³⁵

Scheme 9. Alternative canonical descriptions of **9**.

In light of the synthetic challenges posed by the chloroaminophosphinocarbyne **2b**, attention was redirected to modifications which might provide alternative reactivity of interest. Diaminophosphines $PR(NR'_2)_2$ present a broad manifold of useful reactivity³⁶ and appeared a worthy target. Treatment of **2b** with lithium diphenylamide resulted in formation of the diaminophosphinocarbyne $[W\{\equiv C(P(NPr_2)(NPh_2))(CO)_2(Tp^*)\}]$ (**10**) (Scheme 10). This complex features two distinct amino substituents bonded directly to the phosphorus of the phosphinocarbyne. Rather surprisingly, **2b** does not react at all (at room temperature) with lithium diisopropylamide or lithium diethylamide and **2b** can be recovered near stoichiometrically from the reaction mixtures. As there is no clear electronic reason for this observation it can presumably only be explained by invoking a steric argument; the 'cavity' between the $Tp^*(CO)_2W$ and N^iPr_2 moieties can accommodate the NPh_2 group but not NEt_2 and N^iPr_2 groups. We have also been unsuccessful in forming $[W\{\equiv C(P(NPr_2)_2)(CO)_2(Tp^*)\}]$ from the reaction of **1b** with $nBuLi$ followed by treatment with $PCl(N^iPr_2)_2$ for what we expect is the same reason. Steric protection may also explain the apparently high thermal stability of **10**; the complex remained unchanged after 3 days of heating a toluene solution under reflux, and there was only very minor (*ca* <10%) decomposition when **10** was heated under reflux for 1 day in a 20% v/v methanol/toluene solvent mixture. It is, however, sensitive to acid and reacts rapidly to give as yet unidentified products.

Scheme 10. Synthesis of a diaminophosphinocarbyne.

The two distinct amino groups in **10** result in a loss of the mirror plane and thus each pyrazolyl proton and carbon nuclei give rise to a distinct resonance in their respective NMR spectra. The carbyne carbon resonates at $\delta_C = 300.8$ ($^1J_{CP} = 76$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum and the phosphorus nuclei at $\delta_P = 100.6$ ($^2J_{WP} = 76$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Both of these chemical shifts are similar to other *monoaminophosphinocarbynes* reported herein.

The molecular structure of **10** was determined and the geometry is shown in Figure 7. The $W-C-P$ bond angle ($156.0(2)^\circ$) deviates appreciably from linearity and is one of the most acute angles observed in such a system (typically $160-180^\circ$).³⁷ This is likely to be a combination of solid-state packing effects as well as a consequence of steric interactions between the reasonably bulky amino substituents on phosphorus. Nonetheless, the geometry about phosphorus remains approximately pyramidal ($\Sigma^\circ(P) = 316.7^\circ$) and the geometry about the amino nitrogen atoms are especially close to planarity ($\Sigma^\circ(N7) = 360.0^\circ$, $\Sigma^\circ(N8) = 359.8^\circ$).

Figure 7. Molecular structure of **10** showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances [Å] and angles [$^\circ$]: $W-C1$ 1.822(4), $C1-P$ 1.798(3), $P-N7$ 1.674(3), $P-N8$ 1.728(3), $W-C2$ 1.982(4), $W-C3$ 1.981(4), $W-N1$ 2.284(3), $W-N3$ 2.219(2), $W-N5$ 2.205(3), $N7-C4$ 1.480(4), $N7-C7$ 1.471(5), $N8-C10$ 1.423(4), $N8-C16$ 1.441(4), $W-C1-P$ 156.0(2), $C1-P-N7$ 106.21(15), $C1-P-N8$ 100.62(14), $N7-P-N8$ 109.82(16).

Conclusions

In contrast to the phosphaisocyanide anions $[W(CPR)(CO)_2(Tp^*)]^-$ ($R = Ph, Cy$) which display nucleophilic character at phosphorus, the chloroaminophosphinocarbyne $[W(\equiv CPCIN^iPr_2)(CO)_2(Tp^*)]$ is synthetically equivalent to the cationic phosphaisocyanide complex $[W(\equiv CPN^iPr_2)(CO)_2(Tp^*)]^+$, in particular with respect to nucleophilic halide substitution reactions that demonstrate its synthetic utility. Whilst this cationic complex could not yet be isolated in pure form, circumstantial evidence for its existence comes from halide abstraction reactions.

Experimental

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) glove-box techniques with dried and degassed solvents. NMR spectra were obtained at $25^\circ C$ on Varian Mercury 300 (1H at 300.1 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.5 MHz), Varian Inova 300 (1H at 299.9 MHz, ^{13}C at 75.42 MHz, ^{31}P at 121.4 MHz), Varian MR 400 (1H at 399.9 MHz, ^{13}C at 100.5 MHz, ^{31}P at 161.9 MHz), Bruker Avance 400

(^1H at 400.1 MHz, ^{31}P at 162.0 MHz), Varian Inova 500 (^1H at 500.0 MHz, ^{13}C at 125.7 MHz), Bruker Avance 400 (^1H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{31}P at 162.0 MHz), Bruker Avance 600 (^1H at 600.0 MHz, ^{13}C at 150.9 MHz) or Bruker Avance 700 (^1H at 700.0 MHz, ^{13}C at 176.1 MHz, ^{31}P at 283.4 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^1H , ^{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. In some cases, distinct peaks were observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^1H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. The notation t' denotes an apparent triplet. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental microanalytical data were obtained from the Australian National University or London Metropolitan University microanalytical services. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix. Data for X-ray crystallography were collected with an Agilent Xcalibur CCD diffractometer (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) or an Agilent SuperNova CCD diffractometer (Cu- $\text{K}\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$) using the CrysAlis PRO software.³⁸ The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXL program³⁹ and the WinGX⁴⁰ or Olex2 software.⁴¹ Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.⁴² Calculations were performed at the DFT:B3LYP-LANL2DZ level of theory for gas phase molecules employing the SPARTAN-18^o suite of programs.⁴³ The compound $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]^{7,8}$ was prepared according to a published procedure. The phosphines $\text{PCl}_2\text{N}^i\text{Pr}^{14}$ and $\text{PCl}_2\text{NEt}_2^{44}$ were prepared according to reported methods. All other reagents were used as obtained from commercial sources, except Al_2Cl_6 which was freshly sublimed twice prior to use.

Attempted synthesis and observation of $[\text{W}(\equiv\text{CPCINeEt}_2)(\text{CO})_2(\text{Tp}^*)]$ (2a**).** A solution of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (174 mg, 0.277 mmol) in THF (10 mL) was cooled to -78°C and treated with $n\text{BuLi}$ (0.16 mL, 1.7 M in hexanes, 0.27 mmol). The resulting light brown solution was stirred for one hour and then treated with PCl_2NEt_2 (0.04 mL, 0.3 mmol). The solution instantly turned dark red and was stirred for a further 60 minutes then allowed to warm to room temperature. Volatiles were removed under reduced pressure and the solid residue was extracted with n -pentane (25 mL, then $3 \times 10 \text{ mL}$) and the combined extracts were collected by cannula filtration. Concentration under reduced pressure then cooling to -78°C did not result in precipitation of the product. Methods for the purification of this compound were not successfully identified. Some spectroscopic data for the crude product (ca 80% yield by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy) are: IR (THF, cm^{-1}): 2551w ν_{BH} , 1993s, 1904s ν_{CO} . ^1H NMR (C_6D_6 , 25°C) $\delta_{\text{H}} = 5.56$ (s, 1 H, pzH), 5.55 (s, 1 H, pzH), 5.31 (s, 3 H, pzH), 2.82 (s, 3 H, pzCH₃), 2.71 (s, 3 H, pzCH₃), 2.32 (s, 3 H, pzCH₃), 2.05 (s, 3 H, pzCH₃), 2.03 (s, 3 H, pzCH₃), 1.99 (s, 3 H, pzCH₃), 0.96 (t, 6 H,

NCH_2CH_3 , $^3J_{\text{HH}} = 15.0$). Unfortunately, the ^1H NMR spectrum of the crude product was too complex to confidently assign the resonances attributed to NCH_2 (diastereotopic). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25°C): $\delta_{\text{P}} = 136.7$ ($^2J_{\text{WP}} = 76.4 \text{ Hz}$).

Synthesis of $[\text{W}(\equiv\text{CPCIN}^i\text{Pr}_2)(\text{CO})_2(\text{Tp}^*)]$ (2b**).** A solution of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ (2.000 g, 3.180 mmol) in THF (60 mL) was cooled to -78°C and treated with $n\text{BuLi}$ (1.3 mL, 2.5 M in hexanes, 3.3 mmol). The resulting light brown solution was stirred for 20 minutes and then treated with $\text{PCl}_2\text{N}^i\text{Pr}_2$ (0.59 mL, 3.2 mmol). The solution instantly turned orange and was stirred for a further 30 minutes then allowed to warm to room temperature. Volatiles were removed under reduced pressure. The solid residue was suspended in hexane and filtered through diatomaceous earth which was further washed with hexane and benzene until the washings were colourless. The solvent was removed under reduced pressure to afford an orange solid of pure **2b** (2.193 g, 3.102 mmol, 96%). IR (Nujol, cm^{-1}): 2547w ν_{BH} , 1988vs, 1909sh, 1900vs ν_{CO} . IR (THF, cm^{-1}): 2551w ν_{BH} , 1992vs, 1904vs ν_{CO} . IR (CH_2Cl_2 , cm^{-1}) 1994s, 1904s ν_{CO} . ^1H NMR (700 MHz, 25°C , C_6D_6): $\delta_{\text{H}} = 5.55$ (s, 1 H, pzCH), 5.54 (s, 1 H, pzCH), 5.30 (s, 1 H, pzCH), 4.85 (br, 1 H, NCH), 3.05 (br, 1 H, NCH), 2.83 (s, 3 H, pzCH₃), 2.79 (s, 3 H, pzCH₃), 2.34 (s, 3 H, pzCH₃), 2.05 (s, 3 H, pzCH₃), 2.03 (s, 3 H, pzCH₃), 1.98 (s, 3 H, pzCH₃), 1.36–1.29 (br, 3 H, NCHCH₃), 1.26–1.18 (br, 6 H, NCHCH₃), 1.06–0.98 (br, 3 H, NCHCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, 25°C , C_6D_6): $\delta_{\text{C}} = 291.5$ (d, $\text{W}\equiv\text{C}$, $^1J_{\text{PC}} = 94$, $^1J_{\text{CW}} = 194$), 226.2 (CO, $^1J_{\text{WC}} = 165$), 226.0 (CO, $^1J_{\text{WC}} = 165.5 \text{ Hz}$), 152.7, 152.4, 152.4, 145.1, 144.5, 144.5 (pzCCH₃), 107.2, 107.1, 107.0 (pzCH), 54.5 (br, NCH), 45.9 (br, NCH), 26.9 (br, NCHCH₃), 24.9 (br, NCHCH₃), 22.1, 21.7 (br, NCHCH₃), 17.5, 17.4, 15.1, 12.5 (2 C, coincident), 12.4 (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (283 MHz, C_6D_6 , 25°C): $\delta_{\text{P}} = 129.4$ ($^2J_{\text{WP}} = 83 \text{ Hz}$). Anal. Found: C, 39.93; H, 4.77; N, 13.41%. Calcd. for $\text{C}_{24}\text{H}_{36}\text{BCIN}_7\text{O}_2\text{PW}$: C, 40.28; H, 5.07; N, 13.70%. Satisfactory mass spectrometric data not obtained due to matrix hydrolysis. ESI-MS (MeCN): Unidentified parent fragment $m/z = 730.2631$.

Single crystal X-ray structure determination of $[\text{WCl}\{\eta^2\text{-HOC}\equiv\text{CPH}(\text{O})(\text{OH})\}(\text{CO})(\text{Tp}^*)]\cdot\text{C}_6\text{H}_6$ (3**).** A solution of **2b** in benzene was allowed to stand open to air at 4°C for several days. Bright blue crystals were deposited which were used for structure determination and proved to be a benzene solvate. Insufficient material was obtained for spectroscopic characterisation. Disorder in the $\text{PH}(\text{O})(\text{OH})$ moiety precluded accurate location of the associated hydrogen atoms. *Crystal data for $\text{C}_{24}\text{H}_{36}\text{BCIN}_7\text{O}_4\text{PW}$* : $M_{\text{w}} = 728.63 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.3645(2)$, $b = 15.7367(2)$, $c = 16.4046(2) \text{ \AA}$, $\beta = 115.079(2)^\circ$, $V = 3358.66(9) \text{ \AA}^3$, $Z = 4$, $T = 150.0(1) \text{ K}$, $\mu(\text{Cu K}\alpha) = 7.848 \text{ mm}^{-1}$, $D_{\text{calc.}} = 1.441 \text{ Mg m}^{-3}$, 17851 reflections measured ($8.184^\circ \leq 2\theta \leq 133.186^\circ$), 5926 unique ($R_{\text{int}} = 0.0281$, $R_{\text{sigma}} = 0.0269$) which were used in all calculations. The final R_1 was 0.0466 ($I > 2\sigma(I)$) and wR_2 was 0.1294 (all data) for 351 refined parameters with 48 restraints. CCDC 1908155.

Synthesis of $[\text{W}(\equiv\text{CPMeN}^i\text{Pr}_2)(\text{CO})_2(\text{Tp}^*)]$ (5a**).** A solution of **2b** (100 mg, 0.140 mmol) in THF (10 mL) at -78°C was treated with LiMe (100 μL , 1.6 M in Et_2O , 0.16 mmol), causing the initially orange solution to turn bright yellow. Stirring was continued for 30 min, after which time the solution was warmed to room temperature and the volatiles were removed *in vacuo*.

The residue was dissolved in *n*-pentane (3 x 10 mL) and the soluble component extracted by cannula filtration. Removal of the solvent under reduced pressure gave a yellow solid of pure **5a** (88.0 mg, 0.127 mmol, 90%). IR (Nujol, cm^{-1}): 2542w ν_{BH} , 1987m, 1972s, 1957sh, 1902m, 1883s, 1862m ν_{CO} . IR (THF, cm^{-1}): 2551w ν_{BH} , 1974vs, 1884vs ν_{CO} . IR (CH_2Cl_2 , cm^{-1}): 1976s, 1884s ν_{CO} . ^1H NMR (600 MHz, C_6D_6 , 25 °C) δ_{H} = 5.56 (s, 1 H, pzH), 5.55 (s, 1 H, pzH), 5.35 (s, 1 H, pzH), 3.61 (m, 2 H, NCH), 2.86 (s, 3 H, pzCH₃), 2.72 (s, 3 H, pzCH₃), 2.45 (s, 3 H, pzCH₃), 2.08 (s, 3 H, pzCH₃), 2.07 (s, 3 H, pzCH₃), 2.03 (s, 3 H, pzCH₃), 1.53 (d, $^2J_{\text{PH}}$ = 6.4 Hz, 3 H, PCH₃), 1.41 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, NCH(CH₃)₂), 1.06 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 6 H, NCH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 25 °C) δ_{C} = 313.0 (d, $^1J_{\text{PC}}$ = 80, $^1J_{\text{WC}}$ = 178, W $\equiv$ C), 227.5 (CO, $^1J_{\text{WC}}$ = 171), 227.1 (CO, $^1J_{\text{WC}}$ = 171), 152.5, 152.3, 152.0, 144.7, 144.3, 144.1 (pzCCH₃), 107.0, 106.8, 106.8 (pzCH), 48.6 (br s, NCH), 24.7 (d, $^3J_{\text{PC}}$ = 7.6, NCHCH₃), 24.4 (d, $^3J_{\text{PC}}$ = 5.6, NCHCH₃), 17.5 (br s, pzCH₃), 17.4 (d, $^5J_{\text{PC}}$ = 4.4, pzCH₃), 15.5 (d, $^1J_{\text{PC}}$ = 18.5 Hz, PCH₃), 15.2, 12.5, 12.5, 12.4 (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ_{P} = 53.3 (s, $^2J_{\text{WP}}$ = 80 Hz). MS (ESI, m/z): Found 696.2589. Calcd. for $\text{C}_{25}\text{H}_{40}^{11}\text{BN}_7\text{O}_2\text{P}^{184}\text{W}$: 696.2584. Anal. Found: C, 43.17; H, 5.80; N, 13.98%. Calcd. for $\text{C}_{25}\text{H}_{39}\text{BN}_7\text{O}_2\text{PW}$: C, 43.19; H, 5.65; N, 14.10%. Crystal suitable for X-ray crystallographic analysis were grown by slow evaporation of a CH_2Cl_2 /ethanol mixture at -18 °C. *Crystal data for* $\text{C}_{25}\text{H}_{39}\text{BN}_7\text{O}_2\text{PW}$: M_{w} = 695.26 g mol^{-1} , triclinic, space group *P*-1 (no. 2), a = 11.0365(4), b = 11.7052(3), c = 12.2565(3) Å, α = 81.005(2)°, β = 77.156(3)°, γ = 75.950(3)°, V = 1488.75(8) Å³, Z = 2, T = 150.0(1) K, $\mu(\text{Cu K}\alpha)$ = 7.968 mm^{-1} , $D_{\text{calc.}}$ = 1.551 Mg m^{-3} , 15374 reflections measured ($7.442^\circ \leq 2\theta \leq 147.464^\circ$), 5970 unique (R_{int} = 0.0404, R_{sigma} = 0.0409) which were used in all calculations. The final R_1 was 0.0392 ($I > 2\sigma(I)$) and wR_2 was 0.1029 (all data) for 349 refined parameters with 0 restraints. CCDC 1908156.

Synthesis of [W($\equiv$ CPEtN Pr_2)(CO)₂(Tp*)] (5b). A solution of [W($\equiv$ CBr)(CO)₂(Tp*)] (250 mg, 0.397 mmol) in THF (10 mL) was cooled to -78 °C and treated with *n*BuLi (0.25 mL, 1.6 M in hexanes, 0.40 mmol). The resulting light brown solution was stirred for 1 h at reduced temperature and then treated with $\text{PCl}_2\text{N}^i\text{Pr}_2$ (75 μL , 0.41 mmol). The resulting orange solution was stirred for 30 min at reduced temperature. A solution of EtLi (0.40 mmol) was freshly prepared from EtBr (30 μL) and Li in Et₂O (10 mL) and then added to the *in situ* generated solution of [W($\equiv$ CPCIN Pr_2)(CO)₂(Tp*)] at -78 °C. The mixture was slowly warmed to RT and was stirred for a further 1 h. Volatiles were then removed *in vacuo* and the residue was extracted with *n*-pentane (3 x 25 mL) *via* cannula filtration. Removal of the solvent under reduced pressure gave a yellow solid of **5b** (213 mg, 0.300 mmol, 76%). Further purification was not found to be possible due to the sensitivity of the complex towards chromatography and for this reason a satisfactory elemental analysis was not obtained. IR (CH_2Cl_2 , cm^{-1}): 1975s, 1884s ν_{CO} . ^1H NMR (600 MHz, 25 °C, C_6D_6 , δ): 5.60 (s, 1 H, pzCH), 5.56 (s, 1 H, pzCH), 5.35 (s, 1 H, pzCH), 3.60 (br s, 2 H, NCH), 2.90 (s, 3 H, pzCH₃), 2.76 (s, 3 H, pzCH₃), 2.45 (s, 3 H, pzCH₃), 2.09 (s, 3 H, pzCH₃), 2.06 (s, 3 H, pzCH₃), 2.03 (s, 3 H, pzCH₃), 2.04–1.97 (observed m, 1 H, PCH₂), 1.94–1.85 (m, 1 H, PCH₂), 1.47 (d, $^3J_{\text{HH}}$ = 6.6, NCHCH₃), 1.16 (dt, $^3J_{\text{HP}}$ = 19.0, $^3J_{\text{HH}}$ = 7.6, 3 H, PCH₂CH₃), 1.08 (d, $^3J_{\text{HH}}$ = 6.6 Hz, NCHCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 25 °C, C_6D_6): δ_{P} = 313.4 (d, $^1J_{\text{CP}}$ = 82, $^1J_{\text{CW}}$ = 178, W $\equiv$ C), 227.6 (CO,

$^1J_{\text{CW}}$ = 171), 227.4 (CO, $^1J_{\text{CW}}$ = 171), 152.6, 152.4, 152.1, 144.7, 144.4, 144.2 (pzCCH₃), 107.0, 106.9, 106.7 (pzCH), 48.4 (br s, NCH), 25.0 (br d, $^3J_{\text{CP}}$ = 4.5, NCHCH₃), 24.8 (br d, $^3J_{\text{CP}}$ = 4.7, NCHCH₃), 22.6 (d, $^1J_{\text{CP}}$ = 10.4, PCH₂CH₃), 17.6, 17.2 (d, $^5J_{\text{CP}}$ = 6.2), 15.2, 12.6, 12.5, 12.4 (pzCH₃), 10.4 (d, $^2J_{\text{CP}}$ = 21 Hz, PCH₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 25 °C, C_6D_6): δ_{P} = 68.2 ($^2J_{\text{WP}}$ = 72 Hz). MS (ESI, m/z): Found: 710.2743. Calcd for $\text{C}_{26}\text{H}_{42}^{11}\text{BN}_7\text{O}_2\text{P}^{184}\text{W}$ [$M + \text{H}$]⁺: 710.2735.

Synthesis of [W($\equiv$ CPhN Pr_2)(CO)₂(Tp*)] (5c). A solution of [W($\equiv$ CBr)(CO)₂(Tp*)] (250 mg, 0.397 mmol) in THF (10 mL) was cooled to -78 °C and treated with *n*BuLi (0.25 mL, 1.6 M in hexanes, 0.40 mmol). The resulting light brown solution was stirred for 1 h at reduced temperature and then treated with $\text{PCl}_2\text{N}^i\text{Pr}_2$ (75 μL , 0.41 mmol). The resulting orange solution was stirred for 30 min at reduced temperature and then treated with PhLi (210 μL , 1.9 M in dibutyl ether, 0.40 mmol). The mixture was slowly warmed to room temperature and was stirred for a further 1 h. Volatiles were removed *in vacuo* and the residue was subjected to column chromatography (20 x 1 cm basic alumina column), eluting with petroleum ether (40–60 °C) followed by 30% v/v CH_2Cl_2 /petrol. The major orange band was collected and the solvents were removed under reduced pressure to give an orange solid of pure **5c** (251 mg, 0.331 mmol, 83%). IR (CH_2Cl_2 , cm^{-1}): 1979s, 1888s ν_{CO} . ^1H NMR (400 MHz, 25 °C, CDCl_3): δ_{H} 7.98–7.91 (m, 2H, C₆H₅), 7.02–6.97 (m, 2 H, C₆H₅), 6.96–6.91 (m, 1 H, C₆H₅), 5.64 (s, 1 H, pzCH), 5.54 (s, 1 H, pzCH), 5.36 (s, 1 H, pzCH), 3.54 (br m, 2 H, NCH), 2.66 (s, 3 H, pzCH₃), 2.64 (s, 3 H, pzCH₃), 2.42 (s, 3 H, pzCH₃), 2.08 (s, 3 H, pzCH₃), 2.03 (s, 3 H, pzCH₃), 2.02 (s, 3 H, pzCH₃), 1.58 (d, $^3J_{\text{HH}}$ = 6.5, 6 H, NCHCH₃), 1.10 (d, $^3J_{\text{HH}}$ = 6.5 Hz, 6 H, NCHCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 25 °C, CDCl_3): δ_{C} = 307.8 (d, $^1J_{\text{CP}}$ = 83, W $\equiv$ CP), 230.5 (CO, $^1J_{\text{CW}}$ = 169), 224.3 (d, $^3J_{\text{CP}}$ = 4.0, CO), 152.6 (2 C), 152.2, 144.9, 144.6, 144.4 (pzCCH₃), 141.8 [d, $^1J_{\text{CP}}$ = 5.9, C¹(C₆H₅)], 132.1, 131.9 [C^{2,3,5,6}(C₆H₅)], *ca* 128.2–127.9 (two signals corresponding to [C^{2,3,5,6}(C₆H₅)] carbons, obscured by C_6D_6 , identified by ^1H - ^{13}C HSQC-NMR), 127.7 [C⁴(C₆H₅)], 107.1, 106.8 (pzCH), 49.3 (br s, NCH), 25.1 (d, $^3J_{\text{CP}}$ = 6.9, NCHCH₃), 24.4 (d, $^3J_{\text{CP}}$ = 5.8, NCHCH₃), 17.4 (pzCH₃), 16.8 (d, $^5J_{\text{CP}}$ = 5.5 Hz, pzCH₃), 15.2, 12.6, 12.6, 12.4 (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, 25 °C, CDCl_3): δ_{P} = 69.1 ($^2J_{\text{WP}}$ = 72 Hz). MS (ESI, m/z): Found: 758.2743. Calcd for $\text{C}_{30}\text{H}_{42}^{11}\text{BN}_7\text{O}_2\text{P}^{184}\text{W}$ [$M + \text{H}$]⁺: 758.2735. Anal. Found: C, 47.49; H, 5.62; N, 12.81. Calcd for $\text{C}_{30}\text{H}_{41}\text{BN}_7\text{O}_2\text{PW}$: C, 47.58; H, 5.46; N, 12.95%. *Crystal data for* $\text{C}_{30}\text{H}_{41}\text{BN}_7\text{O}_2\text{PW}$: M_{w} = 757.33 g mol^{-1} , trigonal, space group *P*3₁ (no. 144), a = 10.6921(2), c = 25.0214(2) Å, V = 2477.24(9) Å³, Z = 3, T = 150.0(1) K, $\mu(\text{Cu K}\alpha)$ = 7.238 mm^{-1} , $D_{\text{calc.}}$ = 1.523 Mg m^{-3} , 59289 reflections measured ($9.552^\circ \leq 2\theta \leq 147.544^\circ$), 5942 unique (R_{int} = 0.0403, R_{sigma} = 0.0189) which were used in all calculations. The final R_1 was 0.0353 ($I > 2\sigma(I)$) and wR_2 was 0.0906 (all data) for 389 refined parameters with 1 restraint. CCDC 1908157.

Synthesis of [$i\text{Pr}_2\text{NP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2$] (6). A solution of [W($\equiv$ CBr)(CO)₂(Tp*)] (500 mg, 0.795 mmol) in THF (10 mL) was cooled to -78 °C and treated with *n*BuLi (0.50 mL, 1.6 M in hexanes, 0.80 mmol). The resulting light brown solution was stirred for 1 h at reduced temperature and then treated with $\text{PCl}_2\text{N}^i\text{Pr}_2$ (74 μL , 0.40 mmol). The resulting orange solution was warmed to room temperature and was stirred for a further 15

h. Volatiles were removed under reduced pressure and the residue was subjected to column chromatography (40 x 1 cm basic alumina column), eluting with petroleum ether (40–60 °C) followed by 50% v/v CH₂Cl₂/petrol. The major orange band was collected and the solvents were removed under reduced pressure to give an orange solid of pure **6** (344 mg, 0.280 mmol, 70%). IR (CH₂Cl₂, cm⁻¹) 1981s, 1968s, 1886s ν_{CO}. ¹H NMR (700 MHz, 25 °C, C₆D₆): δ_H = 5.41 (s, 4 H, pzCH), 5.34 (s, 2 H, pzCH), 3.85 (br, 2 H, NCH), 2.59 (br s, 12 H, pzCH₃), 2.40 (s, 6 H, pzCH₃), 2.09 (s, 12 H, pzCH₃), 2.02 (s, 6 H, pzCH₃), 1.60 (d, ³J_{HH} = 6.6 Hz, 12 H, NCHCH₃). ¹³C{¹H} NMR (176 MHz, 25 °C, CDCl₃): δ_C = 297.9 (d, ¹J_{CP} = 79.7, ¹J_{CW} = 180, W≡CP), 226.0 (br, CO), 152.7, 152.6, 144.7, 144.3 (pzCCH₃), 107.0 106.7 (pzCH), 34.4 (NCH), 25.2 (br, NCCH₃), 22.7 (NCCH₃), 16.7, 15.3, 12.6, 12.4 (pzCH₃). ³¹P{¹H} NMR (283 MHz, 25 °C, CDCl₃): δ_P = 112.1 (²J_{WP} = 76 Hz). MS (ESI, *m/z*): Found: 1030.3751. Calcd for C₄₂H₅₉¹¹B₂N₁₃O₄P¹⁸⁴W₂ [M + H]⁺: 1030.3757. Anal. Found: C, 40.83; H, 4.64; N, 14.67. Calcd for C₄₂H₅₈B₂N₁₃O₄PW₂: C, 41.04; H, 4.76; N, 14.81%. Crystals suitable for crystallographic analysis were grown by slow evaporation of a CH₂Cl₂/ethanol mixture and proved to be a dichloromethane solvate. *Crystal data for* C₄₃H₆₀B₂Cl₂N₁₃O₄PW₂: *M_w* = 1314.23 g mol⁻¹, monoclinic, space group *P*2₁/c (no. 14), *a* = 24.5458(5), *b* = 13.8577(3), *c* = 15.7675(4) Å, β = 90.920(2)°, *V* = 5362.6(2) Å³, *Z* = 4, *T* = 150.0(1) K, μ(Mo Kα) = 4.468 mm⁻¹, *D_{calc}* = 1.628 Mg m⁻³, 60001 reflections measured (6.64° ≤ 2θ ≤ 52.742°), 10939 unique (*R_{int}* = 0.0485, *R_{sigma}* = 0.0361) which were used in all calculations. The final *R₁* was 0.0289 (*I* > 2σ(*I*)) and *wR₂* was 0.0623 (all data) for 637 refined parameters with 0 restraints. CCDC 1908158.

Synthesis and observation of [W(≡CPHN/Pr₂)(CO)₂(Tp*)] (7**) as a mixture with **5b**.** A solution of **2b** (0.028 g, 0.039 mmol) in THF (1 mL) was cooled to –78 °C and treated with Li[BHET₃] (0.08 mL, 1.0 M in THF, 0.08 mmol). The resulting orange-brown solution was stirred for 60 minutes then allowed to warm to room temperature. After this time the volatiles were removed under reduced pressure to afford primarily crude **7** as a brown solid. ³¹P{¹H} NMR spectroscopy indicated that the crude product contained approximately 75% **7** and 15% **5b**. Attempts to scale up the procedure (0.150 g **2b**) gave 25% and 38% spectroscopic yields, respectively. As samples of reasonable purity were not obtained, only very limited spectroscopic data are presented. ¹H NMR (400 MHz, 25 °C, CDCl₃): δ_H = 6.46 (d, 1 H, ¹J_{PH} = 228 Hz, PH), 5.55 (s, 2 H, pzH), 5.34 (s, 1 H, pzH). The pzCH₃ and ^{*i*}Pr resonances could not be unambiguously differentiated. ³¹P{¹H} NMR (162 MHz, 25 °C, CDCl₃): δ_P = 22.6 (²J_{WP} = 77.6). ³¹P NMR (162 MHz, 25 °C, CDCl₃): δ_P = 22.6 (dt, ¹J_{PH} = 229.5, ³J_{PH} = 20.8).

Synthesis of [W(≡CP(N^{*i*}Pr₂)(NPh₂))(CO)₂(Tp*)] (10**).** A solution of [W(≡CBr)(CO)₂(Tp*)] (250 mg, 0.397 mmol) in THF (10 mL) was cooled to –78 °C and treated with ^{*n*}BuLi (0.25 mL, 1.6 M in hexanes, 0.40 mmol). The resulting light brown solution was stirred for 1 h at reduced temperature and then treated with PCl₂N^{*i*}Pr₂ (75 μL, 0.41 mmol). The resulting orange solution was stirred for 30 min at reduced temperature. A solution of LiNPh₂ was prepared separately from HNPh₂ (100 mg, 0.591 mmol) and ^{*n*}BuLi (1.6 M in hexanes, 0.36 mL, 0.58 mmol) in THF (5 mL) at –78 °C and subsequently added *via* cannula transfer, causing the orange-red solution to lighten to yellow-orange.

The mixture was warmed to RT and stirring continued for 1 h, after which time all the volatiles were removed *in vacuo*. The residue was extracted with *n*-pentane (5 x 20 mL), ethanol (20 mL) was added and the solvents were removed until ~5 mL of ethanol remained. Cooling the solution overnight at –20 °C caused orange crystals to form, which were collected by filtration and washed with ice-cold ethanol (3 x 2 mL) to give pure **10** (171 mg, 0.202 mmol, 51%). A second crop was obtained from the filtrate with only a marginal reduction in purity (104 mg, 0.123 mmol, 31%). IR (CH₂Cl₂, cm⁻¹) 1982s, 1890s ν_{CO}. ¹H NMR (700 MHz, 25 °C, CDCl₃): δ_H = 7.52 [d, ³J_{HH} = 8.2, 4 H, H^{2,6}(C₆H₅)], 7.03 [t', ³J_{HH} = 7.9, 4 H, H^{3,5}(C₆H₅)], 6.83 [t, ³J_{HH} = 7.5, 4 H, H⁴(C₆H₅)], 5.64 (s, 1 H, pzCH), 5.48 (s, 1 H, pzCH), 5.31 (s, 1 H, pzCH), 3.58 (br, 2 H, NCH), 2.62 (s, 3 H, pzCH₃), 2.44 (s, 3 H, pzCH₃), 2.39 (s, 3 H, pzCH₃), 2.14 (s, 3 H, pzCH₃), 2.02 (s, 3 H, pzCH₃), 2.01 (s, 3 H, pzCH₃), 1.43 (d, ³J_{HH} = 6.8, 6 H, NCHCH₃), 1.07 (d, ³J_{HH} = 6.8 Hz, 6 H, NCHCH₃). ¹³C{¹H} NMR (176 MHz, 25 °C, CDCl₃): δ_C = 300.8 (d, ¹J_{CP} = 76, WCP), 229.8 (CO), 224.4 (d, ³J_{CP} = 6, CO), 152.6, 152.6, 152.4 (pzCCH₃), 149.9 (d, ²J_{CP} = 10, C¹(C₆H₅)), 144.8, 144.5, 144.3 (pzCCH₃), 129.0 [C^{3,5}(C₆H₅)], 125.1 [d, ³J_{CP} = 8, C^{2,6}(C₆H₅)], 122.8 [C⁴(C₆H₅)], 107.1, 107.0, 106.8 (pzCH), 49.4 (br, NCH), 25.3 (d, ³J_{CP} = 6, NCHCH₃), 24.5 (d, ³J_{CP} = 6 Hz, NCHCH₃), 17.1, 16.7 (d, ⁵J_{CP} = 4 Hz), 15.2, 12.7, 12.6, 12.4 (pzCH₃). ³¹P{¹H} NMR (162 MHz, 25 °C, CDCl₃): δ_P = 100.6 (²J_{WP} = 76 Hz). MS (ESI, *m/z*): Found: 849.3152. Calcd for C₃₆H₄₆¹¹BN₈O₂P¹⁸⁴W [M + H]⁺: 849.3162. Anal. Found: C, 50.86; H, 5.53; N, 13.17. Calcd for C₃₆H₄₆BN₈O₂PW: C, 50.96; H, 5.46; N, 13.21%. Single crystals suitable for structure determination were grown by slow evaporation of a CH₂Cl₂/ethanol solution. *Crystal data for* C₃₆H₄₆BN₈O₂PW: *M_w* = 848.44 g mol⁻¹, triclinic, space group *P*-1 (no. 2), *a* = 10.8899(4), *b* = 11.6332(4), *c* = 15.5746(6) Å, α = 83.516(3)°, β = 84.985(3)°, γ = 77.955(3)°, *V* = 1913.13(12) Å³, *Z* = 2, *T* = 150.0(1) K, μ(Mo Kα) = 3.103 mm⁻¹, *D_{calc}* = 1.473 Mg m⁻³, 16590 reflections measured (6.604° ≤ 2θ ≤ 57.496°), 7992 unique (*R_{int}* = 0.0328, *R_{sigma}* = 0.0535) which were used in all calculations. The final *R₁* was 0.0304 (*I* > 2σ(*I*)) and *wR₂* was 0.0644 (all data) for 452 refined parameters with 0 restraints. CCDC 1908159.

Computational details. Geometry optimization of singlet ground-state structures in the gas phase was performed at the Becke 3LYP (B3LYP) level of theory.⁴⁵ The effective core potentials of Hay and Wadt⁴⁶ with a double-ζ valence basis set (LanL2DZ) were used to describe the W and P atoms, while the standard 6-31G basis set was used for all other atoms.⁴⁷ All calculations were performed with the use of the *Spartan-18* package⁴⁸ and the molecular orbitals obtained from B3LYP calculations were plotted using the *Spartan-18* program. Geometry optimisation for the cation [W(CPPH)(CO)₂(Tp*)]⁺ commenced with that for the corresponding anion. Geometry optimisation for the cation [W(CPNMe₂)(CO)₂(Tp*)]⁺ commenced with a geometry derived from that of the phenyl derivative by replacing Ph with NMe₂ (bent phosphorus C–P–N = 120 ° and trigonal nitrogen). The same optimised geometry was arrived at by commencing with the least likely geometry, i.e., one involving linear phosphorus and trigonal pyramidal nitrogen. Two rotational conformers were identified with the CPNMe₂ ligand either bisecting the OC–W–CO unit or alternatively aligning with one carbonyl ligand, consistent with

the low barriers to rotation for phosphino-substituted carbyne ligands in this system,³ and the near degeneracy of the two relevant retrodative orbitals of the (Tp*)(CO)₂W fragment.

Acknowledgements

This work was supported by the Australian Research Council (DP170102685 and DP190100723). The authors declare no conflict of interest.

Notes and references

- 1 T. Agapie, P. L. Diaconescu and C. C. Cummins, *J. Am. Chem. Soc.*, 2002, **124**, 2412 – 2413.
- 2 A. L. Colebatch and A. F. Hill, *J. Am. Chem. Soc.*, 2014, **136**, 17442 – 17445.
- 3 A. L. Colebatch, A. F. Hill and M. Sharma, *Organometallics*, 2015, **34**, 2165 – 2182.
- 4 A. L. Colebatch and A. F. Hill, *Organometallics*, 2016, **35**, 2249 – 2255.
- 5 (a) J. Y. Saillard, D. Grandjean, P. Caillet and A. Le Beuze, *J. Organomet. Chem.*, 1980, **190**, 371 – 379; (b) W. G. Richards, *Trans. Faraday Soc.*, 1967, **63**, 257 – 261.
- 6 (a) S. Chaona, F. J. Lalor, G. Ferguson and M. M. Hunt, *J. Chem. Soc., Chem. Commun.*, 1988, 1606 – 1608; (b) F. J. Lalor and S. A. O'Neill, *J. Organomet. Chem.*, 2003, **684**, 249 – 265; (c) B. E. Woodworth and J. L. Templeton, *J. Am. Chem. Soc.*, 1996, **118**, 7418 – 7419; (d) L. Weber, G. Dembeck, H.-G. Stammer, B. Neumann, M. Schmidtman and A. Müller, *Organometallics*, 1998, **17**, 5254 – 5259; (e) L. Weber, G. Dembeck, R. Boese and D. Bläser, *Organometallics*, 1999, **18**, 4603 – 4607; (f) B. J. Frogley, A. F. Hill, R. A. Manzano and M. Sharma, *Chem. Commun.*, 2018, **54**, 1702–1705; (g) R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 4532 – 4540; (h) L. M. Caldwell, A. F. Hill, R. Stranger, R. N. L. Terrett, K. M. von Nessi, J. S. Ward and A. C. Willis, *Organometallics*, 2015, **34**, 328 – 334.
- 7 F. J. Lalor, T. J. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez and B. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1995, 1709 – 1726.
- 8 R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 5177 – 5179.
- 9 (a) R. L. Cordiner, A. F. Hill, R. Shang and A. C. Willis, *Organometallics*, 2011, **30**, 139 – 144; (b) A. F. Hill and R. Shang, *Organometallics*, 2012, **31**, 4635 – 4638; (c) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 2126 – 2129.
- 10 (a) R. L. Cordiner, P. A. Gugger, A. F. Hill and A. C. Willis, *Organometallics*, 2009, **28**, 6632 – 6635; (b) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, 2017, **46**, 4355 – 4365; (c) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 7649 – 7652; (d) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 1237 – 12376.
- 11 A. L. Colebatch, Y.-S. Han, A. F. Hill, M. Sharma, R. Shang and J. S. Ward, *Chem. Commun.*, 2017, **53**, 1832 – 1835.
- 12 M. Q. Y. Tay, Y. Lu, R. Ganguly and D. Vidović, *Angew. Chem. Int. Ed.*, 2013, **52**, 3132 – 3135.
- 13 S. Stadlbauer, R. Frank, I. Maulana, P. Lönnecke, B. Kirchner and E. Hey-Hawkins, *Inorg. Chem.*, 2009, **48**, 6072 – 6082.
- 14 (a) F. R. Kreissl, P. Friedrich and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 101 – 103.
- 15 A. Mayr and C. M. Bastos, *Prog. Inorg. Chem.*, 1992, **40**, 1 – 98.
- 16 H. P. Kim, S. Kim, R. A. Jacobson and R. J. Angelici, *Organometallics*, 1986, **5**, 2481 – 2488.
- 17 (a) M. H. Chisholm, J. C. Huffman and N. S. Marchant, *J. Chem. Soc., Chem. Commun.*, 1986, 717 – 718; (b) E.-K. Aida, K. Stahl, U. Müller and K. Dehnicke, *J. Organomet. Chem.*, 1986, **317**, C9 – C15; (c) S. G. Bott, D. L. Clark, M. L. H. Green and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1991, 471 – 481; (d) A. J. Nielson, P. D. W. Boyd, G. R. Clark, T. A. Hunt, J. B. Metson, C. E. F. Rickard and P. Schwerdtfeger, *Polyhedron*, 1992, **11**, 1419 – 1421; (e) T. E. Baroni, J. A. Heppert, R. R. Hodel, R. P. Kingsborough, M. D. Morton, A. L. Rheingold and G. P. A. Yap, *Organometallics*, 1996, **15**, 4872 – 4879; (f) T. E. Baroni, V. Kolesnichenko, L. Seib, J. A. Heppert, L. M. Liable-Sands, G. P. A. Yap and A. E. Rheingold, *Polyhedron*, 1998, **17**, 759 – 768; (g) T. W. Hayton, J. M. Boncella, B. L. Scott, K. A. Abboud and R. C. Mills, *Inorg. Chem.*, 2005, **44**, 9506 – 9517.
- 18 (a) P. J. Lim, D. A. Slizys, J. M. White, C. G. Young and E. R. T. Tiekink, *Organometallics*, 2003, **22**, 4853 – 4860; (b) I. M. Bartlett, S. Carlton, N. G. Connelly, D. J. Harding, O. D. Hayward, A. G. Orpen, C. D. Ray and P. H. Rieger, *Chem. Commun.*, 1999, 2403 – 2404; (c) C. J. Adams, I. M. Bartlett, S. Carlton, N. G. Connelly, D. J. Harding, O. D. Hayward, A. G. Orpen, E. Patron, C. D. Ray and P. H. Rieger, *Dalton Trans.*, 2007, 62 – 72; (d) L. M. Caldwell, A. F. Hill and A. C. Willis, *J. Organomet. Chem.*, 2017, **829**, 48 – 57; (e) A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 721 – 722; (f) W. W. Seidel, M. Schaffrath, M. J. Meel, T. Hamilton, S. C. Ariza and T. Pape, *Z. Naturforsch.*, 2007, **62B**, 791 – 798.
- 19 (a) S. G. Feng, C. C. Philipp, A. S. Gamble, P. S. White and J. L. Templeton, *Organometallics*, 1991, **10**, 3504 – 3512; (b) M. B. Wells, P. S. White and J. L. Templeton, *Organometallics*, 1997, **16**, 1857 – 1864; (c) M. B. Wells, J. E. McConathy, P. S. White and J. L. Templeton, *Organometallics*, 2002, **21**, 5007 – 5020; (d) M. A. Collins, S. G. Peng, P. A. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1992, **114**, 3771 – 3775; (e) S. A. O'Reilly, P. S. White and J. L. Templeton, *Chem. Mater.*, 1996, **8**, 93 – 99; (f) K. Helmdach, S. Ludwig, A. Villinger, D. Hollmann, J. Koters and W. W. Seidel, *Chem. Commun.*, 2017, **53**, 5894 – 5897; (g) K. Helmdach, S. Dork, A. Villinger and W. W. Seidel, *Dalton Trans.*, 2017, **46**, 11140 – 11144; (h) K. Helmdach, A. Villinger and W. W. Seidel, *Organometallics*, 2017, **36**, 4844 – 4853; (i) J. Zagermann, K. Merz and N. Metzler-Nolte, *Organometallics*, 2009, **28**, 5090 – 5095.
- 20 (a) J. C. Jeffery, J. C. V. Laurie, I. Moore and F. G. A. Stone, *J. Organomet. Chem.*, 1983, **258**, C37 – C40; (b) J. A. K. Howard, J. C. Jeffery, J. C. V. Laurie, I. Moore, F. G. A. Stone and A. Stringer, *Inorg. Chim. Acta*, 1985, **100**, 23 – 32.
- 21 A. Mayr, C. M. Bastos, R. T. Chang, J. X. Haberman, K. S. Robinson and D. A. Belle-Oudry, *Angew. Chem., Int. Ed.*, 1992, **31**, 747 – 749.
- 22 Although the complex [W(η²-HOCCC₆H₄Me-4)(CO)₂Cl(acac)] has been structurally characterised, neither the C–O bond length nor atomic coordinates are available: E. O. Fischer and P. Friedrich, *Angew. Chem., Int. Ed.*, 1979, **18**, 327 – 328.
- 23 (a) R. Choukroun, B. Donnadieu, I. Malfant, S. Haubrich, R. Frantz, C. Guerin and B. Henner, *Chem. Commun.*, 1997, 2315 – 2316; (b) R. Choukroun, Y. Miquel, B. Donnadieu, A. Igau, C. Blandy and J. P. Majoral, *Organometallics*, 1999, **18**, 1795 – 1797. (c) L. D. Quin, *A Guide to Organophosphorus Chemistry*, John Wiley & Sons, New York, USA, 2000.
- 24 G. M. Jamison, A. E. Bruce, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1991, **113**, 5057 – 5059.
- 25 (a) P. K. Majhi, J. M. Franco, S. Villalba, G. Schnakenburg, T. Sasamori and R. Streubel, *Eur. J. Inorg. Chem.*, 2017, 910 – 914; (b) M. Herberhold, C. Kohler, V. Trobs and B. Wrackmeyer, *Z. Naturforsch.*, 2000, **55B**, 939 – 945; (c) M. Schmitz, S. Leininger, U. Bergstrasser and M. Regitz, *Heteroatom Chem.*, 1998, **9**, 453 – 460; (d) J. Grobe, D. Le Van, S. Martin and J. Szameitat, *Z. Naturforsch.*, 1992, **47B**, 321 – 328; (e) J. F. Janik, E. N. Duesler, W. F. McNamara, M. Westerhausen and R. T. Paine, *Organometallics*, 1989, **8**, 506 – 514; (f) R. R. Ford and R. H. Neilson, *Polyhedron*, 1986, **5**, 643 – 653; (g) E. Niecke, R. Rueger and W. Güth, *Z. Naturforsch.*, 1985, **40B**, 1049 1052; (h) H. R. O'Neal and R. H. Neilson, *Inorg. Chem.*, 1984, **23**, 1372 – 1377; (i) R. H. O'Neal and R. H. Neilson, *Inorg. Chem.*, 1983, **22**, 814 – 818; (j) X. M. Xie and R. H. Neilson, *Organometallics*, 1983, **2**, 921–925.
- 26 (a) O. Back, M. A. Celik, G. Frenking, M. Melaimi, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2010, **132**, 10262 – 10263; (b) T. L. Chan and Z. Xie, *Chem. Commun.*, 2016, **52**, 7280 – 7283; (c) M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem.*, 1988, **27**, 2045 – 2049; (d) H. Nöth, B. Gemund and R. T. Paine, *Eur. J. Inorg. Chem.*, 2007, 4282 – 2497; (e) O. Puntigam, D. Forster, N. A. Giffin, S. Burck, J. Bender, F. Ehret, A. D. Hendsbee, M. Nieger, J. D. Masuda and D. Gudat, *Eur. J. Inorg. Chem.*, 2013, 2041 – 2050. (f)
- 27 A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367 – 382.
- 28 K. Vaheesar, C. M. Kuntz and B. T. Sterenberg, *J. Organomet. Chem.*, 2013, **745** – **746**, 347 – 355.

- 29 (a) J. Sánchez-Nieves, B. T. Sterenberg, K. A. Udachin and A. J. Carty, *J. Am. Chem. Soc.*, 2003, **125**, 2404 – 2405; (b) N. E. Brasch, I. G. Hamilton, E. H. Krenske and S. B. Wild, *Organometallics*, 2004, **23**, 299 – 302; (c) D. C. R. Hockless, M. A. McDonald, M. Pabel and S. B. Wild, *J. Organomet. Chem.*, 1997, **529**, 189 – 196.
- 30 (a) B. T. Sterenberg, K. A. Udachin and A. J. Carty, *Organometallics*, 2001, **20**, 4463 – 4465; (b) N. Burford, P. J. Ragnogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2003, **125**, 14404 – 14410; (c) R. A. Rajagopalan and B. T. Sterenberg, *Organometallics*, 2011, **30**, 2933 – 2938.
- 31 E. Conrad, N. Burford, R. McDonald and M. J. Ferguson, *Inorg. Chem.*, 2008, **47**, 2952 – 2954.
- 32 B. T. Sterenberg, K. A. Udachin and A. J. Carty, *Organometallics*, 2001, **20**, 2657 – 2659.
- 33 A. Jayaraman and B. T. Sterenberg, *Organometallics*, 2013, **32**, 745 – 747.
- 34 K. S. Fongers, H. Hogeveen and R. F. Kingma, *Tetrahedron Lett.*, 1983, **24**, 643 – 646.
- 35 (a) A. E. Bruce, A. S. Gamble, T. L. Tonker and J. L. Templeton, *Organometallics*, 1987, **6**, 1350 – 1352; (b) K. C. Stone, G. M. Jamison, P. S. White and J. L. Templeton, *Inorg. Chim. Acta*, 2002, **330**, 161 – 172; (c) G. M. Jamison, P. S. White and J. L. Templeton, *Organometallics*, 1991, **10**, 1954 – 1959.
- 36 J. Gopalakrishnan, *Appl. Organomet. Chem.*, 2009, **23**, 291 – 318.
- 37 L. M. Caldwell, *Adv. Organomet. Chem.*, 2008, **56**, 1 – 94.
- 38 CrysAlis PRO, Agilent Technologies Ltd, Yarnton, Oxfordshire, England, 2014.
- 39 G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3-8.
- 40 L. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849 – 854.
- 41 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339 – 341.
- 42 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466 – 470.
- 43 *Spartan 18*® (2018) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.
- 44 P. Wucher, J. B. Schwaderer and S. Mecking, *ACS Catalysis*, 2014, **4**, 2672 – 2679.
- 45 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098 – 3100; (b) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200 – 206.
- 46 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299 – 310.
- 47 (a) M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163 – 168; (b) P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta*, 1973, **28**, 213 – 222; (c) R. C. Binning Jr. and L. A. Curtiss, *J. Comput. Chem.*, 1990, **11**, 1206 – 1216.
- 48 *Spartan 18*® (2018) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.

Table of Contents Text

The synthesis of the first *P*-halo-aminophosphinocarbonyne complex is described in addition to and exploration of its ligand-based reactivity towards nucleophilic substitution and *P*-halide abstraction processes as a possible route to cationic aminophosphonitrile derivatives.

Table of Contents Graphic