Coordination Chemistry of Phosphinocarbynes: Phosphorus vs Carbyne Site Selectivity.

Annie L. Colebatch and Anthony F. Hill

The phosphinocarbyne complex \( \left[ W{\equiv CPPh}(\text{CO})_2(Tp^*) \right] \) (1; \( Tp^* = \) hydrotidis(dimethylpyrazolyl)borate) coordinates transition metal fragments via the phosphine to form bimetallic species \([W{\equiv CPPhRhCl}_2(Cp*)](\text{CO})_2(Tp^*)\) (2) and \([W{\equiv CPhPhAuCl}(\text{CO})_2(Tp^*)]\) (3). Appropriately tailored sterics allow for complexation of a second equivalent of AuCl to afford the trimetallic complex \([W{(\eta^5-CuCl)(PPh)(\text{AuCl})(\text{CO})_2(Tp^*)}]\) (4), containing an Au-W-C dimetallacylcopropene connectivity. Similarly, AuCl binds to the carbyne linkage in \([W{(\eta^5-CP=sPPh)(\text{CO})_2(Tp^*)}]\), yielding \([W{(\eta^5-CuCl)(P=sPPh)(\text{CO})_2(Tp^*)}]\) (5). In the case of auration of the ditungsten species \([W_2(\mu-C_2PPh)(\text{CO})_2(Tp^*)]\) (6), variation in the stoichiometry leads to trimetallic \([W_2(\mu-\text{CPhPhAuCl})(\text{CO})_2(Tp^*)]\) (7) and pentametallic \([W_2(\mu-\text{CPhPhAuCl})(\text{CO})_2(Tp^*)]\) (8) complexes, via a proposed tetrametallic intermediate \([W_2(\mu-(\eta^6-\text{CAuCl}))PPh)(\text{CO})_2(Tp^*)]\), the site selectivity being dictated by aurophilic interactions.

Introduction

Phosphines are one of the most widely employed classes of ligands in inorganic and organometallic chemistry, and as such need little introduction. Phosphine ligands containing metal fragments have many advantages, largely due to the range of steric and electronic variation that can be conferred upon such ligands. Perhaps the most well-known example of such is 1,1’-bis(diphenylphosphino)ferrocene (dpff), which has been widely applied in many transition metal mediated catalytic processes.\(^1\) In the case of dpff the metal centre is typically innocent, which is a desirable feature in many cases. There are, however, scenarios in which being able to perform onward reactivity at the metal centre might be advantageous.

We have an ongoing interest in group 6 carbyne complexes bearing heteroatom substituents,\(^2\) and have recently extended this work to phosphinocarbynes of the form \([M{(\equiv CPPh_2)}(\text{CO})_2(Tp^*)]\) (\( M = \) Mo, W; \( Tp^* = \) hydrotidis(3,5-dimethylpyrazol-1-yl)borate).\(^3\) We have found that, in many cases, conventional organophosphorus chemistry protocols, such as electrophilic addition and nucleophilic substitution, can be applied to these systems to impart desired functionality without rupture of the carbyne linkage.\(^4\)

An obvious extension to this is the reactivity of these complexes towards transition metal fragments. In particular, we were interested in \([W{(\equiv CPPh_2)}(\text{CO})_2(Tp^*)]\) (1), as an elaborately-functionanalogue of the ubiquitous triphenylphosphine ligand. Stone extensively researched the coordination of carbyne complexes to transition metals and showed that complexation of the metal-carbon bond to one or two metals occurs readily allowed the strategic construction of polymeric assemblies.\(^5\) Complex 1 is an attractive subject for study as it presents the possibility of competition between the phosphine and carbyne sites, and an opportunity to compare the donor abilities of these two sites within the one molecule. Herein we explore this dichotomy via the reactions of 1, and its bimetallic counterpart \([W_2(\mu-C_2PPh)(\text{CO})_2(Tp^*)]\) (6), with transition metal complexes.

In isolobal terms, complex 1 bears a notional semblance to alkynylphosphines, which themselves demonstrate rich coordination chemistry. Alkynylphosphines have been shown to react with the rhodium and iridium dimers \([M_2(\mu-\text{Cl})_2\text{Cl}_2(Cp^*)]\) via halide bridge cleavage to form P-coordinated species, an example of which is shown in Scheme 1.\(^6\)

![Scheme 1.](image)

These species can undergo subsequent reactions with cis-\([\text{Pt}(\text{CF}_3)_2(\text{THF})_2]\), via displacement of the labile THF ligands, to give bimetallic species with bridging chloride ligands or via coordination of the alkyn.

Results and discussion

Inspired by the report of Forniés and Lalinde,\(^6\) we investigated the reaction of 1 with \([\text{Rh}_2(\mu-\text{Cl})_2\text{Cl}_2(Cp^*)]\). Stirring a \(\text{CH}_2\text{Cl}_2\) solution of 1 and half an equivalent of \([\text{Rh}_2(\mu-\text{Cl})_2\text{Cl}_2(Cp^*)]\) resulted in a dark red solution, the IR spectrum of

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which included two $\nu_{\text{CO}}$ bands at 2008 and 1916 cm$^{-1}$ (cf. 1982, 1891 cm$^{-1}$ for 1). After chromatographic purification the bimetallic species \([W(\text{η}_2\text{-C}(\text{RhCl}_2\text{Cp}^*)\text{PPh}_2\text{RhCl}_2\text{Cp}^*)]\text{(CO)}_2\text{(Tp}^*)\] (2), resulting from P-coordination, was isolated as a red solid (Scheme 2). Electron donation to the Lewis-acidic rhodium is manifest in the shift of $\nu_{\text{CO}}$ to higher frequency with respect to the precursor 1. The $^{31}$P($^1$H) NMR spectrum shows only a very slight downfield shift upon coordination of the phosphate to $^{197}$Pt at 37.0 (cf. $\delta^1_P 32.0$ in 1), with coupling to rhodium ($^{13}$N$_{\text{Rh}}$ 139.2 Hz) within the typical range.7 A dramatic increase in the $W$–$P$ coupling constant is observed upon complexation ($^{32}$J$_{\text{Np}}$ 122.0 Hz cf. 69.0 Hz in 1), consistent with the values observed for other $\lambda^4$ or $\lambda^5$-$P$ adducts \([W(\text{η}_2\text{C}P\text{PPh}_2\text{E})(\text{CO})_2(Tp}^*)\] (E = BH, O, S, Se) with 4-coordinate phosphorus,8 and slightly smaller than the $^{31}$N$_{\text{Rh}}$ values observed for tungsten phosphoniocarbynes \([\text{L}_2\text{W}(\text{η}_2\text{C}P\text{P}^*)]\) (150 – 200 Hz).9

Figure 1. Molecular structure of 2 in a crystal of 2-(CH$_3$Cl)$_2$ (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.824(4), C1–P1 1.798(4), P1–Rh1 2.3198(10), W1–C1–P1 175.8(2), C1–P1–Rh1 119.23(13).

Efforts were therefore redirected towards a smaller metal-ligand fragment to circumvent such steric inhibitions. In this case ‘AuX’ was envisaged as an ideal candidate to fulfill these requirements. The literature hosts numerous reports documenting addition of gold(I) reagents to tungsten carbyne complexes of the form \([W(\text{η}_2\text{CR})(\text{L})]\) in which the metal-carbon triple bond is the reactive site.5e,g,12 In these cases a W–C–Au ‘metallacyclpropene’ is formed, such as that seen in the reaction of \([\text{Au}(\text{PPh}_3)]\text{TIPF}_6\) with a tungsten toluidyne, shown in Scheme 3.5e In this case, mono-addition of the \([\text{Au}(\text{PPh}_3)]^+\) moiety occurred, but solution NMR studies showed that the complex redistributes into \([\text{Au}[W(\text{≡CTol})(\text{CO})_2(\text{Cp})]]\text{TIPF}_6\) and \([\text{Au}(\text{PPh}_3)]\text{PF}_6\). A particularly fascinating example of such chemistry is that of the tetrameric complex \([W(\text{CAu})(\text{CO})_2(\text{Tp}^*)]\), which forms a remarkable CaAu$_4$ ring in which each carbido carbon is bound to two adjacent gold atoms and one \((\text{W}(\text{CO})_2\text{Tp}^*))\) moiety.13

In contrast to this, Weber and co-workers have reported the addition of \([\text{AuCl(CO)}]\) to the phospha-alkenycarbyne series \([M(\text{η}_2\text{C}(\text{NMe})_2)](\text{CO})_2(Tp}^*)\] (M = Mo, W), in which two AuCl moieties add to the phosphorus atom to give

\[
\text{Scheme 3. Addition of } [\text{Au}(\text{PPh}_3)]^+ \text{ to a tungsten carbyne complex.}
\]

The characterisation of 2 included an X-ray crystallographic study, the results of which are summarised in Figure 1. The geometry about rhodium is pseudo-octahedral and is comparable to that found in similar Rh(III) complexes.5,10 The sterically demanding Cp* ligand is oriented away from the tungsten centre so as to minimise repulsive inter-ligand interactions. The W1–C1 (1.824(4) Å) and C1–P1 (1.798(4) Å) distances are unchanged from those of 1 (1.827(2), 1.783(3) Å), but the W1–C1–P1 angle in 2 approaches linearity (175.8(2)°), whereas the equivalent angle in 1 is slightly bent (166.6(2)°).

The possibility of coordination of a third metal to the W=C bond was explored in the reaction of 1 with one equivalent of \([\text{Rh}_2(\text{μ}-\text{Cl})_2\text{Cl}_2(\text{Cp}^*)]_2\) (Scheme 2). Although the reactions of carbyne complexes with the rhodium(II) species \([\text{Rh}_2(\text{μ}-\text{CO})_2(\text{Cp}^*)]_2\) have been described,5b,f,m,11 the reactions of carbyne complexes with trivalent rhodium reagents have not. Stirring a solution of 1 with one equivalent of \([\text{Rh}_2(\text{μ}-\text{Cl})_{2}\text{Cl}_2(\text{Cp}^*)]_2\) at room temperature for three days yielded only the bimetallic species 2. Subsequent heating at 110°C resulted in numerous IR bands in the carbonyl region. The $^{31}$P($^1$H) NMR spectrum showed that a number of phosphorus-containing species were present in the reaction mixture, but none of these peaks displayed $^{103}$Rh coupling. It was thus concluded that the trimetallic species \([W(\text{η}_2\text{-C}(\text{RhCl}_2\text{Cp}^*)\text{PPh}_2\text{RhCl}_2\text{Cp}^*)]\text{(CO)}_2(Tp}^*)\) does not form, which is perhaps not surprising given the demanding steric requirements of these species.

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\[
\text{Scheme 2. Reaction of 1 with } [\text{RhCl}_2(\text{Cp}^*)]_2.
\]
[M(≡CP(AuCl)2(C(NMe2)2))(CO)2(Tp*)] (Scheme 4). Intriguingly, in the case of the arsenic analogues, [AuCl(Te)] instead effects carbene abstraction, and subsequent trimerisation of the resultant arsephide M(CAs)(CO)2(Tp*) fragment gives the fascinating cyclic triarsane structure cyclo-As3[(CO)3(Tp*)].

Upon treatment of 1 with one equivalent of [AuCl(SMe2)], infrared monitoring of the red THF solution showed replacement of the starting material (νCO 1981, 1893 cm\(^{-1}\)) by new bands to higher frequency (2002, 1917 cm\(^{-1}\)). Both the shift in frequency and the intensity profile of the two absorptions were similar to those observed for the formation of 2. Filtration through diatomaceous earth provided [W(≡CPhAuCl)(CO)2(Tp*)] (3) as a red solid in 81% yield (Scheme 5). The \(^{31}\)P\(^1\)H NMR spectrum of 3 comprises a singlet with \(^{183}\)W satellites at δ\(_P\) 37.5, with a \(^{139}\)W value of 139.3 Hz similar to that seen for 2. The carbyne resonance is observed as a doublet accompanied by \(^{183}\)W satellites at δ\(_W\) 263.3 (\(^{139}\)W, \(^{199}\)W = 22.1, \(^{199}\)W = 199.9 Hz).

![Scheme 4. Weber’s reactions of phospha-alkene- and arsa-alkene-substituted carbynes with [AuCl(TO)] (M = Mo, W).](image)

Treatment of complex 1 with an excess (three equivalents) of [AuCl(SMe2)] led to new νCO absorptions at 2222 and 1944 cm\(^{-1}\), attributable to the trimetallic complex [W(η\(^5\)-C(AuCl)PPh₂AuCl)(CO)₂(Tp*)] (4), resulting from AuCl addition across the W=C triple bond (Scheme 5). Complex 4 also forms from addition of [AuCl(SMe₂)] to the pre-isolated mono-aurated species 3. Notably, while studying the reactivity of 1 towards [AuCl(SMe₂)] no evidence for formation of [W(η\(^5\)-C(AuCl)PPh₂)(CO)₂(Tp*)] was obtained, demonstrating that the phosphine, rather than the W≡C bond, is the preferred donor. The ESI(+) mass spectrum (MeCN) clearly demonstrated the presence of two AuCl moieties. A shift of the carbonyl absorptions to higher frequency is observed for 4 compared to that of 3, reflecting the expected decrease in electron density at tungsten that accompanies complexation of AuCl to the carbyne. The intensity profile of the νCO absorption bands suggests an opening of the intercarbonyl angle relative to 3, consistent with what is observed in the solid-state structure. Complex 4 is manifest in the \(^{31}\)P\(^1\)H NMR spectrum as a singlet that displays \(^{183}\)W satellites at δ\(_W\) 53.6, with \(^{139}\)W 84.3 Hz being significantly smaller than that observed for 3 (\(^{139}\)W = 139.3 Hz), in accordance with the decreased s-character along the W–C–P spine. In the \(^{13}\)C\(^1\)H NMR spectrum the carbyne resonance is shifted to lower frequency (δ\(_C\) 253.6). The modification of the carbyne moiety is evident in the significant decrease of both the phosphorus-carbon and tungsten-carbon coupling constants (\(^{139}\)W = 1.5, \(^{199}\)W = 99.6 Hz), reflecting the higher degree of substitution along the W–C–P spine. The magnitude of the tungsten-carbon coupling is half that typically seen in carbyne complexes (e.g. 3 \(^{139}\)W = 199.9 Hz).

![Figure 2. Molecular structure of 3 (50% displacement ellipsoids, hydrogen atoms omitted).](image)

An X-ray crystallographic study of 3 corroborated the ligation of AuCl to the phosphine (Figure 2). The W1–C1 bond length of 1.821(4) Å is consistent with a W=C triple bond, while the C1–P1 bond length of 1.783(4) Å is crystallographically identical to that of the precursor 1 (1.783(3) Å) and that observed in Weber’s diaur compound [W(≡CP(AuCl)2(C(NMe2)2))(CO)2(Tp*)] (1.782(11) Å). The Au1–P1 distance of 2.223(1) Å is consistent with a Au–P single (dative) bond and is slightly shorter than those observed in Weber’s compound of 2.250(3) Å. The P1–Au1–C1 angle approaches linearity (177.17(5)°), which is in contrast to the P–Au–Cl angles observed in Weber’s more sterically congested complexes of 168.06(11) and 169.61(11)°.

![Scheme 5. Reaction of 1 with [AuCl(SMe2)].](image)
Stone has observed semi-bridging carbynes, such as [Au[W(µ-CTol)(CO)]_2(η^5-C_5B_5H_5Me_2)](PPh_3)], in which the toluylidyne moiety asymmetrically bridges the tungsten-gold bond (W−C 1.88(3), Au−C 2.19(3) Å). Although the disparity in 4 is not as pronounced as in Stone’s example, the carbyne ligand is asymmetrically disposed along the W−Au bond (W1−C1 1.897(4), W1−Au2 1.907(10) Å). Coordination of AuCl to the W≡C bond would appear to reduce the usually strong trans influence of the carbyne ligand such that the three W−N bonds are of comparable lengths (2.208(4), 2.189(4), 2.207(4) Å).

The ability of 3 to react with a second equivalent of AuCl at the W≡C bond was surprising as we have previously found that quaternization of the phosphorus centre of 1 deactivate the W≡C bond such that further electrophilic addition is disfavored. This is exemplified by the reaction of 1 with sulfur, wherein, although minor quantities of the thioacyl complex [W(η^5-SCPPh_2)(CO)]_2(Tp*)] are generated, the major product [W(η^5-SCPPh_2)(SMe_2)(CO)]_2(Tp*) does not react further with sulfur. We were thus curious to investigate this contrast in reactivity.

Combination of 3 with sulfur yielded no reaction, even after extended reaction times (six days) (Scheme 6). This implies that, as in the case of [W(η^5-SCPPh_2)(CO)]_2(Tp*)], ligation of the phosphorus moiety deactivates the W≡C bond towards electrophilic addition, which is in contrast to the formation of the diaurated complex 4. The reaction was repeated with reversal of the order of addition of reagents. Treatment of [W(η^5-SCPPh_2)(CO)]_2(Tp*) with 1.5 equivalents of [AuCl(SMe_2)] yielded [W(η^5-C-AuCl)(η^5-SCPPh_2)(CO)]_2(Tp*) (5), which was obtained as an orange powder in 57% yield (Scheme 6).

The ^31P(^1H) NMR spectrum of 5 comprises a broad singlet at δ^p 52.3 with no discernible ^181W satellites. Broad peaks are also seen in the ^13C(^1H) NMR spectrum for the carbyne, carbonyl and Cl−phenyl peaks. This broadening in the NMR spectra is not due to dissociation of the AuCl moiety, since in a ^31P(^1H) NMR spectrum containing both [W(η^5-SCPPh_2)(CO)]_2(Tp*)] and 5, the resonance for [W(η^5-SCPPh_2)(CO)]_2(Tp*)] is a sharp singlet with visible tungsten coupling, whereas the resonance for 5 is a broad singlet. If the AuCl group were dissociating on the NMR timescale one would expect to observe broadening of both peaks. Hence this is most likely due to a non-dissociative intramolecular process, e.g., restricted rotation about the P−C bond, although this was not apparent in the NMR spectra for 4.

The carbyne resonance is observed at δ_C 262.4, intermediate between [W(η^5-SCPPh_2)(CO)]_2(Tp*)] (δ_C 270.1) and 4 (δ_C 253.6). No coupling to either tungsten or phosphorus was observable due to the broad nature of the peak, although the analogous ^1J_{PC} coupling in 4 is only 1.5 Hz, i.e., the absence of discernable coupling may simply reflect its small magnitude. The ^1H and ^13C(^1H) NMR spectra display the typical 2:1 ratio of Tp* peaks, consistent with a time-averaged mirror plane through the W(η^5-C-AuCl)(P=S)(5) functionality.

Crystallographic grade crystals of 5 were obtained from chloroform/hexane and the results of a crystallographic study are presented in Figure 4. The geometry about the metallacyclop propane ring is similar to that seen in 4. As expected, the W1−C1 bond length (1.907(10) Å) is significantly elongated compared to that of [W(η^5-SCPPh_2)(CO)]_2(Tp*)] (1.829(4) Å). A slight shortening of the P1−S1 bond is observed compared to [W(η^5-SCPPh_2)(CO)]_2(Tp*)] (1.992(5) Å cf. 1.9568(16) Å), attributable to the higher degree of stibution along the W−C−P spine. As is inferred from the NMR spectra, an approximate (non-crystallographic) mirror plane is present through W(η^5-C-AuCl)(P=S), bisecting the W(CO)_2 PPh_2 and Tp* moieties. A slight bending out of this mirror plane is seen for the phosphine sulfide, with a W1−C1−P1−S1 torsion angle of 8.43° that is most likely a response to packing effects.

**Scheme 6. Synthesis of [W(η^5-C-AuCl)(P=S)Ph_2](CO)]_2(Tp*)] (5) (L = SMe_2)
The formation of 5 demonstrates that, although the nucleophilicity of the WeC bond decreases upon quantemisation of the phosphorus centre, with an appropriate choice of reagent at this site can still occur. This offers the possibility of targeted reactivity at the WeC bond through the use of a protecting group to inhibit reactivity at the phosphine, such as the borane adduct [W(≡CCPPh₂BH₃)](CO)₅(Tp*)₃. The nucleophilic competition between phosphine and carbyne sites demonstrated by 1 begins the question of whether such chemistry could be extended to the bimetallic complex 6. Based on the success enjoyed with 1, the reagent [AuCl(SMe₂)] was chosen as the electrophile of interest because it displayed the most controllable reactivity towards 1, wherein mono- or bis-addition of AuCl could be effected through stoichiometric control.

When a dichloromethane solution of 6 was treated with one equivalent of [AuCl(SMe₂)] a mixture of products was obtained (Scheme 7). The ³¹P(¹H) NMR spectrum contained three resonances with ¹³W satellites at δₚ 49.4 (JₚWP 143.7, 62%), 63.1 (JₚWP 118.7, 25%) and 75.7 (JₚWP 88.8 Hz, 3%). Addition of a second equivalent of [AuCl(SMe₂)] altered the proportions of these three peaks to 16%, 46% and 34%, respectively. Addition of a third [AuCl(SMe₂)] equivalent gave exclusively δₚ 75.7. The parallel variability in product distribution and amount of [AuCl(SMe₂)] added suggested that these three species correspond to differing nuclearities.

Treatment of 6 with 1.1 equivalents of [AuCl(SMe₂)] followed by chromatography allowed isolation of the complex which corresponded to δₚ 49.4 in 24% yield, which was found to be the product of P-coordination, i.e., [W₂(µ-

C₅PPhAuCl)(CO)₅(Tp*)₂] (7). The ³¹P(¹H) NMR spectrum of 7 comprises a singlet resonance at δₚ 49.4 with JₚWP 143.7 Hz, shifted 30 ppm to higher frequency from that of the precursor 6. In contrast to this, the monometallic complex 1 shifts 5 ppm downfield upon P-complexation of AuCl to give [W(≡CCPPh₂AuCl)(CO)₅(Tp*)] (3; δₚ 32.0 cf. 37.5). However, similar coupling constants are seen for 7 (JₚWP 143.7) and 3 (JₚWP 139.3 Hz), illustrating the recurrent theme throughout this work that the coupling constants are more diagnostic than the chemical shifts.
The molecular structure of 8 shown in Figure 6, reveals a Au···Au interaction between the two carbyne-bound gold moieties. The Au1···Au2 distance of 3.0318(8) Å falls within the typical range for aurophilic bonding (2.8 – 3.3 Å),22 and well within the sum of the van der Waals radii (3.32 Å). The geometric features of 8 mirror those observed in the monotungsten complex 4, and related complexes.54,12a-c,18 As has been seen previously,34 the carbyne ligands bridge the W–Au linkages unsymmetrically (W1–C1 1.874(15), W2–C4 1.884(14), C1–Au1 2.038(17), C4–Au2 2.020(15) Å), consistent with retained W–C multiple bonding. The two C–Au–Cl angles are significantly different, with C4–Au2–Cl2 being almost linear (174.8(4)°) while C1–Au1–Cl1 is considerably distorted from linearity (164.6(4)°). For both Cl1 and Cl2, interactions exist with neighbouring dimethylpyrazolyl groups, and Cl1 also interacts with the CH3Cl solvent molecule. The cumulative effect of these intermolecular interactions may be the observed distortion of the C1–Au1–Cl1 angle.

Unfortunately, attempts to isolate complex 9 (δp 63.1), provided material contaminated with considerable quantities of 7 and 8. However, only the symmetrical formulation depicted in Scheme 7 is consistent with the spectroscopic data (Table 1) which indicate chemically equivalent tungsten centres. In the 31P(1)H NMR spectrum, resonance is straddled by only a single pair of satellites (νJWP = 118.7 Hz).

<table>
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<th>Complex</th>
<th>δP (ppm)</th>
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<td>63.1</td>
<td>118.7</td>
<td>2004, 1916</td>
</tr>
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</table>

NMR spectra were recorded in CDCl₃. IR spectra were recorded in CHCl₃.

*Postulated formula. Tentative assignment as the spectrum also contains bands due to 7 and 8.

Based on the 31P(1)H NMR spectra, scrambling of the three species does occur to a small extent. A mixture containing 16% 7, 36% 8 and 48% 9 was found to contain the three species in 23%, 37% and 40%, respectively, after 22 hours in CDCl₃ at room temperature. The inability to obtain a clean sample of 9 is thus likely hampered by the conversion of 9 to 7 and 8 over time.

For the stepwise conversion of 6 to 8 via 7 and 9, the most likely rationale is that complexation of AuCl to W≡C decreases the nucleophilicity of the phosphorus such that dissociation (or migration) of the P-coordinated AuCl occurs. In the free phosphine 6, the phosphorus is clearly the most nucleophilic site as established by the formation of the 1:1 adduct 7 in which AuCl is bound to phosphorus. Coordination of a second AuCl to one W≡C bond electronically reduces the nucleophilicity of the phosphorus, as well as introducing a degree of proximal steric congestion, which is relieved when the AuCl original complexation is reversed in the phosphine 7. This is rationalized by the conversion of 6 to 7, which in turn leads to the second W≡C bond. The observation of an aurophilic interaction in the tris-AuCl adduct 8 implicates a similar interaction operating in the symmetrical W₂Au₂ adduct 9. Aurophilic interactions have been suggested to span the range 25 – 50 kJ mol⁻¹ and accordingly could be expected to play a role here. Finally, addition of the third AuCl group to the revealed phosphine can occur to yield 8.

In the mononuclear complex 1, electroophilic addition to the phosphine was found to decrease the nucleophilicity of the W≡C bond. It appears that in 6 the nucleophilicities of the three competing sites are also interdependent, wherein complexation to one site alters the nucleophilicity of the other two sites, but in a more complex manner than in 1, potentially due to the additional driving force of aurophilic interactions.

**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°C on Varian Mercury 300 (1H at 300.1 MHz, 13C at 75.47 MHz, 31P at 121.5 MHz), Varian Inova 300 (1H at 299.9 MHz, 13C at 75.42 MHz, 31P at 121.4 MHz), Varian MR 400 (1H at 399.9 MHz, 13C at 100.5 MHz, 31P at 161.9 MHz), Bruker Avance 400 (1H at 400.1 MHz, 31P at 162.0 MHz), Varian Inova 500 (1H at 500.0 MHz, 13C at 125.7 MHz), Bruker Avance 600 (1H at 600.0 MHz, 13C at 150.9 MHz) or Bruker Avance 800 (1H at 800.1 MHz, 13C at 201.2 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (H, 13C) or external 85% H3PO4 (31P) with coupling constants given in Hz. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of 138W satellites. Whilst 13C(N) signals for carbon nuclei of PPh groups could be routinely observed, their narrow spectral range and comparable J values often precluded unequivocal assignment, in which case they are designated as 'C2,3,5,6(PPh)'. In some cases, distinct peaks were observed in the 1H and 13C(H) NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for 1H NMR, 1 decimal place for 13C NMR) they are reported as having the same chemical shift. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental microanalytical data were obtained from the ANU Research School of Chemistry microanalytical service. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetoniitrile as the matrix. Data for X-ray crystallography were collected with a Nonius kappa CCD or Agilent Xcalibur diffractometer. The compounds [W{(C≡CPPh)(CO)2}(Tp*)] (1),a [W{(μ-C5PhCH)(CO)(Tp*)(η2-Rh)}]10 [Rh2{(μ-Cl)(Cp)()}2] (Δ=29.3 °C, 2H, pZCH, 2.38 (s, 3, H, pZCH), 2.36 (s, 3, H, pZCH), 2.31 (s, 3, H, pZCH), 2.24 (s, 6, H, pZCH), 13C NMR (CDCl3) δ/ppm: 7.81 – 7.73 (m, 4, H, CpH3), 7.48 – 7.43 (m, 6, H, CpH3), 5.90 (s, 2, H, pZH), 5.77 (s, 1, H, pZH), 2.38 (s, 6, H, pZCH), 2.36 (s, 3, H, pZCH), 2.31 (s, 3, H, pZCH), 2.24 (s, 6, H, pZCH), 13C NMR (CDCl3) δ/ppm: 263.3 (s, 2, WC, 1J_C=W = 22.1, 1J_W=C = 199.9, 223.6 (d, 2, CO, 1J_C=2 = 2.8, 1J_W=C = 163.4), 152.7 (1C), 151.8 (2C), 145.9 (1C), 145.2 (2C) [13C(pz)], 133.7 [d, 13C(η5=Cp), J_C=13.8], 131.4 [d, 13C(η5=Cp), 1J_C=20.0], 129.7 (d, 13C(η5=Cp), J_C=64.3), 129.0 [d, 13C(η5=Cp), J_C=12.4], 107.3 (1C), 106.9 (2C) [13C(pz)], 16.9 (2C), 15.2 (1C), 12.7 (3C, coincident) (pzCH3). 31P(1H) NMR (CDCl3) δ/ppm: 37.5 (t, 1J_C=W = 139.3), MS-ESI(+): m/z 899.6 [M + Na]+, 911.6 [M = 2CO + H]+, 707.7 [M = 2CO + Au + Na]+, 679.8 [M = 2CO + Au + H]+. Accurate mass: found 991.1151 [M + Na]+. Calcd. for CsH32Au13I8Cl18N10O13P4X4: 991.1149. Anal. found: C, 37.24; H, 3.30; N, 8.42%. Calcd. for CsH32Au2BCl2O7PCW: C, 37.28; H, 3.34; N, 8.69%. Calcd. for CsH32Au3BCl2O7PCW: Mw = 968.66, monolonic, P21/a, a = 10.3172(1) Å, b = 13.5659(2) Å, c = 25.2059(3) Å, β = 86.3935(9), V = 3490.02(7) Å3, Z = 4, ρ_calc = 1.840 Mg m−3, μ(Mo Kα) = 3.08 mm−1, T = 200(2) K, red block, 0.27 × 0.20 × 0.14 mm, 14324 independent reflections. F2 refinement, R = 0.030, wR = 0.067 for 8112 reflections (I > 2σ(I), 2θmax = 60°), 388 parameters, CCD 995724.

Synthesis of [W{(C≡CPPh)(AuCl)(CO)}2(Tp*)] (3). A mixture of [W{(C≡CPPh)(AuCl)(CO)}2(Tp*)] (0.352 g, 0.478 mmol) and [AuCl(SMe)2] (0.143 g, 0.485 mmol) was dissolved in THF (15 mL) resulting in a red solution. The solution was stirred for 18 hours and a small amount of gold precipitate was observed. The solution was filtered through diatomaceous earth and the volatiles were removed in vacuo to afford the product as a red powder. Crystals suitable for crystallographic analysis were obtained by slow diffusion of EtOH into a solution of 3 in CH2Cl2. Yield 0.374 g (0.387 mmol, 81%). IR (Nujol) ν/cm−1: 2552 W (BH), 2001 s, 1907 s (CO). IR (CHCl3) ν/cm−1: 2556 W (BH), 2003 vs, 1916 vs (CO). IR (THF) ν/cm−1: 2553 W (BH), 2002 vs, 1917 vs (CO). 1H NMR (CDCl3) δ/ppm: 7.81 – 7.73 (m, 4, H, CpH3), 7.48 – 7.43 (m, 6, H, CpH3), 5.90 (s, 2, H, pZH), 5.77 (s, 1, H, pZH), 2.38 (s, 6, H, pZCH), 2.36 (s, 3, H, pZCH), 2.31 (s, 3, H, pZCH), 2.24 (s, 6, H, pZCH), 13C NMR (CDCl3) δ/ppm: 263.3 (s, 2, WC, 1J_C=W = 22.1, 1J_W=C = 199.9, 223.6 (d, 2, CO, 1J_C=2 = 2.8, 1J_W=C = 163.4), 152.7 (1C), 151.8 (2C), 145.9 (1C), 145.2 (2C) [13C(pz)], 133.7 [d, 13C(η5=Cp), J_C=13.8], 131.4 [d, 13C(η5=Cp), 1J_C=20.0], 129.7 (d, 13C(η5=Cp), J_C=64.3), 129.0 [d, 13C(η5=Cp), J_C=12.4], 107.3 (1C), 106.9 (2C) [13C(pz)], 16.9 (2C), 15.2 (1C), 12.7 (3C, coincident) (pzCH3). 31P(1H) NMR (CDCl3) δ/ppm: 37.5 (t, 1J_C=W = 139.3), MS-ESI(+): m/z 899.6 [M + Na]+, 911.6 [M = 2CO + H]+, 707.7 [M = 2CO + Au + Na]+, 679.8 [M = 2CO + Au + H]+. Accurate mass: found 991.1151 [M + Na]+. Calcd. for C72H23Au13I8Cl18N10O13P4X4: 991.1149. Anal. found: C, 37.24; H, 3.30; N, 8.42%. Calcd. for C72H23Au2BCl2O7PCW: C, 37.28; H, 3.34; N, 8.69%. Crystals suitable for crystallographic analysis were obtained by slow diffusion of EtOH into a solution of 4 in CH2Cl2. Yield 0.240 g (0.200 mmol, 55%). IR (Nujol) ν/cm−1: 2563 W (BH), 2022 vs,
1936 vs (CO). IR (THF) ν/cm⁻¹: 2562 w (BH), 2022 vs, 1944 vs (CO). 1H NMR (CDCl3) δ/ppm: 8.09 – 8.02 (m, 4 H, C6H4), 7.61 – 7.49 (m, 6 H, C6H5), 5.96 (s, 1 H, pzH), 5.93 (s, 2 H, pzH), 5.20 (s, 3 H, pZCH3), 2.36 (s, 6 H, pZCH3), 2.32 (s, 3 H, pzCH3), 2.25 (s, 6 H, pzCH3). 13C[1]H NMR (CDCl3) δ/ppm: 253.6 (d, WJc = 1.5, δJWC = 99.6), 216.6 (d, CO, δJWC = 7.8, δJWC = 154.2), 154.4 (1 C), 152.5 (2 C), 146.9 (1 C), 146.4 (2 C) [C5(pz)], 134.4 [d, C,3,5,6(C6H5), JC = 13.6], 132.5 [d, C,3(C6H5), JC = 3.0], 129.5 [d, C,3,5,6(C6H5), JC = 12.1], 129.4 [d, C,3(C6H5), JC = 61.9], 109.1 (1 C), 108.2 (2 C) [C5(pz)], 17.4 (2 C), 16.0 (1 C), 13.2 (1 C), 12.7 (2 C) [pzCH3]. 31P[31]H NMR (CDCl3) δ/ppm: 53.6 (δJWP = 84.3). MS-ESI(+) m/z: 220.8 [M + Na]+, 1162.7 [M – Cl]⁺. Accurate mass: found 1212.0532 [M + Na]+. Calculated for C60H33Au11β3Cl5N12O14P5W18: 1212.0533. Anal. found: C, 30.11; H, 2.88; N, 7.04%. Calculated for C60H33Au11β3Cl5N12O14P5W18: C, 30.05; H, 2.69; N, 7.01%.

After six hours of stirring the IR showed almost complete disappearance of starting material and the formation of a compound was observed which was removed under reduced pressure. The residue was chromatographed on silica gel using CH2Cl2 as the eluent. A small initial gray band and yellow band were collected and discarded, and the first orange band (containing the product) was collected. The solvent was removed on the rotary evaporator to afford 7 as a red solid. The remaining two red-orange bands were found to contain a mixture of 7, 8 and 9. Crystals suitable for crystallographic analysis were grown from a solution of 7 in Et2O at –20°C. Yield 0.014 g (0.010 mmol, 24%). IR (Nujol) ν/cm⁻¹: 2553 w (BH), 2000 sh, 1995 s, 1911 s (CO). IR (THF) ν/cm⁻¹: 2553 vw (BH), 1996 s, 1914 vs (CO). 1H NMR (CDCl3) δ/ppm: 8.02 (m, 2 H, C6H5), 7.48 (m, 3 H, C6H5), 5.74 (s, 4 H, pZH2), 5.74 (s, 2 H, pzH), 2.37 (s, 18 H, pZCH3), 2.35 (s, 6 H, pZCH3), 2.34 (s, 6 H, pZCH3), 2.29 (s, 6 H, pZCH3). 13C[31]H NMR (CDCl3) δ/ppm: 262.5 (d, WJC = 25.9, δJWC = 203.2), 225.1 (CO, δJWC = 164.0), 223.7 (CO, δJWC = 164.3), 152.6 (2 C), 152.5 (2 C), 152.2 (2 C), 145.6 (2 C), 144.7 (2 C), 144.7 (2 C) [C5(pz)], 134.4 [d, C,3,5,6(C6H5), JC = 14.6], 131.1 [d, C(C6H5), JC = 65.3], 128.8 [d, C,3,5,6(C6H5), JC = 12.5], 107.1 (2 C), 106.7 (2 C), 106.6 (2 C) [C5(pz)], 17.5 (4 C), 15.2 (12 C), 12.7 (6 C) [pzCH3]. 31P[1]H NMR (CDCl3) δ/ppm: 49.4 (δJWP = 143.7). MS-ESI(+) m/z: 1479.3 [M + MeCN]+, 1460.2 [M + Na – H]+, 1439.2 [M + H]+. Accurate mass: found 1463.2169 [M + Na]+. Calculated for C60H33Au11β3Cl5N12O14P5W18: 1463.2156. Found 1461.2184 [M + Na]+. Calculated for C60H33Au11β3Cl5N12O14P5W18: C, 35.07; H, 3.43; N, 11.68%. Crystallized from CH2Cl2/MeCN.

Synthesis of [W(μ-μ3-CpPPhAu(μ-AuBCl)(CO))(CpTp*)](7). A solution of [W(μ-μ3-CpPPh)(CO)(CpTp*)] (0.050 g, 0.041 mmol) and [AuCl(SMe2)] (0.013 g, 0.044 mmol) in CH2Cl2 (3 mL) was stirred at room temperature for 30 minutes. The volatiles were removed under reduced pressure. The residue was chromatographed on silica gel using CH2Cl2 as the eluent. A small initial grey band and yellow band were collected and discarded, and the first orange band (containing the product) was collected. The solvent was removed on the rotary evaporator to afford 7 as a red solid. The remaining two red-orange bands contained a mixture of 7, 8 and 9. Crystals suitable for crystallographic analysis were grown from a solution of 7 in Et2O at –20°C. Yield 0.014 g (0.010 mmol, 24%). IR (Nujol) ν/cm⁻¹: 2553 w (BH), 2000 sh, 1995 s, 1911 s (CO). IR (THF) ν/cm⁻¹: 2553 vw (BH), 1996 s, 1914 vs (CO). 1H NMR (CDCl3) δ/ppm: 8.02 (m, 2 H, C6H5), 7.48 (m, 3 H, C6H5), 5.74 (s, 4 H, pZH2), 5.74 (s, 2 H, pzH), 2.35 (s, 6 H, pZCH3), 2.34 (s, 6 H, pZCH3), 2.29 (s, 6 H, pZCH3). 13C[31]H NMR (CDCl3) δ/ppm: 262.5 (d, WJC = 25.9, δJWC = 203.2), 225.1 (CO, δJWC = 164.0), 223.7 (CO, δJWC = 164.3), 152.6 (2 C), 152.5 (2 C), 152.2 (2 C), 145.6 (2 C), 144.7 (2 C), 144.7 (2 C) [C5(pz)], 134.4 [d, C,3,5,6(C6H5), JC = 14.6], 131.1 [d, C(C6H5), JC = 65.3], 128.8 [d, C,3,5,6(C6H5), JC = 12.5], 107.1 (2 C), 106.7 (2 C), 106.6 (2 C) [C5(pz)], 17.5 (4 C), 15.2 (12 C), 12.7 (6 C) [pzCH3]. 31P[1]H NMR (CDCl3) δ/ppm: 49.4 (δJWP = 143.7). MS-ESI(+) m/z: 1479.3 [M + MeCN]+, 1460.2 [M + Na – H]+, 1439.2 [M + H]+. Accurate mass: found 1463.2169 [M + Na]+. Calculated for C60H33Au11β3Cl5N12O14P5W18: 1463.2156. Found 1461.2184 [M + Na]+. Calculated for C60H33Au11β3Cl5N12O14P5W18: C, 35.07; H, 3.43; N, 11.68%. Crystallized from CH2Cl2/MeCN.

Synthesis of [W(μ-μ3-CpPPhAu(μ-AuBCl)(CO))(CpTp*)](8). A solution of [W(μ-μ3-CpPPh)(CO)(Cp(Tp*)]) (0.020 g, 0.017 mmol) and [AuCl(SMe2)] (0.015 g, 0.041 mmol) and [AuCl(SMe2)] (0.013 g, 0.044 mmol) in CH2Cl2 (3 mL) was stirred at room temperature for 20 minutes. The volatiles were decanted into a round bottom flask to which hexane (ca. 1 mL) was added and volatiles removed on the rotary evaporator to afford 8 as a pink powder. Crystals suitable for crystallographic analysis were grown from a solution of 8 in CH2Cl2 layered with
hexane. Yield 0.031 g (0.016 mmol, 96%). IR (Nujol) ν/cm⁻¹: 2560 w (BH), 2024 s, 1943 s, br, 1914 sh (CO). IR (THF) ν/cm⁻¹: 2060 vw (BH), 2026 s, 1948 vs (CO). ¹H NMR (CDCl₃) δ/ppm: 8.60 (m, 2 H, CH₃), 7.60 (m, 1 H, CH₃), 7.57 (m, 2 H, CH₃), 5.99 (s, 2 H, pHz), 5.94 (s, 2 H, pHz), 5.89 (s, 2 H, pHz), 2.76 (s, 6 H, pCH₃), 2.45 (s, 6 H, pCH₃), 2.38 (s, 6 H, pCH₃), 2.36 (s, 6 H, pCH₃), 2.32 (s, 6 H, pCH₃). ¹³C(¹H) NMR (CDCl₃) δ/ppm: 252.0 (WC, 1J_C=H = 99.9), 217.5 (d, CO, 1J_C=H = 8.1, 1J_C=O = 153.4), 216.2 (d, CO, 1J_C=O = 8.1, 1J_C=O = 153.4), 154.3 (2 C), 153.5 (2 C), 152.9 (2 C), 146.8 (2 C), 146.3 (2 C), 146.2 (2 C) [C=O(pz)], 136.7 [d, br, C₃,5,6(C₆H₅)], J₁C = 15.4), 133.1 [C(C₆H₅)], 129.1 [d, C₃,5,6(C₆H₅)], J₁C = 12.4), 129.0 [d, C(C₆H₅)], J₂C = 59.3), 109.0 (2 C), 108.1 (2 C), 108.0 (2 C) [C=O(pz)], 19.4 (2 C), 17.9 (2 C), 16.0 (2 C), 13.2 (2 C), 12.8 (2 C), 12.7 (2 C) [pCH₃). ³¹P(¹H) NMR (CDCl₃) δ/ppm: 75.7 (1/2J₁P= 88.8). MS-ESI(+) : m/z 1943.1 (M + K⁺), 1927.1 (M + Na⁺). Accurate mass: found 1929.0847 [M + Na⁺]. Calcd. for C₉₂H₆Au₂₁B₃₅Cl₇₂N₂₂Na₂O₈P₁₄W₁₂: 1929.0844. Found 1927.8075 [M + Na⁺].

Acknowledgements
This work was supported by the Australian Research Council (DP110101611 and DP130102598).

Notes and references


8. These [W(CP)(CO)₂(CO)₂] systems exhibit 1/2J₁P= values of 64.5 – 82.5 Hz for three-coordinate phosphorus (x = 2) or 122.0 – 161.6 Hz in the case of four-coordinate phosphorus (x = 3).²⁴,²⁵

whereas a sample of [AuCl(THT)] was on hand. [AuCl(THT)] (THT = tetrahydrothiophene) was used because A.
A. K. Synth. C. H. in the mass spectra of interpretation is disfavoured by scrambling of AuCl
Neumann, Schneider, Schmidbaur, (a) J. C. Jeffery, P. A. Jelliss and F. G. A. Stone, Organometallics
15 Addition to the W≡C bond would result in an increased coordination number at tungsten, causing a variation in the intercarbonyl angle and thus also in the intensities of νs and νas.
21 Percentages quoted represent the % by 31P({H}) NMR spectroscopy integration and do not sum to 100% due to three other minor peaks present in the spectra.
23 The other possible explanation for this is scrambling of AuCl moieties under mass spectrometry conditions. This interpretation is disfavoured as such scrambling was not seen in the mass spectra of 7 and 8.
27 [AuCl(THT)] (THT = tetrahydrothiophene) was used because all of the [AuCl(SMe2)] sample was consumed in this reaction, whereas a sample of [AuCl(THT)] was on hand. Either reagent serves the same purpose.