Coordination Chemistry of Phosphinocarbynes: Phosphorus vs Carbyne Site Selectivity.

Annie L. Colebatch^a and Anthony F. Hill^a

The phosphinocarbyne complex $[W(\equiv CPh)(CO)_2(Tp^*)]$ (**1**; Tp^* = hydrotris(dimethylpyrazolyl)borate) coordinates transition metal fragments *via* the phosphine to form bimetallic species $[W(\equiv CPh)RhCl_2(Cp^*)](CO)_2(Tp^*)]$ (**2**) and $[W(\equiv CPh)AuCl](CO)_2(Tp^*)]$ (**3**). Appropriately tailored sterics allow for complexation of a second equivalent of AuCl to afford the trimetallic complex $[W\{\eta^2-C(AuCl)PPh_2AuCl\}(CO)_2(Tp^*)]$ (**4**), containing an Au–W–C dimetallacyclopentadiene connectivity. Similarly, AuCl binds to the carbyne linkage in $[W\{\eta^2-C(AuCl)P(=S)Ph_2\}(CO)_2(Tp^*)]$ (**5**). In the case of auration of the tungsten species $[W_2(\mu-C_2PPh)(CO)_4(Tp^*)_2]$ (**6**), variation in the stoichiometry leads to trimetallic $[W_2(\mu-C_2PPhAuCl)(CO)_4(Tp^*)_2]$ (**7**) and pentametallic $[W_2(\mu-(\eta^2-CAuCl)_2PPhAuCl)(CO)_4(Tp^*)_2]$ (**8**) complexes, via a proposed tetrametallic intermediate $[W_2(\mu-(\eta^2-CAuCl)_2PPh)(CO)_4(Tp^*)_2]$, 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 (dppf), which has been widely applied in many transition metal mediated catalytic processes.¹ In the case of dppf 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 $[M(\equiv CPr_2)(CO)_2(Tp^*)]$ ($M = Mo, W$; Tp^* = hydrotris(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 $[W(\equiv CPh)(CO)_2(Tp^*)]$ (**1**), as an elaborately-functionalized analogue 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 polymetallic 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 $[W_2(\mu-C_2PPh)(CO)_4(Tp^*)_2]$ (**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 $[M_2(\mu-Cl)_2Cl_2(Cp^*)_2]$ via halide bridge cleavage to form P-coordinated species, an example of which is shown in Scheme 1.⁶

Scheme 1. Illustrative coordination chemistry of the alkynylphosphine $Ph_2PC\equiv CPh$ ($M = Ir, Rh$)

These species can undergo subsequent reactions with *cis*- $[Pt(C_6F_5)_2(THF)_2]$, via displacement of the labile THF ligands, to give bimetallic species with bridging chloride ligands or via coordination of the alkyne.

Results and discussion

Inspired by the report of Forniés and Lalinde,⁶ we investigated the reaction of **1** with $[Rh_2(\mu-Cl)_2Cl_2(Cp^*)_2]$. Stirring a CH_2Cl_2 solution of **1** and half an equivalent of $[Rh_2(\mu-Cl)_2Cl_2(Cp^*)_2]$ resulted in a dark red solution, the IR spectrum of

^a Research School of Chemistry, Australian National University, Canberra, Australia ACT 2601. a.hill@anu.edu.au.

which included two ν_{CO} bands at 2008 and 1916 cm^{-1} (cf. 1982, 1891 cm^{-1} for **1**). After chromatographic purification the bimetallic species $[\text{W}\{\equiv\text{CPh}_2\text{RhCl}_2(\text{Cp}^*)\}(\text{CO})_2(\text{Tp}^*)]$ (**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 ν_{CO} to higher frequency with respect to the precursor **1**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows only a very slight downfield shift upon coordination of the phosphine to δ_{P} 37.0 (cf. δ_{P} 32.0 in **1**), with coupling to rhodium ($^1J_{\text{RhP}}$ 139.2 Hz) within the typical range.⁷ A dramatic increase in the W–P coupling constant is observed upon complexation ($^2J_{\text{WP}}$ 122.0 Hz cf. 69.0 Hz in **1**), consistent with the values observed for other λ^4 or λ^5 -P adducts $[\text{W}(\equiv\text{CPh}_2\text{E})(\text{CO})_2(\text{Tp}^*)]$ (E = BH₃, O, S, Se) with 4-coordinate phosphorus,⁸ and slightly smaller than the $^2J_{\text{WP}}$ values observed for tungsten phosphoniocarbynes $[\text{L}_n\text{W}(\equiv\text{CPR}_3)]^+$ (150 – 200 Hz).⁹

Scheme 2. Reaction of **1** with $[\text{RhCl}_2(\text{Cp}^*)]_2$

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.^{6,10} 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 $\text{W}\equiv\text{C}$ bond was explored in the reaction of **1** with one equivalent of $[\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{Cp}^*)_2]$ (Scheme 2). Although the reactions of carbyne complexes with the rhodium(I) species $[\text{Rh}_2(\mu\text{-CO})_2(\text{Cp}^*)_2]$ 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 $[\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{Cp}^*)_2]$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{W}\{\eta^2\text{-C}(\text{RhCl}_2\text{Cp}^*)\text{PPh}_2\text{RhCl}_2(\text{Cp}^*)\}(\text{CO})_2(\text{Tp}^*)]$ does not form, which is perhaps not surprising given the demanding steric requirements of these species.

Figure 1. Molecular structure of **2** in a crystal of $2\cdot(\text{CH}_2\text{Cl}_2)_2$ (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 fulfil these requirements. The literature hosts numerous reports documenting addition of gold(I) reagents to tungsten carbyne complexes of the form $[\text{W}(\equiv\text{CR})(\text{L})_n]$ in which the metal-carbon triple bond is the reactive site.^{5e,g,12} In these cases a W–C–Au 'metallacyclopentene' is formed, such as that seen in the reaction of $[\text{AuCl}(\text{PPh}_3)]/\text{TIPF}_6$ with a tungsten toluidyne, shown in Scheme 3.^{5g} In this case, mono-addition of the $[\text{Au}(\text{PPh}_3)]^+$ moiety occurred, but solution NMR studies showed that the complex redistributes into $[\text{Au}\{\text{W}(\equiv\text{CTol})(\text{CO})_2(\text{Cp})\}_2]\text{PF}_6$ and $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$. A particularly fascinating example of such chemistry is that of the tetrameric complex $[\text{W}(\text{CAu})(\text{CO})_2(\text{Tp}^*)]_4$, which forms a remarkable C_4Au_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

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

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

$[M\{\equiv C(P(AuCl)_2C(NMe_2)_2\}(CO)_2(Tp^*)\}]$ (Scheme 4).¹⁴ Intriguingly, in the case of the arsenic analogues, $[AuCl(CO)]$ instead effects carbene abstraction, and subsequent trimerisation of the resultant arsephide 'M(CAs)(CO)₂(Tp*)' fragment gives the fascinating cyclic triarsine structure *cyclo*-As₃[$\equiv CM(CO)_2(Tp^*)$]₃.

Scheme 4. Weber's reactions of phospho-alkene- and arsa-alkene-substituted carbynes with $[AuCl(CO)]$ ($M = Mo, W$).¹⁴

Upon treatment of **1** with one equivalent of $[AuCl(SMe_2)]$, infrared monitoring of the red THF solution showed replacement of the starting material (ν_{CO} 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**.¹⁵ Filtration through diatomaceous earth provided $[W(\equiv CPh_2AuCl)(CO)_2(Tp^*)]$ (**3**) as a red solid in 81% yield (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **3** comprises a singlet with ^{183}W satellites at δ_P 37.5, with a $^2J_{WP}$ 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_C 263.3 ($^1J_{PC}$ 22.1, $^1J_{WC}$ 199.9 Hz).

Scheme 5. Reaction of **1** with $[AuCl(SMe_2)]$

An X-ray crystallographic study of **3** corroborated ligation of AuCl to the phosphine (Figure 2). The W1–C1 bond length of 1.821(4) Å is consistent with a W $\equiv$ C triple bond,¹⁶ while the C1–P1 bond length of 1.773(4) Å is crystallographically identical to that of the precursor **1** (1.783(3) Å) and that observed in Weber's diauro compound $[W\{\equiv C(P(AuCl)_2C(NMe_2)_2\}(CO)_2(Tp^*)\}]$ (1.782(11) Å).¹⁴ The Au1–P1 distance of 2.223(1) Å is consistent with a Au–P single (dative) bond¹⁷ and is slightly shorter than those observed in Weber's compound of 2.250(3) Å. The P1–Au1–Cl1 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)°.

Figure 2. Molecular structure of **3** (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.821(4), C1–P1 1.773(4), P1–Au1 2.2234(10), Au1–Cl1 2.2724(13), W1–C1–P1 165.5(2), C1–P1–Au1 113.02(12), P1–Au1–Cl1 177.17(5).

Treatment of complex **1** with an excess (three equivalents) of $[AuCl(SMe_2)]$ led to new ν_{CO} absorptions at 2022 and 1944 cm^{-1} , attributable to the trimetallic complex $[W\{\eta^2-C(AuCl)PPh_2AuCl\}(CO)_2(Tp^*)\}]$ (**4**), resulting from AuCl addition across the W $\equiv$ C triple bond (Scheme 5). Complex **4** also forms from addition of $[AuCl(SMe_2)]$ to the pre-isolated mono-aurated species **3**. Notably, while studying the reactivity of **1** towards $[AuCl(SMe_2)]$ no evidence for formation of $[W\{\eta^2-C(AuCl)PPh_2\}(CO)_2(Tp^*)\}]$ was obtained, demonstrating that the phosphine, rather than the W $\equiv$ 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 ν_{CO} 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 $^{31}P\{^1H\}$ NMR spectrum as a singlet that displays ^{183}W satellites at δ_P 53.6, with $^2J_{WP}$ 84.3 Hz being significantly smaller than that observed for **3** ($^2J_{WP}$ 139.3 Hz), in accordance with the decreased s-character along the W–C–P spine. In the $^{13}C\{^1H\}$ 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 ($^1J_{PC}$ 1.5, $^1J_{WC}$ 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** $^1J_{WC}$ 199.9 Hz).

The formulation of complex **4** was confirmed by an X-ray crystallographic study (Figure 3). The geometry about the W1–Au2–C1 metallacycle is similar to that observed in related compounds.^{5d,12a-c,18} The W1–C1 bond length of 1.897(4) Å is significantly elongated compared to that in **3** (1.821(4) Å) and falls within the range of both WC double and triple bonds, consistent with a dimetallacyclopropene description.¹⁹

Figure 3. Molecular structure of **4** (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.897(4), W1–Au2 2.8011(3), C1–P1 1.802(4), C1–Au2 2.031(4), P1–Au1 2.2278(12), W1–N11 2.208(4), W1–N21 2.189(4), W1–N31 2.207(4), W1–C1–P1 145.1(3), C1–P1–Au1 110.50(15), C1–Au2–Cl2 167.42(14), W1–C1–Au2 90.90(18), C1–W1–Au2 46.47(13), P1–Au1–Cl1 175.66(6).

Stone has observed *semi-bridging* carbynes, such as $[\text{Au}\{\text{W}(\mu\text{-CTol})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)\}(\text{PPh}_3)]$, in which the toluidyne moiety asymmetrically bridges the tungsten-gold bond (W–C 1.88(3), Au–C 2.19(3) Å).^{5k} 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), Au2–C1 2.031(4) Å). Coordination of AuCl to the $\text{W}\equiv\text{C}$ bond would appear to reduce the usually strong *trans* influence of the carbyne ligand¹⁶ 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 $\text{W}\equiv\text{C}$ bond was intriguing as we have previously found that quarternization of the phosphorus centre of **1** deactivates the $\text{W}\equiv\text{C}$ bond such that further electrophilic addition is disfavored.^{3a} This is exemplified by the reaction of **1** with sulfur, wherein, although minor quantities of the thioacyl complex $[\text{W}(\eta^2\text{-SCPPH}_2)(\text{CO})_2(\text{Tp}^*)]$ are generated, the major product $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ 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 $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$, ligation of the phosphorus moiety deactivates the $\text{W}\equiv\text{C}$ 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 $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ with 1.5 equivalents of $[\text{AuCl}(\text{SMe}_2)]$ yielded $[\text{W}\{\eta^2\text{-C}(\text{AuCl})\text{P}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (**5**), which was obtained as an orange powder in 57% yield (Scheme 6).

Scheme 6. Synthesis of $[\text{W}\{\eta^2\text{-C}(\text{AuCl})\text{P}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (**5**) (L = SMe₂)

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** comprises a broad singlet at δ_{P} 52.3 with no discernible ^{183}W satellites. Broad peaks are also seen in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the carbyne, carbonyl and C^{1,4}-phenyl peaks. This broadening in the NMR spectra is not due to dissociation of the AuCl moiety, since in a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum containing both $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ and **5**, the resonance for $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ 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 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 $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (δ_{C} 270.1) and **4** (δ_{C} 253.6). No coupling to either tungsten or phosphorus was resolvable due to the broad nature of the peak, although the analogous $^1J_{\text{PC}}$ coupling in **4** is only 1.5 Hz, i.e., the absence of discernable coupling may simply reflect its small magnitude. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra display the typical 2:1 ratio of Tp^* peaks, consistent with a time-averaged mirror plane through the $\text{W}\{\eta^2\text{-C}(\text{AuCl})\text{P}(=\text{S})\}$ 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 metallacyclopropene 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 $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (1.829(4) Å). A slight lengthening of the P1–S1 bond is observed compared to $[\text{W}\{\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (1.992(5) cf. 1.9568(16) Å), attributable to the higher degree of substitution along the W–C–P spine. As is inferred from the NMR spectra, an approximate (non-crystallographic) mirror plane is present through $\text{W}\{\eta^2\text{-C}(\text{AuCl})\text{P}(=\text{S})\}$, bisecting the $\text{W}(\text{CO})_2$, 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.

Figure 4. Molecular structure of **5** (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.907(10), W1–Au1 2.7940(5), C1–P1 1.788(10), C1–Au1 2.043(10), P1–S1 1.992(5), W1–C1–P1 146.6(6), C1–P1–S1 113.3(3), C1–Au1–Cl1 166.8(3), W1–C1–Au1 90.0(4), C1–W1–Au1 47.0(3), W1–Au1–C1 43.0(3).

The formation of **5** demonstrates that, although the nucleophilicity of the $W\equiv C$ bond decreases upon quaternization of the phosphorus centre, with an appropriate choice of reagent reaction at this site can still occur. This offers the possibility of targeted reactivity at the $W\equiv C$ bond through the use of a protecting group to inhibit reactivity at the phosphine, such as the borane adduct $[W(\equiv CPh_2BH_3)(CO)_2(Tp^*)]$,^{3a} which might then be removed after addition of the desired electrophile to the $W\equiv C$ bond. The ability of both the phosphine and the carbyne sites of mononuclear phosphinocarbynes to ligate metal centres has thus provided access to a range of bi- and trimetallic complexes.

We have recently reported a bimetallic analogue of **1**, $[W_2(\mu-C_2PPh)(CO)_4(Tp^*)_2]$ (**6**).^{3b,20} However, so far the reactivity of this complex has been confined to its unusual thermal rearrangement to give an unprecedented phospho-acyl complex $[W_2(\mu:\eta^1-C;\eta^2-C,P-CCPPh)(CO)_4(Tp^*)_2]$.²⁰ The nucleophilic competition between phosphine and carbyne sites demonstrated by **1** begs the question of whether such chemistry could be extended to the bimetallic complex **6**. Based on the success enjoyed with **1**, the reagent $[AuCl(SMe_2)]$ 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 $[AuCl(SMe_2)]$ a mixture of products was obtained (Scheme 7). The $^{31}P\{^1H\}$ NMR spectrum contained three resonances with ^{183}W satellites at δ_P 49.4 ($^2J_{WP}$ 143.7, 62%), 63.1 ($^2J_{WP}$ 118.7, 25%) and 75.7 ($^2J_{WP}$ 88.8 Hz, 3%).²¹ Addition of a second equivalent of $[AuCl(SMe_2)]$ altered the proportions of these three peaks to 16%, 46% and 34%, respectively. Addition of a third $[AuCl(SMe_2)]$ equivalent gave exclusively δ_P 75.7. The parallel variability in product distribution and amount of $[AuCl(SMe_2)]$ added suggested that these three species correspond to differing nuclearities.

Treatment of **6** with 1.1 equivalents of $[AuCl(SMe_2)]$ followed by chromatography allowed isolation of the complex which corresponded to δ_P 49.4 in 24% yield, which was found to be the product of P-coordination, i.e., $[W_2(\mu-$

$C_2PPhAuCl)(CO)_4(Tp^*)_2]$ (**7**). The $^{31}P\{^1H\}$ NMR spectrum of **7** comprises a singlet resonance at δ_P 49.4 with $^2J_{WP}$ 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 $[W(\equiv CPh_2AuCl)(CO)_2(Tp^*)]$ (**3**: δ_P 32.0 cf. 37.5). However, similar coupling constants are seen for **7** ($^2J_{WP}$ 143.7) and **3** ($^2J_{WP}$ 139.3 Hz), illustrating the recurrent theme throughout this work that the coupling constants are more diagnostic than the chemical shifts.

Scheme 7. Addition of $[AuCl(SMe_2)]$ to **6**

In the $^{13}C\{^1H\}$ NMR spectrum both the chemical shift and couplings of **7** (δ_C 262.5, $^1J_{PC}$ 25.9, $^1J_{WC}$ 203.2 Hz) mimic those of **3** (δ_C 263.3, $^1J_{PC}$ 22.1, $^1J_{WC}$ 199.9 Hz). The carbyne resonance appears 20 ppm upfield with respect to that of the precursor **6**, along with a considerable reduction in the $^1J_{PC}$ value. The 1H and $^{13}C\{^1H\}$ NMR spectra indicate that the pyrazolyl rings and carbonyl ligands at each tungsten centre are inequivalent, a consequence of their prochirality.

Crystals of **7** were obtained and crystallographically analysed to provide the molecular geometry presented in Figure 5. Unfortunately, the crystals obtained were of low quality, providing poor data that limited the precision of the structural model which will not be discussed in detail. Nevertheless, the structure substantiates the proposed formulation of **7** based on spectroscopic data.

The reaction of **6** with three equivalents of $[AuCl(SMe_2)]$ gave the pentametallic complex $[W_2\{\mu-(\eta^2-C_2AuCl)_2PPhAuCl\}(CO)_4(Tp^*)_2]$ (**8**) in which addition to the phosphine and both $W\equiv C$ bonds has occurred. The phosphorus resonance is shifted to lower frequency (δ_P 75.7) compared to **7** and the $^1J_{WP}$ coupling of 88.8 Hz is comparable to that of $[W\{\eta^2-C(AuCl)PPh_2AuCl\}(CO)_2(Tp^*)]$ (**4**) ($^1J_{WP}$ 84.3 Hz). The carbyne resonance appears at δ_C 252.0 with no resolvable $^1J_{PC}$ coupling and considerably reduced $^1J_{WC}$ coupling (99.9 Hz) akin to **4** (δ_C 253.6, $^1J_{PC}$ 1.5, $^1J_{WC}$ 99.6 Hz). The carbonyl absorption bands are again shifted to higher frequency compared to **6** and **7** as a result of decreased electron density at the tungsten centres. As for **7**, 1H and $^{13}C\{^1H\}$ NMR data demonstrate the prochirality of the carbonyls and pyrazolyl ligands.

Figure 5. Molecular structure of **7** in a crystal of **7**·Et₂O (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.84(2), W2–C4 1.89(2), C1–P1 1.75(2), C4–P1 1.73(2), P1–Au1 2.235(7), W1–C1–P1 170.3(13), W2–C4–P1 173.2(16), C1–P1–C4 106.8(10), P1–Au1–Cl1 178.4(2).

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 literature complexes.^{5d,12a-c,18} As has been seen previously,^{5k} the carbyne ligands bridge the W–Au linkages unsymmetrically (W1–C1 1.874(15), W2–C4 1.884(14) *cf.* 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 (178.4(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 CH₂Cl₂ solvent molecule. The cumulative effect of these intermolecular interactions may be the observed distortion of the C1–Au1–Cl1 angle.

Figure 6. Molecular structure of **8** in a crystal of **8**·CH₂Cl₂ (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.874(15), W2–C4 1.884(14), C1–P1 1.804(16), C4–P1 1.831(15), C1–Au1 2.038(17), C4–Au2 2.020(15), W1–Au1 2.8275(9), W2–Au2 2.7691(9), Au1–Au2 3.0318(8), P1–Au3 2.237(4), W1–C1–P1 148.6(10), W2–C4–P1 148.8(9), C1–P1–C4 107.0(7), W1–C1–Au1 92.5(7), W2–C4–Au2 90.3(6), C1–W1–Au1 46.1(5), C4–W2–Au2 46.8(5), C1–Au1–Cl1 164.6(4), C4–Au2–Cl2 178.4(4).

Unfortunately, attempts to isolate complex **9** (δ_p 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{¹H} NMR spectrum, resonance is straddled by only a single pair of satellites (³J_{WP} = 118.7 Hz).

Table 1. Selected spectroscopic data for **6** and AuCl adducts ([W] = W(CO)₂(Tp*)).

Complex	δ_p ppm	² J _{WP} Hz	ν_{CO} cm ⁻¹
[W] ₂ (μ-C ₂ PPh) (6)	79.5	77.2	1986, 1975, 1892
[W] ₂ (μ-C ₂ PPhAuCl) (7)	49.4	143.7	1998, 1913
[W] ₂ (μ-(CAuCl) ₂ PPhAuCl) (8)	75.7	88.8	2029, 1951
[W] ₂ (μ-(CAuCl) ₂ PPh) ^a (9)	63.1	118.7	2004, 1916 ^b

NMR spectra were recorded in CDCl₃. IR spectra were recorded in CH₂Cl₂.

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

Based on the ³¹P{¹H} 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 originally bound to phosphorus migrates 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.²⁴ Finally, addition of the third AuCl group to the revealed phosphine can occur to yield **8**.

In the monometallic complex **1**, electrophilic 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, ^{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 600 (^1H at 600.0 MHz, ^{13}C at 150.9 MHz) or Bruker Avance 800 (^1H at 800.1 MHz, ^{13}C at 201.2 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^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. Whilst $^{13}\text{C}\{^1\text{H}\}$ signals for carbon nuclei of PPh groups could be routinely observed, their narrow spectral range and comparable J_{PC} values often precluded unequivocal assignment, in which case they are designated as ' $\text{C}^{2,3,5,6}(\text{PPh})$ '. 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. 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 acetonitrile as the matrix. Data for X-ray crystallography were collected with a Nonius Kappa CCD or Agilent Xcalibur diffractometer. The compounds $[\text{W}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$ (**1**),^{3a} $[\text{W}_2(\mu\text{-C}_2\text{PPh})(\text{CO})_4(\text{Tp}^*)_2]$,²⁰ $[\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{Cp}^*)_2]$ ²⁵ and $[\text{AuCl}(\text{L})]$ ($\text{L} = \text{SMe}_2$, THT)²⁶ were prepared according to published procedures. All other reagents were used as obtained from commercial sources.

Synthesis of $[\text{W}(\equiv\text{CPh}_2\text{RhCl}_2(\text{Cp}^*))(\text{CO})_2(\text{Tp}^*)]$ (2**).** A solution of $[\text{W}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$ (0.350 g, 0.477 mmol) and $[\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{Cp}^*)_2]$ ²⁵ (0.147 g, 0.239 mmol) in CH_2Cl_2 (20 mL) was stirred overnight. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 and chromatographed on silica gel. Elution with CH_2Cl_2 gave an initial yellow fraction containing unreacted $[\text{W}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$. Subsequent elution with THF gave a red fraction, which was collected and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and EtOH then concentrated under reduced pressure to afford the product as a red precipitate, which was collected by filtration. Crystals suitable for crystallographic and microanalytical analysis were obtained by slow diffusion of n -hexane into a solution of **2** in CH_2Cl_2 . Yield 0.219 g (0.210 mmol, 44%). IR (Nujol) ν/cm^{-1} : 2552 w (BH), 2004 s, 1913 s (CO). IR (CH_2Cl_2) ν/cm^{-1} : 2554 w (BH), 2008 vs, 1916 vs (CO). IR (THF) ν/cm^{-1} : 2012 vs, 1919 vs (CO), ν_{BH} not visible. ^1H NMR (CDCl_3) δ/ppm : 7.93 – 7.87 (m, 4 H, C_6H_5), 7.39 – 7.36 (m, 6 H, C_6H_5), 5.65 (s, 3 H, pzH, coincident), 2.41 (s, 3 H, pzCH₃), 2.28 (s, 6 H, pzCH₃), 2.23 (s, 3 H, pzCH₃), 1.69 (s, 6 H, pzCH₃), 1.35 (d, 15 H, $^3J_{\text{RhH}} = 3.6$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 273.0 (d, $\text{W}=\text{C}$, $^1J_{\text{PC}} = 28.7$, $^1J_{\text{WC}} = 208.2$), 226.3 (CO, $^1J_{\text{WC}} = 170.5$), 152.8 (3 C, coincident), 144.8 (1 C), 144.3 (2 C) [$\text{C}^{3,5}(\text{pz})$], 134.7 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 9.1$], 132.5 [d, $\text{C}^1(\text{C}_6\text{H}_5)$, $^1J_{\text{PC}} = 45.3$], 130.0 [$\text{C}^4(\text{C}_6\text{H}_5)$], 128.1 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 9.1$], 106.9 (1 C), 106.1 (2 C) [$\text{C}^4(\text{pz})$], 98.5 (C_5Me_5), 15.8 (2 C), 15.2 (1 C), 12.8 (2 C), 12.6 (1

C) (pzCH_3), 8.9 (C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 37.0 (d, $^1J_{\text{RhP}} = 139.2$, $^2J_{\text{WP}} = 122.0$). MS-ESI(+): m/z 1007.8 [$\text{M} - \text{Cl}$]⁺. Accurate mass: found 1007.1848 [$\text{M} - \text{Cl}$]⁺. Calcd. for $\text{C}_{40}\text{H}_{47}^{11}\text{B}^{35}\text{ClN}_6\text{O}_2\text{P}^{103}\text{Rh}^{184}\text{W}$: 1007.1844. Anal. found: C, 41.41; H, 4.32; N, 6.94%. Calcd. for $\text{C}_{40}\text{H}_{47}\text{BCl}_2\text{N}_6\text{O}_2\text{PRhW} \cdot (\text{CH}_2\text{Cl}_2)_2$: C, 41.58; H, 4.24; N, 6.93%. Crystal data for $\text{C}_{40}\text{H}_{47}\text{BCl}_2\text{N}_6\text{O}_2\text{PRhW} \cdot (\text{CH}_2\text{Cl}_2)_2$: $M_w = 1213.16$, orthorhombic, $Pbca$, $a = 20.9517(2)$ Å, $b = 21.1340(2)$ Å, $c = 22.1261(1)$ Å, $V = 9797.29(14)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.645$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 3.08$ mm⁻¹, $T = 200(2)$ K, red block, $0.27 \times 0.20 \times 0.14$ mm, 14324 independent reflections. F^2 refinement, $R = 0.040$, $wR = 0.106$ for 11541 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 60^\circ$), 541 parameters, CCDC 995723.

Synthesis of $[\text{W}(\equiv\text{CPh}_2\text{AuCl})(\text{CO})_2(\text{Tp}^*)]$ (3**).** A mixture of $[\text{W}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$ (0.352 g, 0.479 mmol) and $[\text{AuCl}(\text{SMe}_2)]^{26}$ (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 CH_2Cl_2 . Yield 0.374 g (0.387 mmol, 81%). IR (Nujol) ν/cm^{-1} : 2552 w (BH), 2001 s, 1907 s (CO). IR (CH_2Cl_2) 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 (CDCl_3) δ/ppm : 7.81 – 7.73 (m, 4 H, C_6H_5), 7.48 – 7.43 (m, 6 H, C_6H_5), 5.90 (s, 2 H, pzH), 5.77 (s, 1 H, pzH), 2.38 (s, 6 H, pzCH₃), 2.36 (s, 3 H, pzCH₃), 2.31 (s, 3 H, pzCH₃), 2.24 (s, 6 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 263.3 (d, $\text{W}=\text{C}$, $^1J_{\text{PC}} = 22.1$, $^1J_{\text{WC}} = 199.9$), 223.6 (d, CO, $^3J_{\text{PC}} = 2.8$, $^1J_{\text{WC}} = 163.4$), 152.7 (1 C), 151.8 (2 C), 145.9 (1 C), 145.2 (2 C) [$\text{C}^{3,5}(\text{pz})$], 133.7 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 13.8$], 131.4 [d, $\text{C}^4(\text{C}_6\text{H}_5)$, $^4J_{\text{PC}} = 2.0$], 129.7 [d, $\text{C}^1(\text{C}_6\text{H}_5)$, $^1J_{\text{PC}} = 64.3$], 129.0 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 12.4$], 107.3 (1 C), 106.9 (2 C) [$\text{C}^4(\text{pz})$], 16.9 (2 C), 15.2 (1 C), 12.7 (3 C, coincident) (pzCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 37.5 ($^2J_{\text{WP}} = 139.3$). MS-ESI(+): m/z 989.6 [$\text{M} + \text{Na}$]⁺, 911.6 [$\text{M} - 2\text{CO} + \text{H}$]⁺, 701.7 [$\text{M} - 2\text{CO} - \text{Au} + \text{Na}$]⁺, 679.8 [$\text{M} - 2\text{CO} - \text{Au} + \text{H}$]⁺. Accurate mass: found 991.1151 [$\text{M} + \text{Na}$]⁺. Calcd. for $\text{C}_{30}\text{H}_{32}\text{Au}^{11}\text{B}^{37}\text{ClN}_6\text{NaO}_2\text{P}^{184}\text{W}$: 991.1149. Anal. found: C, 37.24; H, 3.30; N, 8.42%. Calcd. for $\text{C}_{30}\text{H}_{32}\text{AuBClN}_6\text{O}_2\text{PW}$: C, 37.28; H, 3.34; N, 8.69%. Crystal data for $\text{C}_{30}\text{H}_{32}\text{AuBClN}_6\text{O}_2\text{PW}$: $M_w = 966.68$, monoclinic, $P2_1/n$, $a = 10.3172(1)$ Å, $b = 13.5659(2)$ Å, $c = 25.2039(3)$ Å, $\beta = 98.3693(5)^\circ$, $V = 3490.02(7)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.840$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 7.65$ mm⁻¹, $T = 200(2)$ K, orange plate, $0.38 \times 0.28 \times 0.05$ mm, 10247 independent reflections. F^2 refinement, $R = 0.030$, $wR = 0.067$ for 8112 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 60^\circ$), 388 parameters, CCDC 995724.

Synthesis of $[\text{W}\{\eta^2\text{-C}(\text{AuCl})\text{PPh}_2\text{AuCl}\}(\text{CO})_2(\text{Tp}^*)]$ (4**).** A mixture of $[\text{W}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$ (0.351 g, 0.478 mmol) and $[\text{AuCl}(\text{SMe}_2)]^{26}$ (0.428 g, 1.45 mmol) was dissolved in THF (15 mL) resulting in a red solution. The solution was stirred for four days and a small amount of gold precipitate was observed. The solution was decanted by cannula filtration and concentrated to approximately 5 mL in vacuo resulting in precipitation of the product as a peach powder, which was isolated by filtration. Crystals suitable for crystallographic analysis were obtained by slow diffusion of EtOH into a solution of **4** in CH_2Cl_2 . 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 (CDCl_3) δ/ppm : 8.09 – 8.02 (m, 4 H, C_6H_5), 7.61 – 7.49 (m, 6 H, C_6H_5), 5.96 (s, 1 H, pzH), 5.93 (s, 2 H, pzH), 2.50 (s, 3 H, pzCH₃), 2.36 (s, 6 H, pzCH₃), 2.32 (s, 3 H, pzCH₃), 2.25 (s, 6 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 253.6 (d, WC, $^1J_{\text{PC}} = 1.5$, $^1J_{\text{WC}} = 99.6$), 216.6 (d, CO, $^3J_{\text{PC}} = 7.8$, $^1J_{\text{WC}} = 154.2$), 154.4 (1 C), 152.5 (2 C), 146.9 (1 C), 146.4 (2 C) [$\text{C}^{3,5}(\text{pz})$], 134.4 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 13.6$], 132.5 [d, $\text{C}^4(\text{C}_6\text{H}_5)$, $^4J_{\text{PC}} = 3.0$], 129.5 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 12.1$], 129.4 [d, $\text{C}^1(\text{C}_6\text{H}_5)$, $^1J_{\text{PC}} = 61.9$], 109.1 (1 C), 108.2 (2 C) [$\text{C}^4(\text{pz})$], 17.4 (2 C), 16.0 (1 C), 13.2 (1 C), 12.7 (2 C) (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 53.6 ($^2J_{\text{WP}} = 84.3$). MS-ESI(+): m/z 1220.8 [M + Na]⁺, 1162.7 [M – Cl]⁺. Accurate mass: found 1221.0532 [M + Na]⁺. Calcd. for $\text{C}_{30}\text{H}_{32}\text{Au}_2^{11}\text{B}^{35}\text{Cl}_2\text{N}_6\text{NaO}_2\text{P}^{184}\text{W}$: 1221.0533. Anal. found: C, 30.11; H, 2.88; N, 7.04%. Calcd. for $\text{C}_{30}\text{H}_{32}\text{Au}_2\text{BCl}_2\text{N}_6\text{O}_2\text{PW}$: C, 30.05; H, 2.69; N, 7.01%. Crystal data for $\text{C}_{30}\text{H}_{32}\text{Au}_2\text{BCl}_2\text{N}_6\text{O}_2\text{PW}$: $M_w = 1199.10$, monoclinic, $P2_1/n$, $a = 16.5513(2)$ Å, $b = 12.9890(2)$ Å, $c = 17.7921(2)$ Å, $\beta = 113.5027(7)^\circ$, $V = 3507.71(8)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.270$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 11.85$ mm⁻¹, $T = 200(2)$ K, red block, $0.36 \times 0.29 \times 0.26$ mm, 10263 independent reflections. F^2 refinement, $R = 0.034$, $wR = 0.080$ for 8079 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 60^\circ$), 406 parameters, CCDC 995725.

Synthesis of $[\text{W}\{\eta^2\text{-C}(\text{AuCl})\text{P}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (5). $[\text{W}\{\equiv\text{CP}(=\text{S})\text{Ph}_2\}(\text{CO})_2(\text{Tp}^*)]$ (0.095 g, 0.12 mmol) and $[\text{AuCl}(\text{SMe}_2)]^{26}$ (0.037 g, 0.12 mmol) were dissolved in CH_2Cl_2 (6 mL) resulting in a red solution and golden precipitate. The suspension was stirred for two hours after which time IR spectroscopy showed the presence of the starting material (ν_{CO} 2004, 1916 cm^{-1}) and a new compound (ν_{CO} 2031, 1952 cm^{-1}). After 4.5 hours the infrared showed no change, so a further half equivalent of $[\text{AuCl}(\text{THT})]^{27}$ (0.020 g, 0.062 mmol) was added. After six hours of stirring the IR showed almost complete conversion to the product and the reaction was left to sit overnight. The reaction mixture was filtered through diatomaceous earth and washed with CH_2Cl_2 until the washings were colourless. EtOH was added to the filtrate and the solution was concentrated on the rotary evaporator until a bluish precipitate was observed, which was removed by filtration. The crude product was chromatographed on neutral alumina using 2:1 CH_2Cl_2 :MeCN as the eluent. An initial orange fraction was collected containing the starting material, followed by a red fraction containing the product. The solvent was removed under reduced pressure to afford **5** as an orange solid. Yield 0.070 g (0.070 mmol, 57%). IR (Nujol) ν/cm^{-1} : 2560 w (BH), 2028 s, 1948 s, br (CO). IR (CH_2Cl_2) ν/cm^{-1} : 2563 w (BH), 2031 s, 1952 vs, br (CO). IR (THF) ν/cm^{-1} : 2563 w (BH), 2031 vs, 1953 vs, br (CO). ^1H NMR (CDCl_3) δ/ppm : 8.23 – 8.20 (m, 4 H, C_6H_5), 7.55 – 7.50 (m, 6 H, C_6H_5), 5.94 (s, 1 H, pzH), 5.91 (s, 2 H, pzH), 2.54 (s, 3 H, pzCH₃), 2.36 (s, 6 H, pzCH₃), 2.32 (s, 3 H, pzCH₃), 2.20 (s, 6 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 262.4 (br, WCP), 216.4 (br, CO), 154.3 (1 C), 152.5 (2 C), 146.7 (1 C), 146.1 (2 C) [$\text{C}^{3,5}(\text{pz})$], 132.5 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 10.0$], 132.0 [br, $\text{C}^{1,4}(\text{C}_6\text{H}_5)$], 128.8 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 8.9$], 108.8 (1 C), 108.0 (2 C) [$\text{C}^4(\text{pz})$], 17.2 (2 C), 15.9 (1 C), 13.1 (1 C), 12.7 (2 C) (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 52.3 (br). MS-ESI(+): m/z 1962.4 [2 M – Cl + H]⁺, 1729.4 [2 M – Au – 2 Cl]⁺, 1021.1 [M + Na]⁺, 963.1 [M – Cl]⁺. Accurate mass: found 1023.0871 [M + Na]⁺. Calcd. for

$\text{C}_{30}\text{H}_{32}\text{Au}^{11}\text{B}^{37}\text{ClN}_6\text{NaO}_2\text{P}^{184}\text{W}$: 1023.0870. Found 1021.0909 [M + Na]⁺. Calcd. for $\text{C}_{30}\text{H}_{32}\text{Au}^{11}\text{B}^{35}\text{ClN}_6\text{NaO}_2\text{P}^{184}\text{W}$: 1021.0900. Anal. found: C, 35.83; H, 3.25; N, 8.20%. Calcd. for $\text{C}_{30}\text{H}_{32}\text{AuBClN}_6\text{O}_2\text{PSW}$: C, 36.08; H, 3.23; N, 8.41%. Crystal data for $\text{C}_{30}\text{H}_{32}\text{AuBClN}_6\text{O}_2\text{PSW}$: $M_w = 998.74$, monoclinic, $P2_1/c$, $a = 16.6239(3)$ Å, $b = 12.8664(3)$ Å, $c = 17.4284(3)$ Å, $\beta = 116.7247(10)^\circ$, $V = 3329.55(12)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.992$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 8.08$ mm⁻¹, $T = 200(2)$ K, orange block, $0.10 \times 0.09 \times 0.08$ mm, 7648 independent reflections. F^2 refinement, $R = 0.043$, $wR = 0.118$ for 5693 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 55^\circ$), 397 parameters, CCDC 995726.

Synthesis of $[\text{W}_2(\mu\text{-C}_2\text{PPhAuCl})(\text{CO})_4(\text{Tp}^*)_2]$ (7). A solution of $[\text{W}_2(\mu\text{-C}_2\text{PPh})(\text{CO})_4(\text{Tp}^*)_2]$ (0.050 g, 0.041 mmol) and $[\text{AuCl}(\text{SMe}_2)]^{26}$ (0.013 g, 0.044 mmol) in CH_2Cl_2 (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 CH_2Cl_2 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 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 (CDCl_3) δ/ppm : 8.02 (m, 2 H, C_6H_5), 7.48 (m, 3 H, C_6H_5), 5.82 (s, 4H, pzH), 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 262.5 (d, W $\equiv\text{C}$, $^1J_{\text{PC}} = 25.9$, $^1J_{\text{WC}} = 203.2$), 225.1 (CO, $^1J_{\text{WC}} = 164.0$), 223.7 (CO, $^1J_{\text{WC}} = 164.3$), 152.6 (2 C), 152.5 (2 C), 152.2 (2 C), 145.6 (2 C), 144.7 (2 C), 144.7 (2 C) [$\text{C}^{3,5}(\text{pz})$], 134.4 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 14.6$], 131.1 [$\text{C}^4(\text{C}_6\text{H}_5)$], 130.3 [d, $\text{C}^1(\text{C}_6\text{H}_5)$, $^1J_{\text{PC}} = 65.3$], 128.8 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 12.5$], 107.1 (2 C), 106.7 (2 C), 106.6 (2 C) [$\text{C}^4(\text{pz})$], 17.5 (4 C), 15.2 (2 C), 12.7 (6 C) (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 49.4 ($^2J_{\text{WP}} = 143.7$). MS-ESI(+): m/z 1479.3 [M + MeCN]⁺, 1460.2 [M + Na – H]⁺, 1439.2 [M + H]⁺. Accurate mass: found 1463.2169 [M + Na]⁺. Calcd. for $\text{C}_{42}\text{H}_{49}\text{Au}^{11}\text{B}_2^{37}\text{ClN}_{12}\text{NaO}_4\text{P}^{184}\text{W}_2$: 1463.2165. Found 1461.2184 [M + Na]⁺. Calcd. for $\text{C}_{42}\text{H}_{49}\text{Au}^{11}\text{B}_2^{35}\text{ClN}_{12}\text{NaO}_4\text{P}^{184}\text{W}_2$: 1461.2194. Anal. found: C, 34.83; H, 3.63; N, 11.30%. Calcd. for $\text{C}_{42}\text{H}_{49}\text{AuB}_2\text{ClN}_{12}\text{O}_4\text{PW}_2$: C, 35.07; H, 3.43; N, 11.68%. Crystal data for $\text{C}_{42}\text{H}_{49}\text{AuB}_2\text{ClN}_{12}\text{O}_4\text{PW}_2 \cdot \text{C}_4\text{H}_{10}\text{O}$: $M_w = 1512.77$, triclinic, $P - 1$ (No. 2), $a = 12.5001(13)$ Å, $b = 14.7647(14)$ Å, $c = 17.4599(10)$ Å, $\alpha = 66.723(7)^\circ$, $\beta = 69.805(7)^\circ$, $\gamma = 73.373(9)^\circ$, $V = 2735.9(5)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.836$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 7.00$ mm⁻¹, $T = 150(2)$ K, red prism, $0.19 \times 0.08 \times 0.07$ mm, 11228 independent reflections. F^2 refinement, $R = 0.081$, $wR = 0.175$ for 5382 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 52^\circ$), 631 parameters, CCDC 1518123.

Synthesis of $[\text{W}_2\{\mu\text{-(CAuCl)}_2\text{PPhAuCl}\}(\text{CO})_4(\text{Tp}^*)_2]$ (8). A solution of $[\text{W}_2(\mu\text{-C}_2\text{PPh})(\text{CO})_4(\text{Tp}^*)_2]$ (0.020 g, 0.017 mmol) and $[\text{AuCl}(\text{SMe}_2)]$ (0.015 g, 0.051 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 20 minutes. The red solution was 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 CH_2Cl_2 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 (CDCl_3) δ/ppm : 8.60 (m, 2 H, C_6H_5), 7.60 (m, 1 H, C_6H_5), 7.57 (m, 2 H, C_6H_5), 5.99 (s, 2 H, pzH), 5.94 (s, 2 H, pzH), 5.89 (s, 2 H, pzH), 2.76 (s, 6 H, pzCH₃), 2.45 (s, 6 H, pzCH₃), 2.38 (s, 6 H, pzCH₃), 2.36 (s, 6 H, pzCH₃), 2.32 (s, 6 H, pzCH₃), 2.15 (s, 6 H, pzCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 252.0 (WC, $^1J_{\text{WC}} = 99.9$), 217.5 (d, CO, $^3J_{\text{PC}} = 8.0$, $^1J_{\text{WC}} = 153.4$), 216.2 (d, CO, $^3J_{\text{PC}} = 8.1$, $^1J_{\text{WC}} = 153.4$), 154.3 (2 C), 153.5 (2 C), 152.9 (2 C), 146.8 (2 C), 146.3 (2 C), 146.2 (2 C) [$\text{C}^{3,5}(\text{pz})$], 136.7 [d, br, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 15.4$], 133.1 [$\text{C}^4(\text{C}_6\text{H}_5)$], 129.1 [d, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$, $J_{\text{PC}} = 12.4$], 129.0 [d, $\text{C}^1(\text{C}_6\text{H}_5)$, $^1J_{\text{PC}} = 59.3$], 109.0 (2 C), 108.1 (2 C), 108.0 (2 C) [$\text{C}^4(\text{pz})$], 19.4 (2 C), 17.9 (2 C), 16.0 (2 C), 13.2 (2 C), 12.8 (2 C), 12.7 (2 C) (pzCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 75.7 ($^2J_{\text{WP}} = 88.8$). MS-ESI(+): m/z 1943.1 [M + K]⁺, 1927.1 [M + Na]⁺. Accurate mass: found 1929.0847 [M + Na]⁺. Calcd. for $\text{C}_{42}\text{H}_{49}\text{Au}_3^{11}\text{B}_2^{35}\text{Cl}_3^{37}\text{Cl}_2\text{N}_{12}\text{NaO}_4\text{P}^{184}\text{W}_2$: 1929.0844. Found 1927.0875 [M + Na]⁺. Calcd. for $\text{C}_{42}\text{H}_{49}\text{Au}_3^{11}\text{B}_2^{35}\text{Cl}_2^{37}\text{ClN}_{12}\text{NaO}_4\text{P}^{184}\text{W}_2$: 1927.0873. Anal. found: C, 26.51; H, 2.58; N, 8.71%. Calcd. for $\text{C}_{42}\text{H}_{49}\text{Au}_3\text{B}_2\text{Cl}_3\text{N}_{12}\text{O}_4\text{PW}_2$: C, 26.50; H, 2.59; N, 8.83%. Crystal data for $\text{C}_{42}\text{H}_{49}\text{Au}_3\text{B}_2\text{Cl}_3\text{N}_{12}\text{O}_4\text{PW}_2 \cdot \text{CH}_2\text{Cl}_2$: $M_w = 1988.42$, monoclinic, $P2_1/c$, $a = 23.7948(4)$ Å, $b = 10.6312(2)$ Å, $c = 24.9238(5)$ Å, $\beta = 116.0601(9)^\circ$, $V = 5663.91(19)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.332$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 12.11$ mm⁻¹, $T = 200(2)$ K, red prism, $0.17 \times 0.04 \times 0.03$ mm, 9980 independent reflections. F^2 refinement, $R = 0.056$, $wR = 0.160$ for 7173 reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 50^\circ$), 649 parameters.

Observation of $[\text{W}_2\{\mu\text{-(CAuCl)}_2\text{PPh}\}(\text{CO})_4(\text{Tp}^*)_2]$ (9**).** $[\text{W}_2\{\mu\text{-C}_2\text{PPh}\}(\text{CO})_4(\text{Tp}^*)_2]$ (0.020 g, 0.017 mmol) and $[\text{AuCl}(\text{SMe}_2)]$ (0.010 g, 0.034 mmol) were dissolved in CDCl_3 (0.5 mL) in an NMR tube. After 15 minutes, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated the solution contained a mixture of **7** (16.0%), **8** (34.2%) and **9** (45.8%) as well as two small singlets without resolvable ^{183}W satellites at δ_{P} 37.5 (0.5%) and 30.2 (3.6%). Attempts to chromatograph mixtures containing **9** did not lead to isolation of pure **9**; instead it was isolated contaminated with **7**, or both **7** and **8**. Limited spectroscopic data for the crude product are given here. IR (CH_2Cl_2) ν/cm^{-1} : 2004 s, 1916 vs (CO) (tentative assignments as the spectrum also contains bands due to **7** and **8**). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ/ppm : 63.1 ($^2J_{\text{WP}} = 118.7$). MS-ESI(+): m/z 1693.2 [M + MeCN]⁺. Accurate mass: found 1693.1543 [M + Na]⁺. Calcd. for $\text{C}_{42}\text{H}_{49}\text{Au}_2^{11}\text{B}_2^{35}\text{Cl}_2\text{N}_{12}\text{NaO}_4\text{P}^{184}\text{W}_2$: 1693.1548.

Conclusions

The work presented here highlights the ability of phosphinocarbyne complexes to coordinate transition metal fragments. Preferential ligation is seen at the phosphine over the carbyne linkage, although this apparent preference may be dictated by steric factors. In both mono- and bimetallic phosphinocarbyne complexes the nucleophilicities of the phosphine and carbyne sites are linked, wherein complexation to one site alters the nucleophilicity of the remaining site(s). The synthetic versatility of such complexes may have interesting implications for future chemistry of these and related species.

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