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ARTICLE

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Metal coordination to bipyridyl carbynes

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The Pd^0/Au^I-mediated coupling of the stannylcarbyne $[W(\equiv CSn^nBu_3)(CO)_2(Tp^*)]$ (**1**) and 6-bromo-2,2′-bipyridine or 6,6′-dibromo-2,2′-bipyridine gives new carbynes functionalised on the carbyne carbon(s) with a bipyridyl group. These new 'metallo-ligands' undergo protonation at the pyridyl nitrogens, metallation of the tungsten–carbon triple bond with $[AuCl(SMe_2)]$, and metallation of the bipyridyl moiety with $K[PtCl_3(C_2H_4)]\cdot H_2O$, $[ReBr(CO)_5]$ and $[MCl(COD)]_2$ (M = Ir, Rh; COD = η^4-cycloocta-1,5-diene).

Introduction

The chemistry of transition metal carbyne complexes, $L_nM{\equiv}CR$, have historically been limited to those bearing alkyl, aryl and amino 'R' substituents,[1] whereas those bearing other functional groups — particularly those with heteroatoms in the vicinity of the metal centre — have arisen only sporadically. This is not necessarily a comment on the stability of such species but rather a consequence of the currently available synthetic protocols. The vast majority of carbynes have been prepared by Fischer's seminal oxide/alkoxide abstraction,[2] Schrock's α-metal-hydride elimination[1b,3] or alkyne scission/metathesis[4] approaches. While a boon for hydrocarbyl and amino-substituted carbynes, these strategies are generally not applicable for the synthesis of carbynes bearing heavier heteroatoms or functional substituents capable of coordinating to metal centres or electrophiles *en route*. Alternative strategies commencing from halocarbynes $[M(\equiv CX)(CO)_2(Tp^*)]$ (M = Mo, W; X = Cl, Br; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate)[5] or their lithiocarbyne derivatives $[M(\equiv CLi)(CO)_2(Tp^*)]$,[6] overcome some of these issues,[7] but these are not without their own significant shortcomings. Motivation for the inclusion of one or more 'C_1' carbyne units on the periphery of more elaborate assemblies originates from the plethora of bi- and poly-metallic species in which multiple metal alkynyl 'C_2' connectivities are appended to electronically conducting spacers. Given that carbyne ligands are considerably more potent π-acceptors than alkynyls, unusual communication phenomena might be anticipated, in turn reflected in electro-optical responses.

Our own interests lie in using metallacarbynes as one or more termini in bi- and polymetallic assemblies bridged by electronically conductive ligands, and it was during this research that we recently fell foul of the shortcomings of the aforementioned strategies. Reaction of the tungsten lithiocarbyne $[W(\equiv CLi)(CO)_2(Tp^*)]$ with $[PtCl_2(phen)]$ (phen = 1,10-phenanthroline) resulted in attack not only at the platinum metal centre (halide metathesis), as expected, but also on the coordinated phenanthroline ligand to give the trimetallic complex $[(Tp^*)(CO)_2W{\equiv}CPtCl(phen\{C{\equiv}W(CO)_2(Tp^*)\text{-}2\}]$ (Chart 1a).[8] This result both confounded our expectations and posed a new synthetic challenge of how to strategically prepare similar "free ligand" analogues which would be available for coordination to a variety of metal centres as opposed to the singular platinum(II) example obtained. With regard to the classical synthetic strategies, the Fischer route is inappropriate because it involves treatment of an acylate or alkoxycarbene with strong Lewis acids (e.g., BBr_3, $[Me_3O]BF_4$, $(CF_3CO)_2O$, $O_2C_2Cl_2$, *etc*), which are incompatible with the desired nitrogen donor atoms. The Schrock α-elimination strategy requires coordinatively unsaturated metal centres which are deactivated by proximate donor atoms. Hopkins has succeeded in preparing the only other comparable examples *via* scission of 4-butynyl-3,5-lutidine or 3-butynylpyridine with $[W(\equiv CEt)(O^tBu)_3]$ or $[W_2(O^tBu)_6]$ to give oligomeric pyridylcarbynes (Chart 1b).[9]

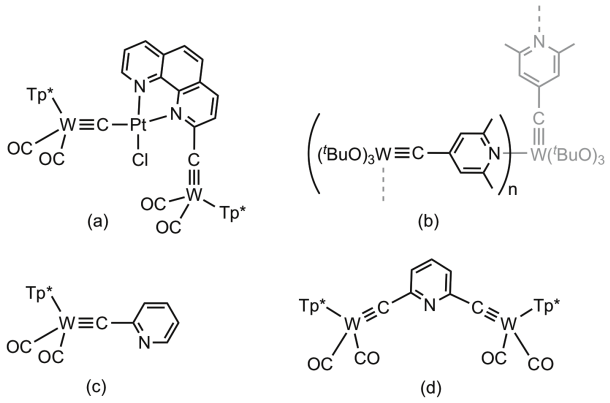

Chart 1. Pyridyl and phenanthroline functionalised carbynes.

These, and the current studies were motivated by the possibility of moderating the electro-optical properties of carbyne complexes by appending extraneous metal centres to the pendant nitrogen donor. This principle has been developed extensively by Koutsantonis who incorporated pyridyl or bipyridyl units into σ-alkynyl, vinylidene and allenylidene organometallic 'tectons' for heterobimetallic assembly.[10]

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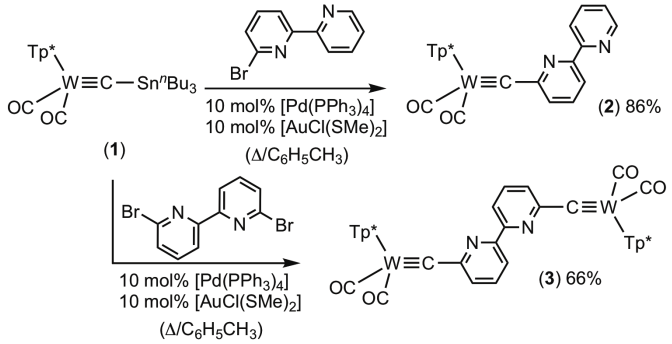
CCDC 1968076–1968086 contain the supplementary crystallographic data for this paper and are available free of charge from The Cambridge Crystallographic Data Centre.

We recently communicated our initial foray into a new synthetic strategy which allows carbyne complexes to be prepared with substituents bearing *inter alia* donor functionalities. A Pd^0/Au^I-mediated C–C cross-coupling reaction between the tungsten stannylcarbyne [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**1**)[11] and bromopyridines gave *ortho*-pyridylcarbynes and bis(carbynes) (Chart 1c and d, respectively), protonation and methylation of which gave the first examples of *N*-heterocyclic vinylidenes.[12] Herein we extend this strategy to the synthesis of bipyridyl-substituted carbynes and demonstrate their protonation and metallation reactions at two alternate sites.

Results and discussion

Reaction of the tungsten stannylcarbyne [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**1**)[11] and 6-bromo-2,2′-bipyridyl in the presence of catalytic amounts of [Pd(PPh$_3$)$_4$] and [AuCl(SMe$_2$)] (10 mol%) in refluxing toluene furnishes [6-{(Tp*)(CO)$_2$W≡C}bipy] (**2**, bipy = 2,2′-bipyridyl throughout this paper) as a dark red solid in good yield (Scheme 1). This complex features a tungsten carbyne with a bipyridyl group directly bound to the carbyne carbon. The necessity of the Au^I additive has been noted previously in the syntheses of pyridylcarbynes,[12] with transmetallation from tin to gold occurring *en route* to Pd^{II} in a manner reminiscent of the promotional "copper effect" observed for traditional Stille couplings.[13] If **1** is instead treated with 6,6′-dibromo-2,2′-bipyridyl under the same conditions the disubstituted derivative [6,6′-{(Tp*)(CO)$_2$W≡C}$_2$bipy] (**3**) is formed, also as a dark red solid, with one alkylidyne substituted on each pyridyl ring. In both cases purification was effected by column chromatography with silica gel as the support. The dark red bands containing **2** or **3** elute with frustrating recalcitrance using 100% CH_2Cl_2 as the eluent, however attempts to accelerate their egress by increasing the eluent polarity with even very low proportions of acetonitrile or methanol causes a range of unidentified impurities to elute with and contaminate the products.



Scheme 1. Synthesis of bipyridyl-substituted tungsten carbynes.

Selected spectroscopic and structural data for **2**, **3** and all other compounds reported in this paper are presented in Table 1.

Table 1. Selected spectroscopic and structural data for **2**–**10**.

	$\delta_{\equiv C}$ [a]	$r_{W\equiv C}$ (Å)	$\angle_{W\equiv C-C}$ (°)	ν_{CO} [b]
2	276.1	1.824(6)	173.3(5)	1981, 1890
3	276.5	1.824(8) 1.831(9)	162.1(7) 162.1(7)	1981, 1890
[**4**]$^+$	266.2	1.822(4)	163.5(3)	2010, 1923
[**5**]$^+$	–[c]	1.831(4) 1.818(5)	167.3(3) 166.8(5)	2010, 1924
6	262.2	1.895(7)	148.3(5)	2014, 1933
7	–[c]	1.890(4)	151.17(3)	2013, 1937
8	–[d]	1.832(7)	167.2(5)	–[d]
9	–[c]	1.833(4)	164.6(3)	1982, 1882
10	265.6	1.838(4)	157.8(5)	2025, 1985, 1926, 1898
[**11**]$^+$	262.3	1.838(6)	160.5(5)	1995, 1907
[**12**]$^+$	261.2	1.833(5)	160.2(4)	1996, 1909

[a] Measured in $CDCl_3$ (**2**–**7**, **11**–**12**) or CD_2Cl_2 (**9**–**10**) (ppm). [b] Measured in CH_2Cl_2 (cm^{-1}). [c] Too broad or low signal-to-noise to determine accurately. [d] Not isolated.

The ^{1}H NMR spectral data contain the typical Tp* signatures[1d] and several new resonances relating to the bipyridyl substituent. Seven distinct aromatic resonances, corresponding to the bipyridyl moiety, were located in the ^{1}H NMR spectrum of **2**, whereas only three were observed for **3**, indicating that both ends of the molecule are chemically equivalent in the latter complex. The carbyne carbons resonate at δ_C = 276.1 and 276.5, respectively, well within the standard range for tungsten arylcarbynes[1d] and close to those of related pyridylcarbynes (275–277 ppm).[12] The molecular structures of **2** and **3** have been crystallographically determined (Figures 1 and 2, respectively) and conform well with reported arylcarbyne precedent.[1d]

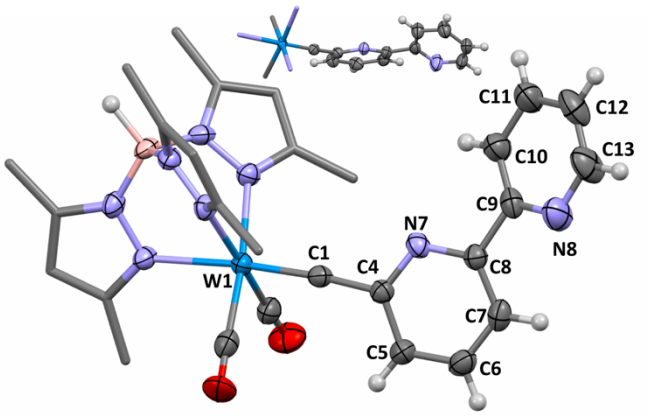


Figure 1. Molecular structure of **2** showing 50% displacement ellipsoids (one of three crystallographically independent molecules). Pyrazolyl groups are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.824(6), C1–C4 1.443(8), W1–C1–C4 173.3(5).

As with free 2,2′-bipyridyl,[13] the two pyridine rings orient close to coplanarity and the nitrogen atoms adopt a *trans* disposition. The W≡C distances are crystallographically identical (**2** 1.824(6); **3** 1.824(8), 1.831(9) Å). The W≡C–C angle in **2** (173.3(5)°) lies much closer to linearity than it does in **3** (162.1(7)°) although deformations from linearity are

commonplace for carbyne ligands and are generally attributed to solid-state packing effects.

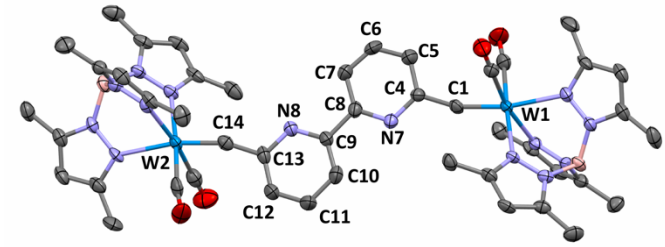
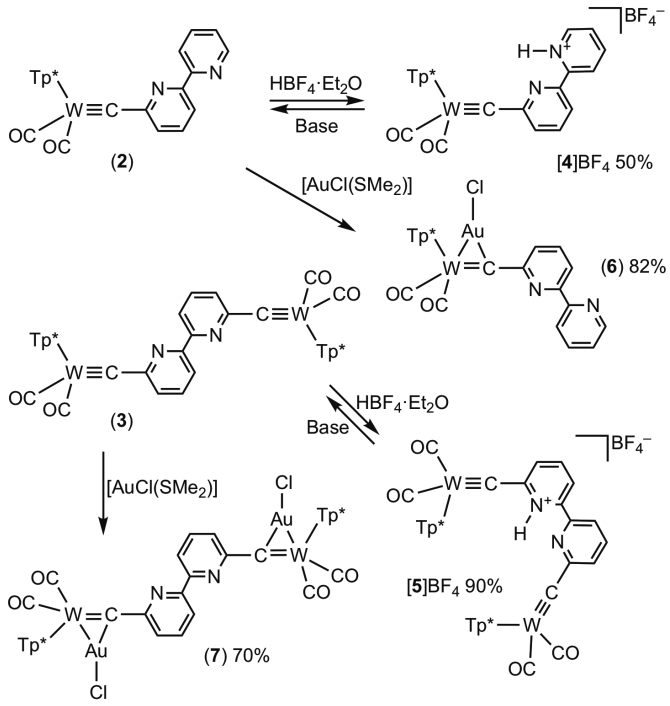


Figure 2. Molecular structure of **3** (50% displacement ellipsoids, pyrazolyl groups simplified and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.824(8), C1–C4 1.441(11), W2–C14 1.831(9), C13–C14 1.453(12), W1–C1–C4 162.1(7), W2–C14–C13 162.1(7).

The related pyridylcarbynes were shown to reversibly protonate at the pyridine nitrogen to give what can be described as *N*-heterocyclic vinylidene derivatives.[11] Treatment of the bipyridyl analogues **2** or **3** with $HBF_4{\cdot}Et_2O$ in diethyl ether results in rapid formation of yellow-green precipitates corresponding to the singly protonated derivatives, [6-{(Tp*)$(CO)_2$W≡C}bipyH]BF_4 [**5**]BF_4 and [6,6'-{(Tp*)$(CO)_2$W≡C}$_2$bipyH]BF_4 [**5**]BF_4, respectively (Scheme 2). Protonation is readily reversed by treatment with bases such as NEt_3 allowing **2** or **3** to be recovered essentially quantitatively. Indeed, both complexes are so susceptible to deprotonation that simply washing the solids with non-acidified solvents begins to effect deprotonation.



Scheme 2. Protonation and addition of gold(I) chloride to tungsten bipyridylcarbynes.

Both pyridyl N are available for protonation and the N*H* proton can in principle hop between the two rapidly in solution. The facile deprotonation necessitated both IR and NMR experiments being conducted in the presence of excess $HBF_4{\cdot}Et_2O$. Nonetheless, the apparent fluxional N*H* exchange leads to many resonances exhibiting appreciable broadening and hinders the extraction of useful data. The characterisation therefore relies primarily on the crystallographic molecular structure determinations (Figures 3 and 4). Compound [**4**]BF_4 crystallises with one equivalent of ethanol of solvation, the oxygen of which forms a hydrogen bond with the NH of the protonated pyridine ring (NH···O distance 1.96 Å) while the hydroxylic proton weakly associates (O-H···F = 2.21 Å) with the counter-anion. This fortuitous solvent inclusion most likely prevents disorder of the proton between the two nitrogen sites. As found for simple monoprotonated bipyridiniums,[15] in both structures the two pyridyl nitrogens lie on the same edge due to favourable electrostatic (N···H-N) interactions. For [**5**]BF_4 this requires substantial structural reorganisation to orient both '(Tp*)$(CO)_2$W' groups, which in the solid state are configured *trans* in the precursor, onto the same side of the molecule. This also results in some interdigitation of pyrazolyl groups on adjacent Tp* ligands to minimise the steric clash. It is clear from the space-filling representation (Figure 4 inset) that the potential 'metallo-ligand' **3** is unlikely to be able to coordinate to metal centres through the pyridyl nitrogens, as the required orientation of the Tp* ligands results in an available cavity too small to accommodate an extraneous metal and associated co-ligands, indeed anything much larger than a proton.

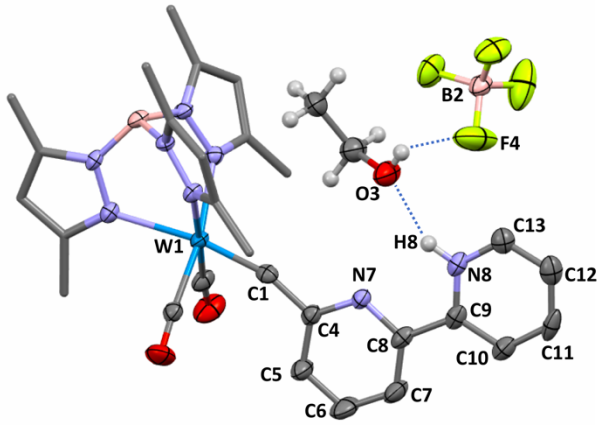


Figure 3. Molecular structure of [**4**]$BF_4{\cdot}C_2H_5OH$ in a crystal (50% displacement ellipsoids, pyrazolyl groups simplified and most hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.822(4), C1–C4 1.449(6), W1–C1–C4 163.5(3).

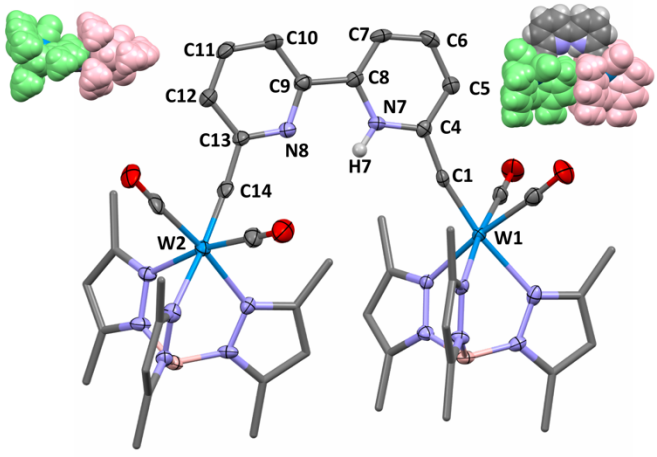


Figure 4. Molecular structure of [**5**]BF_4 in a crystal of [**5**]BF_4·$(CH_2Cl_2)_2$ (50% displacement ellipsoids, pyrazolyl groups simplified, solvent, counter anion and most hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.831(4), C1–C4 1.437(6), C13–C14 1.447(6), C14–W2 1.818(5), W1–C1–C4 167.3(3), W2–C14–C13 166.8(4). Insets: space-fill representations with the 'W$(CO)_2$(Tp*)' groups coloured green and pink.

The bipyridylcarbynes in principle present two possible sites for metal coordination. Treatment of **2** or **3** with [AuCl(SMe_2)] ("AuCl" has a well-documented proclivity for alkylidynes[16]) results in displacement of the labile thioether ligand and coordination of 'AuCl' across the tungsten–carbon multiple bonds, furnishing [6-{(Tp*)$(CO)_2$W(AuCl)(μ-C)}bipy] (**6**) and [6,6'-{(Tp*)$(CO)_2$W(AuCl)(μ-C)}$_2$bipy] (**7**), respectively (Scheme 2). Coordination of gold(I) results in a minor up-field shift of the carbyne carbon $^{13}C\{^1H\}$ NMR signal of *ca* 10 ppm but has little influence on the chemical shifts of other nuclei. The molecular structures of **6** and **7** are in good agreement with related compounds,[16] exhibiting characteristic elongation of the tungsten–carbon bond and more pronounced bending of the W–C1–C4 angle.

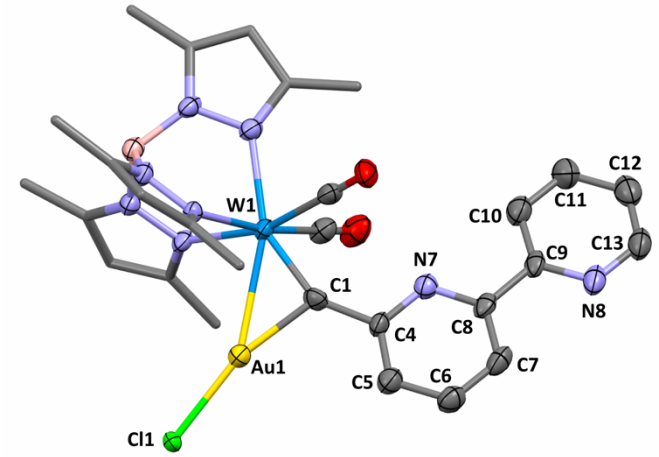


Figure 5. Molecular structure of **6** (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.895(7), C1–C4 1.477(10), W1–Au1 2.7913(4), C1–Au1 2.025(7), Au1–Cl1 2.3256(13), W1–C1–C4 148.3(5), W1–Au1–Cl1 152.46(4), C1–Au1–Cl1 164.7(2).

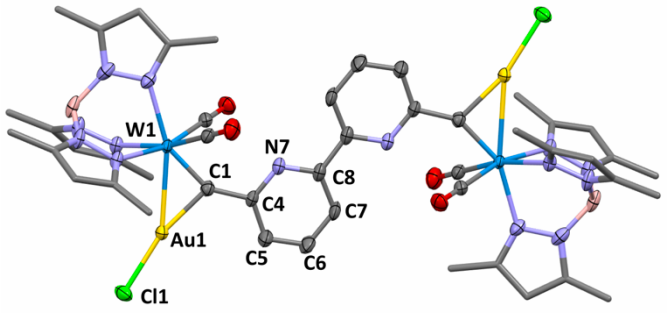
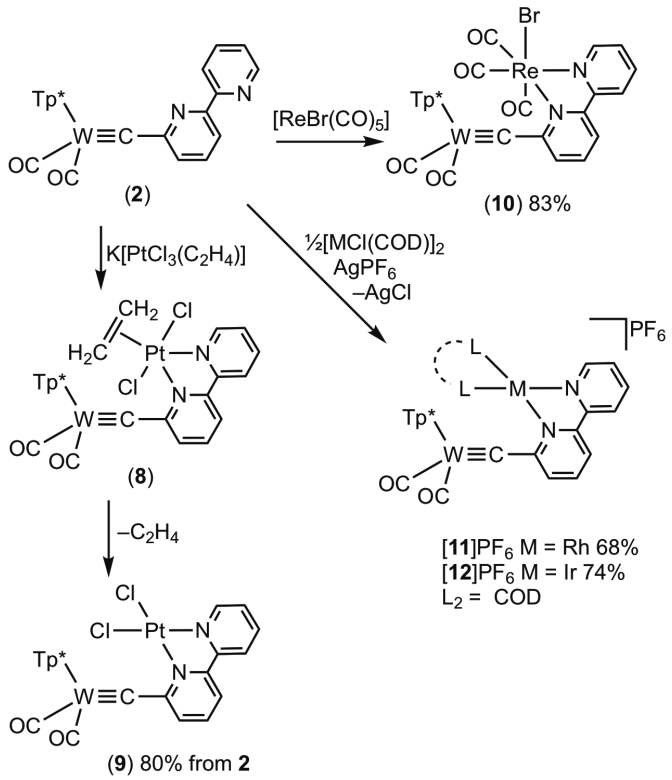


Figure 6. Molecular structure of **7** in a crystal of **7**.$(CH_2Cl_2)_2$ (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms and solvent omitted for clarity). Only one-half of the centrosymmetric molecule is crystallographically unique. Selected distances [Å] and angles [°]: W1–C1 1.890(4), C1–C4 1.474(5), W1–Au1 2.7847(2), C1–Au1 2.025(4), Au1–Cl1 2.2905(10), W1–C1–C4 147.3(3), W1–Au1–Cl1 151.17(3), C1–Au1–Cl1 166.1(1).

For the bipyridyl bis(carbyne) complex **3**, arranging the bipyridyl nitrogens onto the same edge (*S-cis*) orients the bulky 'W$(CO)_2$(Tp*)' groups together such that they provide considerable steric protection (Fig. 4). This provides a nigh insurmountable barrier for metal coordination to the bipyridyl nitrogens — one which we have not yet managed to overcome. The mono(carbyne) complex **2**, however, offers greater accessibility to its nitrogen donor atoms such that coordinated derivatives could be obtained. Whilst no reaction occurs with [$PtCl_2(NCMe)_2$], a reaction quickly ensues between **2** and K[$PtCl_3(C_2H_4)$]·H_2O (Zeise's salt) to give a dirty-brown mixture of two products which foiled any attempt at bulk separation. Crystallisation of this mixture at low temperature allowed orange blocks to be selected from the crude material which were determined by X-ray crystallography to be the five-coordinate platinum(II) complex [6-{(Tp*)$(CO)_2$W≡C}bipy{$PtCl_2(\eta$-$C_2H_4)$}] (**8**) (Scheme 3). Retention of the ethene ligand was also observed in the comparable reaction with pyridylcarbynes (i.e., monodentate metallo-ligands) but was not necessarily expected in this case (despite limited precedent for five-coordinate Pt(II) ethylene complexes[17]) in light of the presumed lability of the ethene ligand and the predilection of platinum(II) for four-coordinate geometries. Indeed, on standing for prolonged periods at room temperature or refluxing briefly in $CHCl_3$/ethanol a bright green product precipitates and was determined to be the four-coordinate derivative [6-{(Tp*)$(CO)_2$W≡C}bipy{$PtCl_2$}] (**9**), formed in good yield by loss of the ethylene ligand.

Complex **9** was found to be profoundly insoluble in all common organic solvents, with dichloromethane being the only solvent in which its sparing solubility allowed at least some spectroscopic data to be acquired. The infrared and (limited) NMR data for **9** differ little from the 'free ligand' **2** and indicate that bipyridyl coordination has little influence on the electronic environment at tungsten.



Scheme 3. Metal coordination to the bipyridyl moiety of bipyridylcarbynes.

The molecular structures of **8** and **9** (Figures 7 and 8, respectively) reveal that accommodating the platinum metal and its ancillary ligands entails further bending of the W≡C–C angles away from linearity (167.2(5)˚ and 164.6(3)˚, respectively, *cf*. 173.3(5)˚ in **2**), although the tungsten–carbon triple bond distances are not unduly influenced and remain crystallographically identical to that of **2**. The five-coordinate Pt(II) centre in **8** has approximately trigonal bipyramidal geometry, the ethene ligand is oriented into the cleft between pyrazolyl groups of the Tp* ligand. Loss of ethene to give **9** results in a rearrangement to an approximately square-planar platinum(II) geometry with a chloride now occupying the cleft between pyrazolyl groups. Platinum and its four ligand donors are essentially coplanar (largest deviation from the Pt1, N7, N8, Cl1, Cl2 least-squares plane of 0.07 Å by Pt1) but the aromatic bipyridyl rings are surprisingly puckered. The two C_5N least-squares planes subtend an angle of 18.4˚, which is amongst the largest reported.[18] This distortion is presumably the result of steric pressures between the ancillary ligands of both metals overwhelming the electronic preference for planarity.

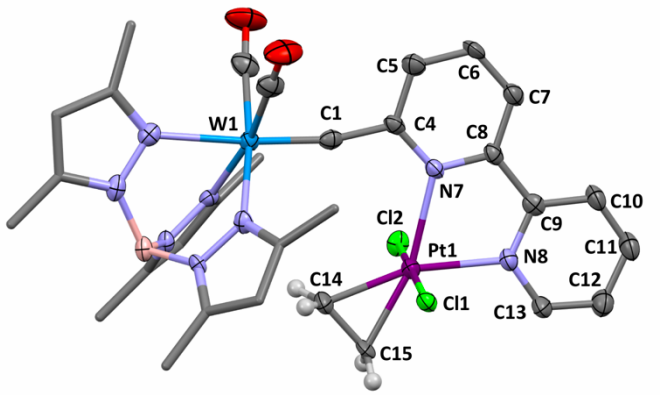


Figure 7. Molecular structure of **8** (50% displacement ellipsoids, pyrazolyl groups simplified, most hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.832(7), C1–C4 1.448(9), Pt1–N7 2.292(5), Pt1–N8 2.187(5), Pt1–C14 2.060(6), Pt1–C15 2.054(6), Pt1–Cl1 2.3447(17), Pt1–Cl2 2.3154(16), W1–C1–C4 167.2(5), N7–Pt1–N8 72.9(2).

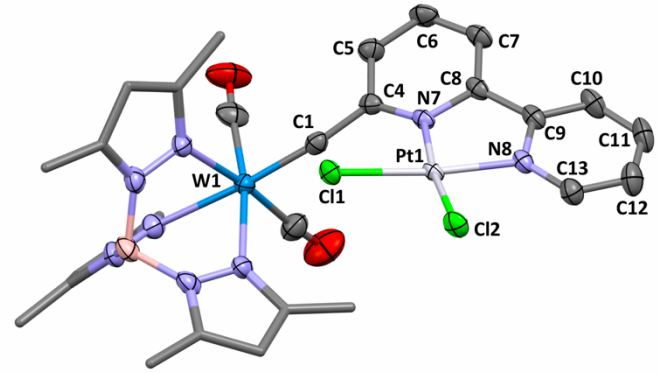


Figure 8. Molecular structure of **9**·$CHCl_3$ (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms and solvent omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.833(4), C1–C4 1.440(5), Pt1–N7 2.034(3), Pt1–N8 2.000(3), Pt1–Cl1 2.2825(8), Pt1–Cl2 2.2977(8), W1–C1–C4 164.6(3), N7–Pt1–N8 81.17(11).

Metallation of the bipyridyl moiety is not limited to platinum and treatment of **2** with $[ReBr(CO)_5]$ in refluxing toluene results in displacement of two of the rhenium carbonyl ligands and formation of [6-{(Tp*)$(CO)_2$W≡C}bipy{$ReBr(CO)_3$}] (**10**) as a lime-green solid in good yield (Scheme 3). A total of four strong carbonyl absorbances were identified in the infrared spectrum of **10** and the NMR spectroscopic data (collected in CD_2Cl_2 due to the poor solubility in $CDCl_3$) confirmed that each Tp* proton and carbon environment is distinct (i.e., there is no longer a mirror plane in the molecule). The carbyne carbon resonates at δ_C = 265.6 in the $^{13}C\{^1H\}$ NMR spectrum, a shift of *ca* 10 ppm up-field from the "free ligand" **2**. The molecular structure of **10** has been determined and structural data are summarised in Figure 9. Nonetheless, it is worth noting that the steric pressures operating in **10** result in substantial distortion of the W≡C–C angle from linearity (157.8(5)˚) in order to accommodate rhenium and its ancillary ligands, although (in contrast to **9**) the bipyridyl rings themselves are essentially coplanar.

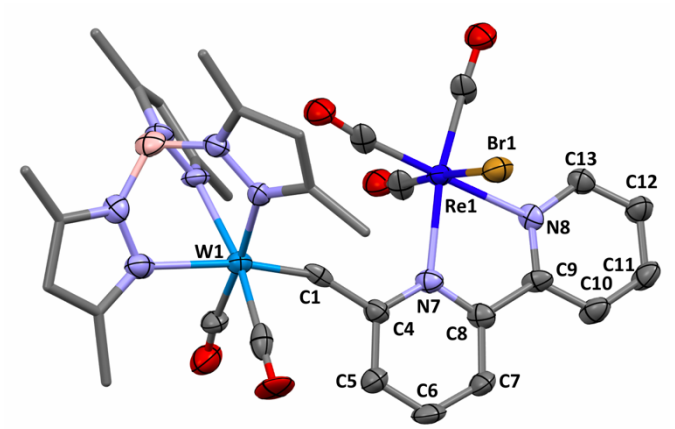


Figure 9. Molecular structure of **10** in a crystal of **10**·CH_2Cl_2 showing 50% displacement ellipsoids. Pyrazolyl groups are simplified, hydrogen atoms and solvent are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.838(4), C1–C4 1.443(5), Re1–N7 2.221(3), Re1–N8 2.162(3), W1–C1–C4 158.5(3), N7–Re1–N8 75.43(11).

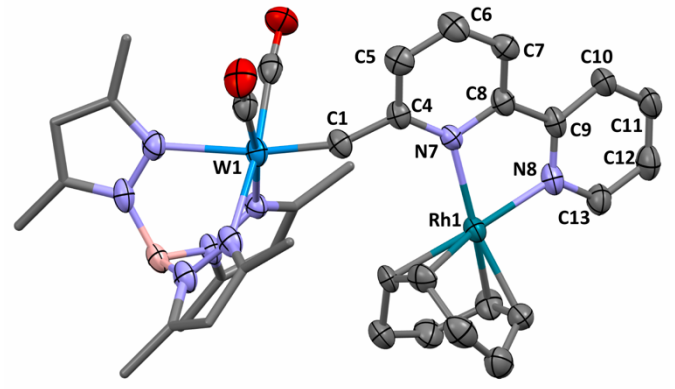


Figure 10. Molecular structure of the cation of [**11**]PF_6 in a crystal (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms and counter anion omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.838(6), C1–C4 1.441(8), Rh1–N7 2.164(4), Rh1–N8 2.089(5), W1–C1–C4 160.0(5), N7–Rh1–N8 78.66(18).

Finally, treatment of **2** with $[M_2(\mu\text{-}Cl)_2(COD)_2]$ (M = Rh, Ir; COD = η^4-cycloocta-1,5-diene) and $AgPF_6$ rapidly furnishes the cationic derivatives [6-{(Tp*)$(CO)_2$W≡C}bipy{M(COD)}]PF_6 (M = Rh [**11**]PF_6; M = Ir [**12**]PF_6) as yellow-brown and green solids, respectively. Metallation once again has little impact on NMR resonances associated with the 'W$(CO)_2$(Tp*)' moiety, though the carbyne carbons again resonate *ca*. 10 ppm up-field (δ_C = 262.3 and 261.2, respectively) in the $^{13}C\{^1H\}$ NMR spectra compared to uncomplexed **2**. Signals related to the cyclooctadiene ligand are too broadened to be confidently assign for the rhodium complex [**11**]PF_6, presumably due to a combination of fluxional coordination character and coupling with the spin-active ^{103}Rh (I = ½, 100% abundance). Broad resonances could, however, be identified in the spectra for [**12**]PF_6 and confirm that the cycloocta-1,5-diene presents with two distinct =CH and four distinct CH_2 environments. The molecular structures of [**11**]PF_6 and [**12**]PF_6 (Figures 10 and 11, respectively) reveal that twisting of their bipyridyl rings is

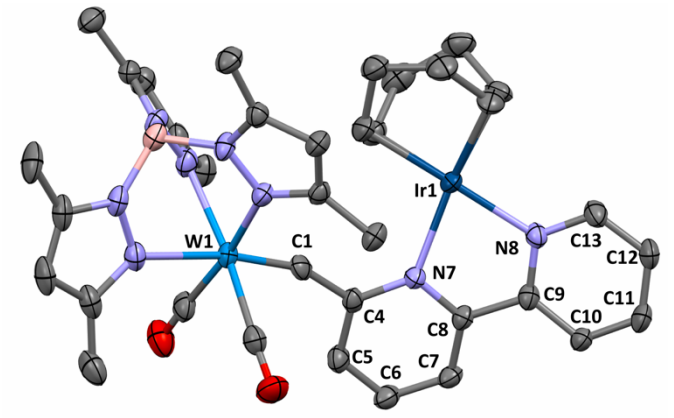


Figure 11. Molecular structure of the cation of [**12**]PF_6 showing 50% displacement ellipsoids. Pyrazolyl groups are simplified, hydrogen atoms and solvent are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.833(5), C1–C4 1.450(7), Ir1–N7 2.139(4), Ir1–N8 2.080(4), W1–C1–C4 160.2(4), N7–Ir1–N8 78.82(16).

required in both cases to accommodate the cyclooctadiene ligand near the sterically protuberant Tp* and carbonyl ligands on tungsten (angle between C_5N least-squares planes is 17.8° and 18.6° in [**11**]PF_6 and [**12**]PF_6, respectively). This also requires substantial bending of the W≡C–C angle away from linearity (W1–C1–C4 157.8(5) and 160.2(4)°, respectively); complexes **10**–**12** possess some of the most bent carbyne angles reported.[1d]

Extensive solution infrared data (ν_{CO}) for an wide range of complexes of the form [M(CR)$(CO)_2$(L)] (M = Cr, Mo, W; L = Tp, Tp*) have been previously collated.[1d] Within the largest neutral 'W(Tp*)' sub-set series, the coupled symmetric (1953-1999 cm^{-1}) and antisymmetric (1862-1918 cm^{-1}) oscillators provide a direct indication of variation in the tungsten π-basicity as a response to changes in the carbyne substituent R. For meaningful inferences to be made, it is essential that the same solvent is employed since considerable solvent dependence is often observed and accordingly the majority of published data are derived from dichloromethane solutions. Narrower lines are typically observed in alkane solvents, however the complexes are less generally soluble. For the compounds described herein, it is clear that appending a proton ([**4**]$^+$, [**5**]$^+$) to the remote bipyridyl donors results in a substantial increase (20-35 cm^{-1}) in the ν_{CO} frequencies, indicating a substantial change on the electron density at the tungsten centres. This may be explained by considering an *N*-heterocyclic vinylidene contribution to the resonance description[12] for which a positive charge is assigned to tungsten. In contrast, coordination of neutral 'PtCl_2' in **9** results in a barely discernible change (1982, 1882 cm^{-1}). On that basis, in the case of **10**, for which multiple ν_{CO} absorptions are observed, we are inclined to assign the W$(CO)_2$ vibrational modes to the bands at 1985 and 1898 cm^{-1} given that [ReBr$(CO)_3$(bipy)] has absorptions at 2025, 1923 and 1900 cm^{-1} (CH_2Cl_2), i.e., we assume negligible coupling operates between remote WCO and ReCO oscillators but that one *fac*-Re$(CO)_3$ mode overlaps with the antisymmetric W$(CO)_2$ mode. For the complexes [**11**]$^+$ and [**12**]$^+$, the ν_{CO} frequencies are somewhat (ca 15-19 cm^{-1}) higher than those for **2**, **9** or **10** but the shift is not as pronounced as for simple protonation (i.e., [**4**]$^+$ and [**5**]$^+$). Taking these observations together, we might surmise that the

electronic impact of addition of a proton (a purely σ-Lewis acid) is manifested at the tungsten centre. For the coordination of neutral metal-ligand fragments, however, the π-acidity of the bipy ligand helps to off-set this. Such retrodonation would be expected to be less effective from the cationic iridium and rhodium centres in [**11**]$^+$ and [**12**]$^+$ resulting in a more pronounced increase in ν_{CO} frequencies. Although a similar increase is observed upon appending 'AuCl' fragments to the W≡C linkages of **2** and **3**, direct comparison is less prudent due to the change in geometry including an increase in coordination number at tungsten in **6** and **7**.

Carbon-13 NMR chemical shifts for carbyne ligands are responsive to variations in the nature of substituents, e.g., positively mesomeric substituents from groups 15-17 tend to result in resonances appearing at higher frequency than hydrocarbyl-substituted alkylidynes. For benzylidynes, the observed isotropic chemical shift comprises three anisotropic components, viz δ_{33} (by far the smallest) directed along the metal-carbon vector, orthogonal to δ_{11} and δ_{22} with δ_{11} being orthogonal to the aryl ring and typically having the largest magnitude due to paramagnetic contributions associated with conjugation of the M≡C* orbital to the aromatic ring.[19] The bipyridyl carbynes **2** and **3** may therefore be considered as special cases of benzylidynes but uniquely present the opportunity to moderate bonding in one plane by appending Brønsted or Lewis acids to the nitrogen lone pairs without the need for variations in the carbyne geometry. Because δ_{22} typically contributes less to δ_{iso}, any changes to this in plane bonding would be expected to impact less than variation in δ_{11}, which appears to be the case. Thus conversion of **2** to [**4**]$^+$, **10**, [**11**]$^+$ or [**12**]$^+$ is accompanied by only a rather modest ($\Delta\delta_{iso}$ ~ 10-14 ppm) *increase* in shielding of the carbyne nuclei corresponding to an increase in the energy gap between occupied and unoccupied in plane orbitals).

Conclusions

The synthesis of new bipyridyl-functionalised carbyne 'metalloligands' has been achieved by a Pd^0/Au^I-mediated coupling between the stannylcarbyne [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**1**) and 6-bromo-2,2'-bipyridyl or 6,6'-dibromo-2,2'-bipyridyl. This strategy offers considerable generality, potentially allowing for a wide range of carbynes with previously inaccessible functional substituents to be prepared. The new 'metalloligands' reported herein undergo protonation on the bipyridyl nitrogens, and metallation at either the tungsten–carbon triple bond or the bipyridyl nitrogen donors to give bi- tri- and tetrametallic derivatives. The reported results are suggestive of broad scope for future work, ranging from application of the 'metallo-ligands' as supports for (hetero)polymetallic complexes or extended frameworks, to utilisation of the strong tungsten–ligand interaction for moderation or perhaps even enhancement of electronic, optical and/or photo-physical properties of the derived complexes. Exploration of these and other possibilities form the basis of ongoing work we hope to report on shortly.

Experimental

Unless otherwise stated, experimental work was carried out at room temperature under a dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques with dried and degassed solvents.

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{19}F at 376.5 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C at 176.1 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent peak, or external references ($CFCl_3$ for $^{19}F\{^1H\}$, 85% H_3PO_4 in H_2O for $^{31}P\{^1H\}$), 1.2M Na_2PtCl_6 in H_2O for ^{195}Pt). The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. 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 ^{1}H and $^{13}C\{^1H\}$ NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The ^{1}H NMR spectra of new compounds reported here include resonances in the region $4 < \delta_H < 5$ ppm due to the BH hydrogen of the Tp* ligand which are broad due to the quadrupolar nature of $^{10/11}$B nuclei, compromising the precision of both the chemical shift and associated integrals. Being remote from the metal centre, in our experience these are of limited diagnostic value and are not listed.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br (broad). Elemental microanalytical data were provided the London Metropolitan University. High-resolution 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 or SuperNova CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) and the CrysAlis PRO software.[20] The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXS or SHELXT and SHELXL programs.[21] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[22]

The synthesis of [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**2**)[10b] has been described previously. The reagents 6-bromo-2,2'-bipyridine,[23] 6,6'-dibromo-2,2'-bipyridine,[24] [AuCl(SMe$_2$)],[25] K[PtCl$_3$(C$_2$H$_4$)].H$_2$O,[26] [RhCl(COD)]$_2$,[27] and [IrCl(COD)]$_2$[28] were prepared by literature methods.

[6-{(Tp*)(CO)$_2$W≡C}bipy] (2). A solution of [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**1**) (500 mg, 0.596 mmol), 6-bromo-2,2′-bipyridine (71 mg, 0.30 mmol), [Pd(PPh$_3$)$_4$] (69 mg , 0.060 mmol) and [AuCl(SMe$_2$)] (17 mg, 0.058 mmol) in toluene (30 mL) was heated under reflux for 14 h, during which time the solution turned dark red. The solvent was then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting with CH_2Cl_2. A slow-moving red band was collected and the volatiles were removed under reduced pressure to give a dark red solid of pure **2** (360 mg, 0.511 mmol, 86%). IR (CH_2Cl_2, cm^{-1}): 1981s, 1890s ν_{CO}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ_H = 2.40 (s, 3H, pzC*H$_3$*), 2.43 (s, 6H, pzC*H$_3$*), 2.53 (s, 3H, pzC*H$_3$*), 2.71 (s, 6H, pzC*H$_3$*), 5.85 (s, 1H, pzC*H*), 5.96 (s, 2H, pzC*H*), 7.29 (t′, $^3J_{HH}$ = 6.2, 1H, *bipy*), 7.46 (d, $^3J_{HH}$ = 7.7, 1H, *bipy*), 7.80 (m, 2H, *bipy*), 8.39 (d, $^3J_{HH}$ = 7.7, 1H, *bipy*), 8.53 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.68 (d, $^3J_{HH}$ = 4.2, 1H, *bipy*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ_C = 12.7, 15.3, 16.8 (pz*C*H$_3$), 106.6, 106.8 (pz*C*H), 118.9, 121.5, 123.8, 123.8, 136.7, 136.9 (*bipy*), 144.5, 145.3 (pz*C*CH$_3$), 148.9 (*bipy*), 152.2, 152.4 (pz*C*CH$_3$), 155.5, 156.3 (*bipy*), 164.5 (W≡C*C*, $^2J_{CW}$ = 45), 224.2 (W*C*O, $^1J_{CW}$ = 164), 276.1 (W≡*C*, $^1J_{CW}$ = 190). MS (ESI, *m/z*): Found: 705.20858. Calcd for $C_{28}H_{30}{}^{11}BN_8O_2{}^{184}W$ [M+H]$^+$: 705.20890. Anal. Found: C, 47.61; H, 4.03; N, 15.75. Calcd for $C_{28}H_{29}BN_8O_2W$: C, 47.75; H, 4.15; N, 15.91%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 °C. *Crystal data for* $C_{28}H_{29}BN_8O_2W$ (M_w =704.25 gmol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 10.7913(3), *b* = 19.8212(7), *c* = 22.1761(9) Å, *α* = 112.852(4)°, *β* = 94.189(3)°, *γ* = 98.719(3)°, *V* = 4275.0(3) Å^3, *Z* = 6, *T* = 150.0(1) K, μ(Cu Kα) = 7.841 mm^{-1}, D_{calc} = 1.641 Mgm^{-3}, 24097 reflections measured (7.808° ≤ 2Θ ≤ 133.192°), 14957 unique (R_{int} = 0.0405, R_{sigma} = 0.0875) which were used in all calculations. The final R_1 was 0.0376 ($I > 2\sigma(I)$) and wR_2 was 0.0812 (all data) for 1111 refined parameters with 0 restraints. CCDC 1968076.

[6,6′-{(Tp*)(CO)$_2$W≡C}$_2$bipy] (3). A solution of [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**1**) (500 mg, 0.596 mmol), 6,6′-dibromo-2,2′-bipyridine (92 mg, 0.29 mmol), [Pd(PPh$_3$)$_4$] (69 mg, 0.060 mmol) and [AuCl(SMe$_2$)] (17 mg, 0.058 mmol) in toluene (30 mL) was heated under reflux for 14 h, during which time the solution turned dark red. The solvent was then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting with CH_2Cl_2. A slow-moving, dark red band (sometimes appearing orange on the column) was collected and the volatiles were removed under reduced pressure to give a dark red solid of pure **3** (248 mg, 0.198 mmol, 66%). IR (CH_2Cl_2, cm^{-1}): 1981s, 1890s ν_{CO}. ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ_H = 2.36 (s, 6H, pzC*H$_3$*), 2.39 (s, 12H, pzC*H$_3$*), 2.48 (s, 6H, pzC*H$_3$*), 2.65 (s, 12H, pzC*H$_3$*), 5.81 (s, 2H, pzC*H*), 5.92 (s, 4H, pzC*H*), 7.38 (d, $^3J_{HH}$ = 7.7, 2H, *bipy-5,5′*), 7.72 (t′, $^3J_{HH}$ = 7.6, 2H, *bipy-4,4′*), 8.41 (d, $^3J_{HH}$ = 7.8, 2H, *bipy-3,3′*). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 15.3, 16.8 (pz*C*H$_3$), 106.7, 106.8 (pz*C*H), 119.4 (*bipy-3,3′*), 123.9 (*bipy-5,5′*), 136.5 (*bipy-4,4′*), 144.5, 145.3, 152.3, 152.5 (pz*C*CH$_3$), 155.5 (*bipy-2,2′*), 164.3 (*bipy-6,6′*), 224.2 (W*C*O, $^1J_{CW}$ = 164), 276.5 (br, W≡*C*). MS (ESI, *m/z*): Found: 1253.3427. Calcd for $C_{46}H_{51}{}^{11}B_2N_{14}O_4{}^{184}W_2$ [M+H]$^+$: 1253.3428. Anal. Found: C, 44.01; H, 3.95; N, 15.65. Calcd for $C_{46}H_{50}B_2N_{14}O_4W_2$: C, 44.12; H, 4.02; N, 15.66%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 ˚C. *Crystal data for* $C_{46}H_{50}B_2N_{14}O_4W_2$ (*M* =1252.32 g.mol^{-1}): orthorhombic, space group Aea2 (no. 41), *a* = 16.0592(2), *b* = 26.2160(3), *c* = 27.9017(3) Å, *V* = 11746.8(2) Å^3, *Z* = 8, *T* = 150.0(1) K, μ(Cu Kα) = 7.525 mm^{-1}, D_{calc} = 1.416 Mgm^{-3}, 12098 reflections measured (9.258° ≤ 2Θ ≤ 141.916°), 7573 unique (R_{int} = 0.0163, R_{sigma} = 0.0273) which were used in all calculations. The final R_1 was 0.0317 ($I > 2\sigma(I)$) and wR_2 was 0.0944 (all data) for 628 refined parameters with 1 restraint. CCDC 1968077.

[6-{(Tp*)(CO)$_2$W≡C}bipy(H)]BF$_4$ [4]BF$_4$. To a solution of **2** (50 mg, 0.071 mmol) in diethyl ether (10 mL) was added HBF$_4$·Et$_2$O (one drop). Stirring was continued for 2 minutes, after which time volume of diethyl ether was reduced to *ca*. 1 mL and *n*-pentane (10 mL) was added. The resulting precipitate was collected by filtration, washed with acidified *n*-pentane (3 x 5 mL) to give a yellow-green solid of [**4**]BF$_4$ (28 mg, 0.035 mmol, 50%). IR (CH_2Cl_2 + trace HBF$_4$, cm^{-1}): 2010s, 1923s ν_{CO}. Due to how prone this complex is to deprotonation, the NMR sample used was prepared by direct addition of one drop of HBF$_4$·Et$_2$O to **2** in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ_H = 2.36 (s, 3H, pzC*H$_3$*), 2.41 (s, 6H, pzC*H$_3$*), 2.46 (s, 3H, pzC*H$_3$*), 2.56 (s, 3H, pzC*H$_3$*), 5.82 (s, 1H, pzC*H*), 5.96 (s, 2H, pzC*H*), 7.47–7.57 (m, 2H, *bipy*), 8.0–8.16 (m, 2H, *bipy*), 8.50 (d, $^3J_{HH}$ = 7.8, 1H, *bipy*), 8.58 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.74 (d, $^3J_{HH}$ = 4.4, 1H, *bipy*). N*H* not observed. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 12.8, 15.4,16.9 (pz*C*H$_3$), 107.0, 107.2 (pz*C*H), 120.0, 123.3, 125.9 (2C), 140.4, 141.0 (br s, *bipy*), 145.1, 145.9 (pz*C*CH$_3$), 147.6 (*bipy*), 152.0, 152.7 (pz*C*CH$_3$), 161.4 (br, W≡C*C*), 223.8 (W*C*O, $^1J_{CW}$ = 162), 266.2 (W≡*C*). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –152.1 (s, B*F$_4$*). MS (ESI, *m/z*): Found: 705.2093. Calcd for $C_{28}H_{30}{}^{11}BN_8O_2{}^{184}W$ [M–BF$_4$]$^+$: 705.2094. Satisfactory elemental microanalytical data not acquired presumably due to the complex being only stable in the presence of acid. Found: C, 41.54; H, 3.49; N, 12.84. Calcd for $C_{28}H_{30}B_2F_4N_8O_2W$: C, 42.46; H, 3.84; N, 14.15%. A crystal suitable for structure determination was grown by slow evaporation of an acidified CH_2Cl_2/ethanol mixture at 4 °C and proved to be an ethanol solvate. *Crystal data for* $C_{30}H_{36}B_2F_4N_8O_3W$ (M_w =838.14 gmol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 10.9320(4), *b* = 12.4024(5), *c* = 13.3168(5) Å, *α* = 91.062(3)°, *β* = 106.316(3)°, *γ* = 100.294(3)°, *V* = 1700.40(12) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(Mo Kα) = 3.463 mm^{-1}, D_{calc} = 1.637 Mgm^{-3}, 14832 reflections measured (6.696° ≤ 2Θ ≤ 57.908°), 7151 unique (R_{int} = 0.0337, R_{sigma} = 0.0567) which were used in all calculations. The final R_1 was 0.0337 (I > 2σ(I)) and wR_2 was 0.0650 (all data) for 449 refined parameters with 0 restraints. CCDC 1968078.

[6,6′-{(Tp*)(CO)$_2$W≡C}$_2$bipy(H)]BF$_4$ [5]BF$_4$. To a solution of **3** (50 mg, 0.040 mmol) in diethyl ether (10 mL) was added HBF$_4$·Et$_2$O (one drop). Stirring was continued for 2 minutes, after which time the resulting yellow precipitate was collected by filtration and washed with acidified diethyl ether (3 x 5 mL) to give a yellow solid of [**5**]BF$_4$ (48 mg, 0.036 mmol, 90%). IR (CH_2Cl_2, cm^{-1}): 2010s, 1989s, 1924s, 1898s ν_{CO}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ_H = 2.36 (s, 6H, pzC*H$_3$*), 2.40 (s, 30H, pzC*H$_3$*), 5.81 (s, 2H, pzC*H*), 5.86 (br s, 4H, pzC*H*), 7.30–8.90 (several br and m resonances, 7H, *bipy* & N*H*). ^{13}C{^{1}H} NMR (101 MHz,

$CDCl_3$, 25 °C): δ_C = 12.8, 12.8, 15.3, 16.8, 106.9, 107.2 (br, pz*C*H), 128.0 (t', *J* = 5.5, *bipy*), 130.0 (*bipy*), 135.3 (t', *J* = 6.0, *bipy*), 145.0, 152.0, 152.8 (br, pz*C*CH_3), 223.3 (*C*O). The breadth of signals resulting from fluxional protonation prohibited confident assignment of other signals. The reason two of these signals appear as apparent triplets is unclear, however we suspect ion-pairing with the BF_4^- counter anion may play a role. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –153.1 (s, B*F*$_4$). MS (ESI, *m/z*): Found: 1253.3435. Calcd for $C_{46}H_{51}{}^{11}B_2N_{14}O_4{}^{184}W_2$ $[M–BF_4]^+$: 1253.3428. Anal. Found: C, 41.09; H, 3.76; N, 14.52. Calcd for $C_{46}H_{51}B_3F_4N_{14}O_4W_2$: C, 41.23; H, 3.84; N, 14.63%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 °C and proved to be a dichloromethane disolvate. *Crystal data for* $C_{48}H_{55}B_3Cl_4F_4N_{14}O_4W_2$ (M_w =1509.99 gmol^{-1}): monoclinic, space group *P2*$_1$/*c* (no. 14), *a* = 17.5492(6), *b* = 20.7960(8), *c* = 16.0536(5) Å, *β* = 90.562(3)°, *V* = 5858.5(4) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(Mo Kα) = 4.174 mm^{-1}, D_{calc} = 1.712 Mgm^{-3}, 32573 reflections measured (6.602° ≤ 2Θ ≤ 57.992°), 12503 unique (R_{int} = 0.0410, R_{sigma} = 0.0531) which were used in all calculations. The final R_1 was 0.0336 (I > 2σ(I)) and wR_2 was 0.0744 (all data) for 678 refined parameters with 0 restraints. CCDC 1968079.

[6-{(Tp*)(CO)$_2$W(AuCl)(μ-C)}bipy] (6). To a flask containing **2** (25 mg, 0.035 mmol) and [AuCl(SMe$_2$)] (11 mg, 0.037 mmol) was added CH_2Cl_2 (2 mL) and the mixture was stirred for 5 min. After this time, the solution was filtered through diatomaceous earth (washed with CH_2Cl_2 until the washings ran clear), petroleum spirits (40–60 °C, 20 mL) was added to the filtrate and removal of the CH_2Cl_2 under reduced pressure gave an orange precipitate, which was collected by filtration to give an orange solid of **6** (27 mg, 0.029 mmol, 82%). IR (CH_2Cl_2, cm^{-1}): 2014s, 1933s ν_{CO}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ_H = 2.38 (s, 3H, pzC*H*$_3$), 2.42 (s, 6H, pzC*H*$_3$), 2.48 (s, 6H, pzC*H*$_3$), 2.67 (s, 3H, pzC*H*$_3$), 5.97 (s, 2H, pzC*H*), 5.98 (s, 1H, pzC*H*), 7.29–7.35 (m, *bipy*), 7.84 (t', $^3J_{HH}$ = 7.9, 1H, *bipy*), 7.86–7.93 (m, 2H, *bipy*), 8.43 (d, $^3J_{HH}$ = 7.7, 1H, *bipy*), 8.65 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.66–8.70 (m, 1H, *bipy*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 13.2, 15.8, 17.6 (pz*C*H$_3$), 107.8, 108.4 (pz*C*H), 121.3, 121.8, 122.3, 124.2, 137.5 (2C, *bipy*), 145.8, 146.3 (pz*C*CH$_3$), 148.7 (*bipy*), 152.4, 153.5 (pz*C*CH$_3$), 155.6 (*bipy*), 155.9 (br. *bipy)* 163.1 (W≡C*C*), 216.5 (W*C*O, $^1J_{CW}$ = 154), 262.2 (W≡*C*). MS (ESI, *m/z*): Found: 937.1447. Calcd for $C_{28}H_{30}Au^{11}B^{35}ClN_8O_2{}^{184}W$ $[M+H]^+$: 937.1447. Found: C, 30.30; H, 2.87; N, 9.22. Calcd for $C_{28}H_{30}AuBCl_2F_4N_8O_2W.3(CH_2Cl_2)$: C, 30.32; H, 2.96; N, 9.1%. Crystals suitable for structure determination were grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 ˚C. *Crystal data for* $C_{28}H_{29}BN_8O_2ClWAu$ (*M* =936.67 g.mol^{-1}): monoclinic, space group P2$_1$/n (no. 14), *a* = 10.1932(2), *b* = 15.8341(4), *c* = 18.7606(4) Å, *β* = 90.182(2)°, *V* = 3027.95(12) Å^3, *Z* = 4, *T* = 293(2) K, μ(CuKα) = 17.043 mm^{-1}, *Dcalc* = 2.055 g.cm^{-3}, 8792 reflections measured (7.306° ≤ 2Θ ≤ 133.176°), 5307 unique (R_{int} = 0.0261, R_{sigma} = 0.0416) which were used in all calculations. The final R_1 was 0.0351 (I > 2σ(I)) and wR_2 was 0.0892 (all data) for 389 refined parameters with 1 restraint. CCDC 1968080.

[6,6'-{(Tp*)(CO)$_2$W(AuCl)(μ-C)}$_2$bipy] (7). To a flask containing **3** (20 mg, 0.016 mmol) and [AuCl(SMe$_2$)] (10 mg, 0.034) was added CH_2Cl_2 (2 mL) and the mixture was stirred for 10 min. After this time, the solution was filtered through diatomaceous earth (washed with CH_2Cl_2 until the washings ran clear) and the filtrate was dried under reduced pressure to give an orange solid of pure **7** (19 mg, 0.011 mmol, 70%). IR (CH_2Cl_2, cm^{-1}): 2013s, 1937s ν_{CO}. ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ_H = 2.39 (s, 6H, pzC*H*$_3$), 2.43 (s, 12H, pzC*H*$_3$), 2.49 (s, 12H, pzC*H*$_3$), 2.69 (s, 6H, pzC*H*$_3$), 5.97 (s, 4H, pzC*H*), 5.99 (s, 2H, pzC*H*), 7.97 (br m, 4H, *bipy*), 8.64 (br, 2H, *bipy*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ_C = 12.9, 13.2, 14.2, 17.7 (pz*C*H$_3$), 107.9, 108.5 (pz*C*H), 122.1, 137.8 (br, *bipy*), 145.9, 146.4, 152.4, 153.7 (pz*C*CH$_3$), 216.6 (W*C*O). Other *bipy* and the W≡*C* resonances are presumably too broad to observe. MS (ESI, *m/z*): Found: 1739.1931. Calcd for $C_{46}H_{50}Au_2{}^{11}B_2{}^{35}Cl_2N_{14}O_4{}^{184}W_2Na$ $[M+Na]^+$: 1739.1952. Found: 1681.2343. Calcd for $C_{46}H_{50}Au_2{}^{11}B_2{}^{35}ClN_{14}O_4{}^{184}W_2$ $[M–Cl]^+$: 1681.2369. Found: C, 29.25; H, 2.99; N, 9.50%. Calcd for $C_{46}H_{50}Au_2B_2Cl_2N_{14}O_4W_2.(CH_2Cl_2)_4$: C, 29.20; H, 2.84, N, 9.53%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol solution at 4 ˚C and proved to be a dichloromethane disolvate. *Crystal data for* $C_{48}H_{54}Au_2B_2Cl_6N_{14}O_4W_2$ (M =1887.00 g.mol^{-1}): monoclinic, space group P2$_1$/n (no. 14), a = 14.5705(4), b = 12.1669(3), c = 19.1692(7) Å, β = 102.297(3)°, V = 3320.31(18) Å^3, Z = 2, T = 150.0(1) K, μ(MoKα) = 8.148 mm^{-1}, Dcalc = 1.887 g.cm^{-3}, 28425 reflections measured (6.698° ≤ 2Θ ≤ 52.744°), 6781 unique (R_{int} = 0.0281, R_{sigma} = 0.0268) which were used in all calculations. The final R_1 was 0.0230 (I > 2σ(I)) and wR_2 was 0.0534 (all data) for 369 refined parameters with 0 restraints. CCDC 1968081.

Structure determination of [6-{(Tp*)(CO)$_2$W≡C}bipy{PtCl$_2$(C$_2$H$_4$)}] (8). To a flask containing **2** (50 mg, 0.071 mmol) and K[PtCl$_3$(C$_2$H$_4$)]·H$_2$O (28 mg, 0.072) was added CH_2Cl_2 (5 mL) and ethanol (5 mL) and the mixture was stirred for 2 min. After this time, the solution was filtered through diatomaceous earth (washed with CH_2Cl_2 until the washings were clear) and the filtrate was dried under reduced pressure to give an orange-brown residue. This was recrystallised by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 ˚C. An orange block was selected from the crude mixture for crystallographic analysis. *Crystal data for* $C_{30}H_{33}BCl_2N_8O_2PtW$ (*M* =998.29 g.mol^{-1}): monoclinic, space group P2$_1$/n (no. 14), *a* = 9.5931(4), *b* = 19.9775(7), *c* = 17.8132(6) Å, *β* = 104.236(4)°, *V* = 3309.0(2) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 7.900 mm^{-1}, *Dcalc* = 2.004 g.cm^{-3}, 16935 reflections measured (6.818° ≤ 2Θ ≤ 57.732°), 6984 unique (R_{int} = 0.0363, R_{sigma} = 0.0503) which were used in all calculations. The final R_1 was 0.0375 (I > 2σ(I)) and wR_2 was 0.0878 (all data) for 413 refined parameters with 0 restraints. CCDC 1968082. Whilst the structural model for **8** is consistent with the synthetic sequence, it should be noted that, as one reviewer has observed, slightly improved residuals emerge from a model in which both heavy metals are assigned as being tungsten. We are unable to account for this crystallographic artefact.

[6-{(Tp*)(CO)$_2$W≡C}bipy(PtCl$_2$)] (9). To a flask containing **2** (50 mg, 0.071 mmol) and K[PtCl$_3$(C$_2$H$_4$)].H$_2$O (28 mg, 0.072) was added $CHCl_3$ (5 mL) and ethanol (5 mL) and the mixture was

heated under reflux for 30 min, during which time a lime green solid precipitated. This was collected by filtration and washed with ethanol (3 x 10 mL) and *n*-pentane (5 x 10 mL) to give a green solid of pure **9** (55 mg, 0.057 mmol, 80%). This complex was found to be insoluble in all common organic solvents and only very sparingly soluble in chloroform and dichloromethane, the latter of which was used for NMR experiments. As such, only limited data could be obtained. IR (CH_2Cl_2, cm^{-1}): 1982s, 1882s ν_{CO}. ^1H NMR (700 MHz, CD_2Cl_2, 25 °C): δ_H = 2.36 (s, 3H, pzC*H*$_3$), 2.41 (s, 3H, pzC*H*$_3$), 2.44 (s, 6H, pzC*H*$_3$), 2.74 (s, 6H, pzC*H*$_3$), 5.83 (s, 1H, pzC*H*), 5.99 (s, 2H, pzC*H*), 7.53 (t', $^3J_{HH}$ = 6.8, 1H, *bipy*), 7.66 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.2, 1H, *bipy*), 7.81 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 7.92 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.00 (t', $^3J_{HH}$ = 7.8, 1H, *bipy*), 8.12 (t'd, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.2, 1H, *bipy*), 9.66 (d, $^3J_{HH}$ = 5.9, 1H, *bipy*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ_C = 12.8, 12.9, 15.4, 17.7 (pz*C*H$_3$), 106.8, 107.1 (pz*C*H), 119.3, 123.1, 137.6, 139.2 (*bipy*), 145.2, 146.4, 152.3, 153.0 (pz*C*CH$_3$). MS (ESI, *m/z*): Found: 974.1594. Calcd for $C_{30}H_{32}{}^{11}B^{35}ClN_9O_2{}^{194}Pt^{184}W$ [M–Cl+CH_3CN]$^+$: 974.1595. Found: 991.0918. Calcd for $C_{28}H_{29}{}^{11}B^{35}Cl_2N_8O_2{}^{194}Pt^{184}WNa$ [M+Na]$^+$: 991.0916. Anal. Found: C, 34.54; H, 3.18; N, 11.51. Calcd for $C_{28}H_{29}BCl_2N_8O_2PtW$: C, 34.66; H, 3.01; N, 11.55%. A crystal suitable for structure determination was grown by slow evaporation of a chloroform solution and proved to be a chloroform solvate. *Crystal data for* $C_{29}H_{30}BCl_5N_8O_2PtW$ (*M* =1089.61 g.mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 17.2205(4), *b* = 12.6997(3), *c* = 17.2216(3) Å, *β* = 97.909(2)°, *V* = 3730.46(14) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 7.224 mm^{-1}, *Dcalc* = 1.940 g.cm^{-3}, 74931 reflections measured (6.848° ≤ 2Θ ≤ 52.744°), 7619 unique (R_{int} = 0.0311, R_{sigma} = 0.0153) which were used in all calculations. The final R_1 was 0.0208 (I > 2σ(I)) and wR_2 was 0.0476 (all data) for 434 refined parameters with 0 restraints. CCDC 1968083.

[6-{(Tp*)(CO)$_2$W≡C}bipy{ReBr(CO)$_3$}] (10). A solution of **2** (50 mg, 0.071 mmol) and [ReBr(CO)$_5$] (30 mg, 0.073 mmol) in toluene (20 mL) was heated under reflux for 1 h, during which time a lime green precipitate formed. The mixture was cooled to RT and the precipitate collected by filtration, washed with toluene (3 x 10 mL) and cold *n*-pentane (3 x 10 mL) and dried *in vacuo* to give a lime green solid of pure **10** (62 mg, 0.059 mmol, 83%). IR (CH_2Cl_2, cm^{-1}): 2025s, 1985s, 1926s, 1898s ν_{CO}. ^1H NMR (700 MHz, CD_2Cl_2, 25 °C): δ_H = 2.35 (s, 3H, pzC*H*$_3$), 2.41 (s, 3H, pzC*H*$_3$), 2.43 (s, 3H, pzC*H*$_3$), 2.48 (s, 3H, pzC*H*$_3$), 2.63 (s, 3H, pzC*H*$_3$), 2.66 (s, 3H, pzC*H*$_3$), 5.86 (s, 1H, pzC*H*), 5.98 (s, 1H, pzC*H*), 6.00 (s, 1H, pzC*H*), 7.48 (t', $^3J_{HH}$ = 6.8, 1H, *bipy*), 7.74 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 7.98 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.03 (t', $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.07 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.18 (d, $^3J_{HH}$ = 8.3, 1H, *bipy*), 9.03 (d, $^3J_{HH}$ = 6.0, 1H, *bipy*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ_C = 12.7, 12.8, 12.9, 15.5, 17.9, 18.3 (pz*C*H$_3$), 106.6, 106.7, 107.2 (pz*C*H), 120.6, 123.9, 127.1, 136.5, 138.2, 139.1 (*bipy*), 145.2, 145.4, 146.5, 151.9, 152.9, 153.0 (pz*C*CH$_3$), 153.3, 156.0, 156.5 (*bipy*), 168.0 (W≡C*C*), 189.8, 194.5, 197.5 (Re*C*O), 224.9, 225.0 (W*C*O), 265.6 (W≡*C*). MS (ESI, *m/z*): Found: 1055.0673. Calcd for $C_{31}H_{30}{}^{11}B^{79}BrN_8O_5{}^{187}Re^{184}W$ [M+H]$^+$: 1055.0634. Found: 1077.0496. Calcd for $C_{31}H_{29}{}^{11}B^{79}BrN_8O_5{}^{187}Re^{184}W$ [M+Na]$^+$: 1077.0454. Anal. Found: C, 35.37; H, 2.76; N, 10.54. Calcd for $C_{31}H_{29}BBrN_8O_5ReW$: C, 35.31; H, 2.77; N, 10.63%. A crystal suitable for structure determination was grown by slow evaporation of a CH_2Cl_2/ethanol mixture at 4 ˚C and proved to be a dichloromethane solvate. *Crystal data for* $C_{32}H_{31}BBrCl_2N_8O_5ReW$ (M_w =1139.32 gmol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 18.07780(10), *b* = 12.51640(10), *c* = 17.18700(10) Å, *β* = 97.4230(10)°, *V* = 3856.29(4) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(Cu Kα) = 14.379 mm^{-1}, D_{calc} = 1.962 Mgm^{-3}, 68065 reflections measured (8.616° ≤ 2Θ ≤ 141.452°), 7360 unique (R_{int} = 0.0393, R_{sigma} = 0.0162) which were used in all calculations. The final R_1 was 0.0246 (I > 2σ(I)) and wR_2 was 0.0650 (all data) for 480 refined parameters with 4 restraints. CCDC 1968084.

[6-{(Tp*)(CO)$_2$W≡C}bipy{Rh(COD)}]PF$_6$ [11]PF$_6$. A solution of **2** (50 mg, 0.071 mmol), [RhCl(COD)]$_2$ (18 mg, 0.037 mmol) and $AgPF_6$ (18 mg, 0.071 mmol) in dichloromethane (10 mL) stirred at RT for 30 min. After this time, the solution was filtered through diatomaceous earth, *n*-hexane was added and on slow removal of the CH_2Cl_2 under reduced pressure a yellow-brown precipitate formed. This was collected by filtration, washed with *n*-pentane (3 x 20 mL) and dried *in vacuo* to give a yellow solid of pure [**11**]PF_6 (51 mg, 0.048 mmol, 68%). IR (CH_2Cl_2, cm^{-1}): 1995s, 1907s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 25 °C): δ_H = 2.34 (s, 3H, pzC*H*$_3$), 2.39 (s, 3H, pzC*H*$_3$), 2.44 (s, 6H, pzC*H*$_3$), 2.70 (s, 6H, pzC*H*$_3$), 5.81 (s, 1H, pzC*H*), 6.04 (s, 2H, pzC*H*), 7.48 (d, $^3J_{HH}$ = 7.7, 1H, *bipy*), 7.56 (t', $^3J_{HH}$ = 6.7, 1H, *bipy*), 7.74 (d, $^3J_{HH}$ = 5.2, 1H, *bipy*), 8.04 (t', $^3J_{HH}$ = 7.7, 1H, *bipy*), 8.14 (t', $^3J_{HH}$ = 7.7, 1H, *bipy*), 8.24 (d, $^3J_{HH}$ = 7.7, 1H, *bipy*), 8.34 (d, $^3J_{HH}$ = 7.7, 1H, *bipy*). Resonances associated with the cyclooctadiene at *ca*. 1.6 and 4.7 ppm were too broad to confidently assign. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.8, 12.9, 15.4, 17.5 (pz*C*H$_3$), 29.8 (br, COD{*C*H$_2$}), 107.0, 107.3 (pz*C*H), 120.7, 124.5, 127.2, 132.5, 140.1, 141.2 (*bipy*), 145.3, 146.3 (pz*C*CH$_3$), 147.8, 152.0, 152.8 (*bipy*), 155.8, 156.6 (pz*C*CH$_3$), 167.9 (W≡C*C*), 223.3 (*C*O, $^1J_{CW}$ = 160), 262.3 (W≡*C*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ_P = –144.3 (septet, $^1J_{PF}$ = 712, *P*F$_6$). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –73.3 (d, $^1J_{FP}$ = 712, P*F*$_6$). MS (ESI, *m/z*): Found: 915.2014. Calcd for $C_{36}H_{41}{}^{11}BN_8O_2Rh^{184}W$ [M–PF_6]$^+$: 915.2021. Anal. Found: C, 40.66; H, 3.91; N, 10.50. Calcd for $C_{36}H_{41}BF_6N_8O_2PRhW$: C, 40.78; H, 3.90; N, 10.57%. A crystal suitable for structure determination was grown by slow evaporation of a $CHCl_3$/ethanol mixture at 4 ˚C and was found to be a chloroform hemisolvate. The solvent was, however, found to be highly disordered and was removed from the refinement using a solvent mask. *Crystal data for* $C_{36}H_{41}BF_6N_8O_2PRhW$ (M_w =1060.31 gmol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 12.8374(6), *b* = 13.7806(5), *c* = 14.5580(7) Å, *α* = 108.818(4)°, *β* = 110.939(4)°, *γ* = 105.013(4)°, *V* = 2062.60(18) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(Cu Kα) = 9.286 mm^{-1}, D_{calc} = 1.707 Mgm^{-3}, 11288 reflections measured (7.482° ≤ 2Θ ≤ 133.202°), 7246 unique (R_{int} = 0.0303, R_{sigma} = 0.0492) which were used in all calculations. The final R_1 was 0.0418 (I > 2σ(I)) and wR_2 was 0.1154 (all data) for 537 refined parameters with 6 restraints. CCDC 1968085.

[6-{(Tp*)(CO)$_2$W≡C}bipy{Ir(COD)}]PF$_6$ [12]PF$_6$. A solution of **2** (50 mg, 0.071 mmol), [IrCl(COD)]$_2$ (24 mg, 0.036 mmol) and $AgPF_6$ (18 mg, 0.071 mmol) in dichloromethane (10 mL) stirred at RT for 30 min. After this time, the solution was filtered through diatomaceous earth, *n*-hexane was added and on slow removal of the CH_2Cl_2 under reduced pressure a green

precipitate formed. This was collected by filtration, washed with *n*-pentane (3 x 20 mL) and dried *in vacuo* to give a green solid of pure [**12**]PF_6 (70 mg, 0.052 mmol, 74%). IR (CH_2Cl_2, cm^{-1}): 1996s, 1909s ν_{CO}. ^1H NMR (700 MHz, $CDCl_3$, 25 °C): δ_H = 1.37 (br, 2 x 2H overlapping, COD{C*H*$_2$}), 1.59 (br, 2H, COD{C*H*$_2$}), 2.01 (br, 2H, COD{C*H*$_2$}), 2.34 (s, 3H, pzC*H*$_3$), 2.38 (s, 3H, pzC*H*$_3$), 2.44 (s, 6H, pzC*H*$_3$), 2.64 (s, 6H, pzC*H*$_3$), 3.93 (br, 2H, COD{=C*H*}), 5.23 (br, 2H, COD{=C*H*}), 5.81 (s, 1H, pzC*H*), 6.02 (s, 2H, pzC*H*), 7.57 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 7.67 (t', $^3J_{HH}$ = 6.7, 1H, *bipy*), 8.02 (d, $^3J_{HH}$ = 5.1, 1H, *bipy*), 8.11 (t', $^3J_{HH}$ = 7.8, 1H, *bipy*), 8.23 (t', $^3J_{HH}$ = 7.8, 1H, *bipy*), 8.31 (d, $^3J_{HH}$ = 7.9, 1H, *bipy*), 8.42 (d, $^3J_{HH}$ = 8.1, 1H, *bipy*). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 25 °C): δ_C = 12.7, 12.9, 15.3, 17.6 (pz*C*H$_3$), 30.5, 30.5 (br, COD{*C*H$_2$}), 67.8, 75.1 (COD{=*C*H}), 107.0, 107.3 (pz*C*H), 120.9, 124.7, 127.8, 133.9, 140.5, 141.7 (*bipy*), 145.3, 146.4 (pz*C*CH$_3$), 147.6 (*bipy*), 151.9, 152.8 (pz*C*CH$_3$), 157.1, 157.4 (*bipy*), 168.6 (W≡C*C*), 223.6 (*C*O, $^1J_{CW}$ = 159), 261.2 (W≡*C*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ_P = –144.3 (septet, $^1J_{PF}$ = 714, *P*F_6). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ_F = –73.1 (d, $^1J_{FP}$ = 714, P*F*$_6$). MS (ESI, *m/z*): Found: 1003.2565. Calcd for $C_{36}H_{41}{}^{11}B^{193}IrN_8O_2{}^{184}W$ $[M–PF_6]^+$: 1003.2570. Anal. Found: C, 35.21; H, 2.67; N, 8.50. Calcd for $C_{36}H_{41}BF_6IrN_8O_2PW{\cdot}CHCl_3$: C, 35.02; H, 3.34; N, 8.83%. Crystals suitable for structure determination were grown by slow evaporation of a $CHCl_3$/*n*-heptane mixture and proved to be a solvate of chloroform, although the solvent was found to be highly disordered and necessitated elimination using a solvent mask. *Crystal data for* $C_{36}H_{41}BF_6IrN_8O_2PW$ (*M* =1149.60 g.mol^{-1}): triclinic, space group P-1 (no. 2), *a* = 12.8493(4), *b* = 13.8233(5), *c* = 14.5185(5) Å, *α* = 114.140(4)°, *β* = 106.442(3)°, *γ* = 103.774(3)°, *V* = 2064.34(14) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 12.194 mm^{-1}, *Dcalc* = 1.849 $g.cm^{-3}$, 12056 reflections measured (7.388° ≤ 2Θ ≤ 141.526°), 7682 unique (R_{int} = 0.0259, R_{sigma} = 0.0421) which were used in all calculations. The final R_1 was 0.0354 (I > 2σ(I)) and wR_2 was 0.0972 (all data) for 515 refined parameters with 1 restraint. CCDC 1968086.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. (a) A. J. L. Pombeiro, M. F. C. Guedes da Silva and R. A. Michelin, *Coord. Chem. Rev.*, 2001, **218**, 43-74; (b) R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145-180; (c) G. Jia, *Coord. Chem. Rev.*, 2007, **251**, 2167-2187; (d) L. M. Caldwell, *Adv. Organomet. Chem.*, 2008, **56**, 1-94; (e) C. Shi and G. Jia, *Coord. Chem. Rev.*, 2013, **257**, 666-701.
2. E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem., Int. Ed.*, 1973, **12**, 564-565.
3. (a) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 2935-2935; (b) R. R. Schrock, *Chem. Commun.*, 2005, 2773-2777.
4. M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74-83.
5. S. Chaona, F. J. Lalor, G. Ferguson and M. M. Hunt, *J. Chem. Soc., Chem. Commun.*, 1988, 1606-1608.
6. R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 5177-5179.
7. (a) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75-77; (b) L. Weber, G. Dembeck, R. Boese and D. Bläser, *Chem. Ber.*, 1997, **130**, 1305-1308; (c) L. Weber, G. Dembeck, R. Boese and D. Bläser, *Organometallics*, 1999, **18**, 4603-4607; (d) R. L. Cordiner, A. F. Hill, R. Shang and A. C. Willis, *Organometallics*, 2011, **30**, 139-144; (e) A. L. Colebatch and A. F. Hill, *J. Am. Chem. Soc.*, 2014, **136**, 17442-17445; (f) A. L. Colebatch, Y.-S. Han, A. F. Hill, M. Sharma, R. Shang and J. S. Ward, *Chem. Commun.*, 2017, **53**, 1832-1835; (g) B. J. Frogley, A. F. Hill, R. A. Manzano and M. Sharma, *Chem. Commun.*, 2018, **54**, 1702-1705; (h) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 2126-2129; (i) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 7649-7652; (j) B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2018, **54**, 12373-12376; (k) A. L. Colebatch, B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2019, **48**, 10628-10641; (l) B. J. Frogley, A. F. Hill and L. J. Watson, *Dalton Trans*, 2019, **48**, 12598-12606.
8. B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2019, **55**, 12400-12403.
9. T. P. Pollagi, S. J. Geib and M. D. Hopkins, *J. Am. Chem. Soc.*, 1994, **116**, 6051-6052.
10. P. A. Schauer, B. W. Skelton and G. A. Koutsantonis, *Organometallics*, 2015, **34**, 4975-4988. (b) C. F. R. Mackenzie, S. Bock, C.-Y. Lim, B. W. Skelton, C. Nervi, D. A. Wild, P. J. Low and G. A. Koutsantonis, *Organometallics*, 2017, **36**, 1946-1961. (c) G. A. Koutsantonis, P. J. Low, C. F. R. Mackenzie, B. W. Skelton and D. S.Yufit, *Organometallics*, 2014, **33**, 4911-4922. (d) G. A. Koutsantonis, G. I. Jenkins, P. A. Schauer, B. Szczepaniak, B. W. Skelton, C. Tan and A. H. White, *Organometallics*, 2009, **28**, 2195-2205. (e) M. P. Cifuentes, M. G. Humphrey, G. A. Koutsantonis, N. A. Lengkeek, S. Petrie, V. Sanford, P. A. Schauer, B. W. Skelton, R. Stranger and A. H. White, *Organometallics*, 2008, **27**, 1716-1726.
11. (a) E. S. Borren, A. F. Hill, R. Shang, M. Sharma and A. C. Willis, *J. Am. Chem. Soc.*, 2013, **135**, 4942-4945; (b) A. Reinholdt, J. Bendix, A. F. Hill and R. A. Manzano, *Dalton Trans.*, 2018, **47**, 14893-14896.
12. B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2019, **55**, 15077-15080.
13. (a) V. Farina, S. Kapadia, B. Krishnan, C. Wang and L. S. Liebeskind, *J. Org. Chem.*, 1994, **59**, 5905-5911; (b) S. P. H. Mee, V. Lee and J. E. Baldwin, *Angew. Chem. Int. Ed.*, 2004, **43**, 1132-1136.
14. L. L. Merritt and E. Schroeder, *Acta Cryst.*, 1956, **9**, 801-804.
15. S. J. Kavitha, K. Panchanatheswaran, J. N. Low, G. Ferguson and C. Glidewell, *Acta Crystallogr. Section C*, 2006, **62**, o165-o169.
16. (a) G. A. Carriedo, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597-1603; (b) S. H. F. Becke, M. D. Bermúdez, N. H. Tran-Huy, J. A. K. Howard, O. Johnson and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 1229-1234; (c) G. A. Carriedo, V. Riera, G. Sánchez and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1988, 1957-1962; (d) J.-L. Cabioch, S. J. Dossett, I. J. Hart, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1991, 519-527; (e) C. E. Strasser, S. Cronje and H. G. Raubenheimer, *New J. Chem.*, 2010, **34**, 458-469; (f) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, 2017, **46**, 4355-4365; (g) B. J. Frogley, A. F. Hill and C. S. Onn, *Dalton Trans*, 2019, **48**, 11715-11723; (h) B. J. Frogley

and A. F. Hill, *Angew. Chem., Int. Ed. Engl.*, 2019, **58**, 8044-8048; (i) A. R. Delaney, B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2019, **48**, 13674-13684; (j) B. J. Frogley, A. F. Hill and L. J. Watson, *Chem. Commun.*, 2019, **55**, 14450-14453.

17. (a) F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio and G. Pacchioni, *J. Chem. Soc., Chem. Commun.*, 1992, 333-335; (b) Francesco P. Fanizzi, N. Margiotta, M. Lanfranchi, A. Tiripicchio, G. Pacchioni and G. Natile, *Eur. J. Inorg. Chem.*, 2004, 1705-1713.
18. (a) A. Hazell, O. Simonsen and O. Wernberg, *Acta Crystallogr. Sect. C*, 1986, **42**, 1707-1711; (b) A. Hazell, *Polyhedron*, 2004, **23**, 2081-2083.
19. (a) C. P. Gordon, C. Raynaud, R. A. Andersen, C. Copéret and O. Eisenstein, *Acc. Chem. Res.*, 2019, **52**, 2278-2289. (b) D. P. Estes, C. P. Gordon, A. Fedorov, W.-C. Liao, H. Ehrhorn, C. Bittner, M. L. Zier, D. Bockfeld, K. W. Chan, O. Eisenstein, C. Raynaud, M. Tamm and C. Copéret, *J. Am. Chem. Soc.*, 2017, **139**, 17597-17607.
20. Agilent, *CrysAlis PRO*, Agilent Technologies Ltd, Yarnton, Oxfordshire, England, 2014.
21. (a) G. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3-8.
22. (a) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457; (b) 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.
23. T. N. Y. Hoang, M. Humbert-Droz, T. Dutronc, L. Guénée, C. Besnard and C. Piguet, *Inorg. Chem.*, 2013, **52**, 5570-5580.
24. H. Shimada, T. Sakurai, Y. Kitamura, H. Matsuura and T. Ihara, *Dalton Trans.*, 2013, **42**, 16006-16013.
25. R. Uson, A. Laguna, M. Laguna , D. A. Briggs , H. H. Murray and J. P. Fackler Jr, in *Inorg. Synth.*, ed. H. D. Kaesz, 1989, vol. 26, ch. 17, pp. 85-91.
26. P. B. Chock, J. Halpern, F. E. Paulik, S. I. Shupack and T. P. Deangelis, in *Inorg. Synth.*, ed. R. J. Angelici, 1990, vol. 28, pp. 349-351.
27. G. Giordano, R. H. Crabtree, R. M. Heintz, D. Forster and D. E. Morris, in *Inorg. Synth.*, ed. R. J. Angelici, 1990, vol. 28, pp. 88-90.
28. J. L. Herde, J. C. Lambert, C. V. Senoff and M. A. Cushing, in *Inorg. Synth.*, ed. G. W. Parshall, 1974, vol. 15, pp. 18-20.