Carbyne decorated porphyrins

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The Pd⁰/Au^I-mediated coupling between stannylcarbyne $[W(\equiv CSn^rBu_3)(CO)_2(Tp^*)]]$ (**1**) and *meso*-5,10,15,20-tetrakis(3' or 4'-bromophenyl)porphyrins gives tetrametallic derivatives where a central porphyrin unit is formally substituted at the four *meso* positions by tungsten benzylidyne moieties. These new 'metallo-porphyrins' undergo metallation at the porphyrin centres with Zn(OAc)₂·2H₂O to give a pentametallic W₄Zn complexes or at the tungsten–carbon triple bonds with [AuCl(SMe₂)] to give an octametallic W₄Au₄ complex. The Zn(II)-metalloporphyrin derivatives are capable of reversibly coordinating further axial ligands such as 4-dimethylaminopyridine or *meta*-pyridylcarbynes, which themselves are prepared *via* a coupling between **1** and the appropriate (di)bromopyridine.

Introduction

The coupling of the stannylcarbyne $[W(\equiv CSn^rBu_3)(CO)_2(Tp^*)]]$ (**1**) with appropriate aryl¹ or main group halides² has recently been shown to be mediated by [Pd(PPh₃)₄] in combination with [AuCl(SMe₂)], *via* the intermediacy of gold³ and palladium⁴ μ -carbido complexes. This protocol offers a versatile, potentially generalisable, strategy towards the preparation of transition metal carbynes bearing substituents that are not otherwise accessible by the classical Fischer⁵ or Schrock⁶ synthetic protocols. Specifically, the stannylcarbyne coupling procedure overcomes historical limitations regarding (i) intolerance to heteroatoms or other substituent functionality within the vicinity of the carbyne fragment and (ii) difficulties associated with incorporating two or more carbyne units within a single molecule. Towards confirming the utility of the coupling procedure, we have sought targets which would be otherwise problematic in both regards.

Mixed porphyrin-alkylidyne complexes are one class of compound that is conspicuously under-represented. Hopkins has reported the only example where a carbyne fragment has been included in the porphyrin backbone itself, which was prepared by a palladium-catalysed coupling between Zn(TPP-mono-*p*-I) (TPP = tetraphenylporphyrinate) and $[W(\equiv CC_6H_4C\equiv CH)Cl(dppe)_2]$ (Chart 1). It was shown that the porphyrin and carbyne units are (weakly) electronically coupled and that this led to substantial improvements in emission lifetimes compared to the uncoupled components. It was further shown that axial ligand coordination to Zn(II) could also influence the photochemical properties.⁷

Chart 1. Reported complexes incorporating both porphyrin and alkylidyne motifs. L = no ligand, pyridine, 4-picoline, 4-(dimethylamino)pyridine or imidazole.⁷⁻⁹

Hopkins also explored the porphyrin/carbyne interplay from an alternative stand-point: a cross-coupling reaction between the same alkylidyne precursor and 4-iodopyridine gave the tungsten carbyne $[W(\equiv CC_6H_4C\equiv C(C_5H_4N-4))Cl(dppe)_2]$. The terminal pyridyl group of this ligand axially coordinates to Zn(TPP), which substantially modifies the photochemical properties of both species.⁶ Further modification of the porphyrin backbone to include a pyridyl group coordinated to 'Re(bipy)(CO)₃' (bipy = 2,2'-bipyridyl) enabled this photochemistry to be directed towards applications such as H₂ and CO₂ activation.⁹ To the best of our knowledge, Hopkins' work represents the entirety of reported mixed porphyrin-alkylidyne species, with the exception of a dubious report of a rhenium-tin carbido complex that is almost certainly incorrectly formulated as $[Sn\{CRe(CO)_3\}_2(TPP)]$ (most likely $[Sn(OReO_3)_2(TPP)]$).¹⁰ The only other incidentally related compounds are those where porphyrins and related tetraazamacrocycles serve as ancillary ligands in bimetallic cumulenic μ -carbido complexes, $L_nM=C=ML_n$.¹¹

Herein we report the synthesis of tetrakis(alkylidynyl)porphyrin complexes prepared by a Pd⁰/Au^I-mediated coupling between the stannylcarbyne **1** and tetrakis(bromophenyl)porphyrins. Furthermore, we report the metallation at the porphyrin core with Zn(OAc)₂·2H₂O or at the tungsten–carbon triple bonds with [AuCl(SMe₂)]. The zinc(II) derivative remains capable of coordinating axial pyridine

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ligands in the same manner as classical Zn(TPP), which was demonstrated with 4-dimethylaminopyridine (DMAP). The 3- and 4-pyridylcarbynes and the 3,5-pyridylbis(carbyne) complexes, prepared by a related Pd⁰/Au^I-mediated coupling between **1** and the appropriate (di)bromopyridine, also appear capable of weak, reversible coordination to the Zn(II) core of the prepared 'W₄Zn 'metalloporphyrins' on the basis of spectroscopic evidence.

Results and discussion

The readily available *meso*-5,10,15,20-tetrakis(4'-bromophenyl)porphyrin has proven to be a versatile starting point for the construction of more elaborate porphyrins *via* a range of carbon–carbon coupling reactions,¹² and this extends to the Pd⁰/Au^I-mediated stannylcarbyne coupling recently developed for the synthesis of otherwise inaccessible transition-metal carbyne substituents.¹ Thus, reaction of the stannylcarbyne complex [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (**1**) (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) with slightly less than one-quarter an equivalent of *meso*-5,10,15,20-tetrakis(4'-bromophenyl)porphyrin in the presence of catalytic (10 mol%) [Pd(PPh₃)₄] and [AuCl(SMe₂)] in refluxing toluene furnishes the tetrasubstituted 'metalloporphyrin' **2**, where a '(Tp*)(CO)₂W≡C' unit has been appended in place of each of the four bromine atoms (Scheme 1). Under these conditions, there was no evidence for the incorporation of either palladium or gold within the porphyrin. Solutions of **2** vary in colour, but generally appear dark red/purple whereas the isolated solid was found to be very dark purple in all instances. The necessity of the Au(I) additive has been noted previously,¹ with transmetalation from tin to gold(I) occurring *en route* to Pd(II) in a manner reminiscent of the "copper effect" observed for traditional Stille couplings.¹³

The synthesis is not limited to the *para*-derivative and under the same conditions, the reaction of **1** with *meso*-5,10,15,20-tetrakis(3'-bromophenyl)porphyrin gives the related 'metalloporphyrin' **3**, where the '(Tp*)(CO)₂W≡C' units have been appended at the *meta*- or 3-position of the four phenyl rings. Solutions and the isolated solid samples of **3** are a comparable red/purple hue.

The four tungsten environments in **2** are spectroscopically equivalent, giving rise to just two ν_{CO} absorbances (CH₂Cl₂: 1974, 1883 cm⁻¹, Table 1) and one set of Tp* resonances in the ¹H and ¹³C{¹H} NMR spectra in the usual 2:1 ratio expected for the locally C_s symmetric 'W(CO)₂(Tp*)' environment. A broad resonance at δ_H = -2.73 in the ¹H NMR spectra, integrating for two protons, corresponds to the porphyrin NH groups. The W≡C carbyne carbon resonates at 278.2 ppm in the ¹³C{¹H} NMR spectrum, barely displaced from that observed for the benzyldiyne [W(≡CPh)(CO)₂(Tp*)] (δ_C = 277.9)¹⁴ and are not far removed from other tungsten alkylidynes ligated by poly(pyrazolyl)borate ligands (*ca* 270–310 ppm).¹⁵ Resonances associated with the tetraphenylporphyrin core are generally unperturbed by the comparatively remote substitution.

In the case of **3**, each of the four tungsten environments are equivalent but the symmetry within each '(Tp*)(CO)₂W' unit has been reduced. Signals are located in very similar positions to

those in **2** but present in a 1:1:1 ratio for the Tp* ligands of **3**. The diastereotopic CO ligands also give rise to ever-so-slightly different ¹³C{¹H} chemical shifts. This effect is especially small (differences being 0.03 ppm or less between the otherwise related nuclei) but does indicate that there may be a degree of restricted rotation in this complex.

Scheme 1. Synthesis of 'tetrakis(alkyldiynylphenyl)porphyrins' and their coordination to Zn(II).

The molecular structure of **2** has been determined (Fig. 1) revealing that only one-half of the molecule of **2** is crystallographically unique. The W≡C (1.816(6), 1.814(5) Å) and C_{carbyne}–C_{aryl} (1.468(8), 1.448(8) Å) distances and are in good agreement with tungsten alkylidynes with aromatic carbyne substituents.¹⁵ The W≡C–C angles (161.9(5), 167.6(5)°) deviate substantially from linearity although this, too, is not uncommon for tris(pyrazolyl)-ligated alkylidynes and is typically attributed to solid state packing effects. Unsurprisingly, structural parameters associated with the porphyrin core of **2** are largely uninfluenced by the distal substitution and are nearly identical to tetrakis(4-bromophenyl)porphyrin itself.¹⁶ The molecules are staggered in the crystal but the rather imposing steric bulk of

the Tp* ligands still results in large void spaces that are occupied, in this case, by six equivalents of *n*-heptane of solvation.

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

	$\delta_{\text{EC}}^{\text{a}}$	$r_{\text{W}\equiv\text{C}}^{\text{b}}$ (Å)	$\angle_{\text{W}\equiv\text{C}-\text{C}}^{\text{b}}$ (°)	$\nu_{\text{CO}}^{\text{b}}$	$\lambda_{\text{max}}^{\text{c}}$
2	278.2	1.816(6) 1.814(5)	161.9(5) 167.6(5)	1974, 1883	433, 522, 562, 653
3	278.0			1974, 1883	421, 516, 551, 591, 645
4	278.5	1.848(15) 1.807(13)	171.6(14) 172.9(13)	1973, 1883	437, 510, 558, 601
5	278.5			1974, 1883	428, 514, 554, 595
6	262.6	1.75(3) 1.90(3)	161(2) 156(2)	2005, 1923	436, 485, 561, 654, 703
7				1973, 1883	444, 526, 571, 615
8				1974, 1885	436, 567, 607
9	271.9	1.804(15)	165.5(11)	1979, 1888	503br
10	^d			1980, 1891	516br
11	271.3			1983, 1892	521br

^a Measured in CDCl₃ (**2–7**, **11–12**) or CD₂Cl₂ (**9–10**) (ppm). ^b Measured in CH₂Cl₂ (cm^{−1}). ^c Measured in CH₂Cl₂ (nm). ^d Too broad or low signal-to-noise to determine accurately. ^e Not isolated.

Figure 1. Molecular structure of **2** in a crystal of **2**·(C₇H₁₆)₆ (50% displacement ellipsoids, one-half of the molecule is crystallographically unique, most hydrogen atoms and solvent omitted and pyrazolyl groups simplified for clarity). Selected distances [Å] and angles [°]: W1–C1 1.816(6), C1–C4 1.468(8), W2–C26 1.814(5), C26–C23 1.448(8), W1–C1–C4 161.9(5), W2–C26–C23 167.6(5). Inset: Alternative views of the ‘core’ of **2** excluding the ancillary ligands on tungsten and space-filling representation.

Unsurprisingly, the porphyrin cores of **2** and **3** are capable of being deprotonated and metalated. Heating **2** or **3** with excess Zn(OAc)₂ in chloroform and methanol under reflux results in metalation of the porphyrin cores to give the ‘zinc(II) metalloporphyrins’ **4** and **5**, respectively (Scheme 1). The colour of these complexes differ rather substantially; the *para*-derivative **4** is dichroic red-green in solution and was isolated as a dark forest-green solid, whereas the *meta*-complex **5** is a comparatively bright red in both solution and as a solid. Complex **4** was also prepared, albeit in slightly reduced yield, through coupling of the stannylcarbyne **1** with Zn(TPP-tetra-*p*-

Br), where the zinc has been pre-ligated to the tetrabrominated porphyrin.

Zinc coordination has little influence on the spectroscopic properties of the metalloporphyrins. The most profound differences are the absence of the broad up-field (negative region) resonances in the ¹H NMR spectra, which confirms deprotonation has occurred in both cases. The carbyne carbon resonances in the ¹³C{¹H} NMR spectrum are barely shifted by Zn(II) coordination (from 278.2 in **2** to 278.5 ppm in **4**; from 278.0 in **3** to 278.5 ppm in **5**). The infrared carbonyl absorbances are also essentially unchanged upon Zn(II) coordination, indicating that it has little if any influence on the electron density at tungsten. The molecular structure of **4** has been determined (Fig. 2) and this also confirms that zinc(II) coordination has occurred at the central porphyrin moiety. Although structural comparisons with **2** are made with some trepidation due to the lower bond precision for the structural model **4**, the data suggest that Zn(II) coordination has minimal influence on the tungsten carbyne fragments.

Figure 2. Molecular structure of **3** (50% displacement ellipsoids, only one-half of the molecule is crystallographically unique, most hydrogen atoms omitted and pyrazolyl groups simplified for clarity). Selected distances [Å] and angles [°]: W1–C1 1.848(15), C1–C4 1.403(18), W2–C26 1.807(13), C26–C23 1.458(16), Zn1–N13 2.030(7), Zn1–N14 2.018(9), W1–C1–C4 171.6(14), W2–C26–C23 172.9(13).

Metal coordination to **2** is possible not only at the porphyrin centre but at the W≡C multiple bonds as well. Treatment of **2** with four equivalents of [AuCl(SMe₂)] (a reagent with a well-documented proclivity for alkylidynes¹⁷) results in displacement of the labile thioether ligand and coordination of ‘AuCl’ across the tungsten–carbon multiple bond, furnishing the octametallic metalloporphyrin **6** (Scheme 2) which was found to have a dark orange colour both in solution and when isolated as a solid. The retention of a broad resonance at $\delta_{\text{H}} = -2.68$ in the ¹H NMR spectrum of **5**, integrating for two protons, confirms the presence of NH protons and implies that the porphyrin core does not directly sequester gold and is uninvolved in the reaction. The carbyne carbon resonance in the ¹³C{¹H} NMR spectrum identified at 281.9 ppm, displays a small but appreciable down-field shift of just under 4 ppm compared to its precursor. In comparable examples, ‘AuCl’ coordination gives rise to shifts of less than 10 ppm in either direction for the

carbyne carbon resonance.^{1a,17f,17g} The molecular structure of **5** was crystallographically determined (Fig. 3) but the extremely weak high angle data allowed only a low-quality dataset to be obtained. For this reason the structural model is included only as evidence of bond connectivity. Unexpectedly, reaction of **3** with four or more equivalents of $[\text{AuCl}(\text{SMe}_2)]$ is not as simple and gives a complex mixture of unidentified products. Coordination to $\text{W}\equiv\text{C}$ is no doubt possible but the ^1H NMR spectra of crude mixtures were devoid of high-frequency signals which would correspond to NH protons, implying competitive reactions may be occurring which involve the porphyrin core.

Scheme 2. Gold(I) coordination to the $\text{W}\equiv\text{C}$ bonds of the 'metalloporphyrin' **2**.

Figure 3. Molecular structure of **4** (30% displacement ellipsoids, most hydrogen atoms omitted and pyrazolyl groups are simplified for clarity). This structural model is of low precision and is presented only as evidence of connectivity.

Attempts to prepare a derivative containing both $\text{Zn}(\text{II})$ coordinated to the porphyrin core and $\text{Au}(\text{I})$ coordinated to the four tungsten-carbon multiple bonds were unfortunately not met with success. Addition of four equivalents of $[\text{AuCl}(\text{SMe}_2)]$ to the zinc(II) metalloporphyrin **3** gave complex mixtures of products containing multiple distinct or broad Tp^* and pyrrolic proton signatures in the ^1H NMR spectrum. On the other hand, the fragility of the gold(I) coordination means that solutions slowly demetallate, often forming gold mirrors on glassware. This precludes addition of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ to the tetraaurated complex **5** as the necessary reaction conditions (refluxing chloroform and methanol solution) accelerates this decomposition.

Despite the impressive steric bulk of the four ' $\text{W}(\text{CO})_2(\text{Tp}^*)$ ' groups in **4** and **5**, they are sufficiently removed from the porphyrin core that the zinc(II) centre remains capable of

coordinating further axial ligands. Addition of an excess of 4-dimethylaminopyridine (4-DMAP) to a solution of **4** results in an immediate colour change from dark red-green to bright, lime green corresponding to formation of the five-coordinate 'zinc(II) metalloporphyrin' complex **7**. Room-temperature ^1H NMR spectra of this mixture are nearly indistinguishable from those of the pure complex **4**, with the most noticeable deviation being a 0.08 ppm up-field shift for the resonance relating to the pyrrolic proton and a very broad signal at 2.88 ppm corresponding to the NMe_2 group, while the 4-DMAP aromatic resonances were too broadened to unambiguously identify. Other resonances are shifted marginally if at all, most differing by less than 0.03 ppm (see ESI for a stacked spectra comparison). These observations are in accord with an (expected) fast coordination/dissociation equilibrium on the NMR timescale and are very similar to changes observed for simple pyridine-based ligand coordination to $\text{Zn}(\text{TPP})$.¹⁸ Several resonances begin to emerge or sharpen as the temperature is lowered (see ESI for stacked variable-temperature ^1H NMR spectra), including those related to the 4-DMAP aromatic protons, but even at -60°C these remain too ill-defined for any meaningful kinetic information to be derived. Both the ν_{CO} absorbances in the infrared spectrum and the Soret band in the UV-Vis spectrum of **7** are nigh indistinguishable from those of **4**, although the broad visible-region absorbance does shift substantially corresponding to the profound colour change observed. Hopkins also noted little change in the Soret band upon axial ligand coordination for his mixed porphyrin-alkylidyne complex.⁸

Addition of excess of 4-DMAP to **5** results in a less profound colour change, from bright to dark red, but does give rise to a substantial increase in the complexity of the ^1H NMR spectra as many resonances arise associated with the Tp^* ligands. A similar *ca.* 0.1 ppm up-field shift was observed for the pyrrolic CH protons but these were split into two distinct resonances. It is not clear whether the increased complexity is due to inequivalence upon coordination or the kinetics are sufficiently slow that multiple components are being simultaneously observed. Cooling to -60°C does little to alleviate these problems and so in both cases we are unable to draw any robust meaningful conclusions. Two Soret peaks observed in the electronic spectra imply that, even with a large excess of 4-DMAP, a mixture of four- and five-coordinate $\text{Zn}(\text{II})$ porphyrin may be present simultaneously in solution. However, we again note that the breadth of these absorbances mean conclusions can be drawn only with reservation.

Scheme 3. Reversible 4-dimethylaminopyridine coordination to the 'zinc(II) metalloporphyrins' **4** and **5**.

We recently reported the synthesis of *ortho*-pyridylcarbynes^{1a} and bipyridylcarbynes^{1b} and demonstrated their coordination to a variety of metal centres. Although these are presumably far weaker donor ligands than 4-DMAP by virtue of the strongly π -acidic carbyne substituent, we have considered whether pyridylcarbynes might nonetheless be capable of coordination to the Zn(II) centre of the metalloporphyrins **4** or **5**. The previously-reported *ortho* complexes are not suited for this purpose as the nitrogen donor is located too close to the sterically prohibitive 'W(CO)₂(Tp*)' moiety. However, the derivatives in which the carbyne fragment is located *meta* or *para* to the pyridyl nitrogen could be prepared in a similar manner.

Treatment of the stannylcarbyne **1** with 3-bromopyridine or 3,5-dibromopyridine under the standard catalytic conditions (10 mol% [Pd(PPh₃)₄] and [AuCl(SMe₂)] in refluxing toluene) furnishes the *meta*-substituted pyridylcarbyne complexes [NC₅H₄{C≡W(CO)₂(Tp*)}-3] (**9**) and [NC₅H₃{C≡W(CO)₂(Tp*)}₂-3,5] (**10**), respectively, as bright orange-red solids in modest yield (Scheme 4). The *para* complex, [NC₅H₄{C≡W(CO)₂(Tp*)}-3] (**11**) can be isolated in trace amounts (9%) as a purple solid from 4-bromopyridine hydrochloride under the same conditions (adapted to include NEt₃ to remove hydrochloride). We attribute the disappointing yield to the sensitivity of free 4-bromopyridine, which is presumably exacerbated by the harsh reaction conditions (toluene reflux). An alternative strategy was attempted involving treatment of the bromocarbyne [W(≡CBr)(CO)₂(Tp*)] with 4-lithiopyridine (generated *in situ* from 4-bromopyridine hydrochloride and two equivalents of *n*-butyllithium), but in this case there was no evidence of the formation of **11** at all. Unfortunately, insufficient material was obtained for this complex to be used in any of the subsequent reactions.

Scheme 4. Synthesis of 3- and 4-pyridylcarbynes and a 3,5-pyridyl bis(carbyne) complex.

The spectroscopic data for the pyridylcarbynes **9–11** are in good agreement with their substitution patterns and are comparable to the reported *ortho* substituted complexes. The chemical shifts and couplings observed for the pyridylcarbynes in their ¹H and ¹³C{¹H} NMR spectra are largely unsurprising. The carbyne carbons in **9** and **11** resonate at $\delta_c = 271.9$ and 271.3, respectively, in the ¹³C{¹H} NMR spectra, which is slightly up-field of that found for the *ortho*-pyridylcarbyne [NC₅H₄{C≡W(CO)₂(Tp*)}-2] (275.9 ppm).^{1a} The two '(Tp*)(CO)₂W≡C' groups in **10** are equivalent by infrared, ¹H and ¹³C{¹H} NMR spectroscopies although in stark contrast to each of the other pyridylcarbynes reported, the pyridyl carbon nuclei were found to give rise to unexpectedly broad resonances in the ¹³C{¹H} NMR spectrum. Carbons in the 2,6- (δ_c 146.5), 3,5- (145.7) and 4- (135.7) positions of the pyridine ring could be identified but the carbyne resonance could not unequivocally be assigned. The molecular structure of **9** has been determined (Figure 4) and, although complicated by disorder and twinning, it confirms the formulation as a 3-pyridylcarbyne structurally similar to related tungsten carbyne complexes.^{1a,1b,12}

Coordination of pyridylcarbynes to the metalloporphyrins was first explored with the most sterically accommodating pair available. We note that while the 4-pyridylcarbyne **11** would presumably provide the least steric prohibition to Zn(II) coordination, the very small amount of material obtained prevented its use in these preliminary test reactions. Thus, addition of an excess of the 3-pyridylcarbyne **9** to a solution of the zinc(II) metalloporphyrin **4** results in a *ca.* 0.09 ppm up-field shift in the ¹H NMR resonance associated with the pyrrolic CH protons and the resonances corresponding to the aromatic 3-pyridyl protons are substantially shifted and broadened (see ESI for a stacked spectra comparison). These changes are congruent with the observations made for the 4-DMAP species and imply that a similarly rapid coordination/dissociation equilibrium may operate. Some sharpening of signals occurs upon cooling to -60 °C but again these remain too poorly resolved for any meaningful conclusions on kinetics to be drawn. These trends continue for each of the other three pairs of metalloporphyrins **4** or **5** and pyridylcarbynes **9** or **10**, suggesting that even the

more sterically rotund complexes are capable of at least some degree of weak coordinative interaction.

Figure 4. Molecular structure of **9** (50% displacement ellipsoids, one of two crystallographically distinct molecules shown, pyrazolyl groups simplified for clarity). Selected distances [Å] and angles [°]: W1–C1 1.804(15), C1–C4 1.460(19), W1–C1–C4 165.5(11).

The question of whether electronic communication might occur between the distal metal centres in these polymetallic assemblies is best addressed by electrochemical interrogation. The cyclic voltammogram of complex **2** is displayed in Figure 5 and clearly shows that only a single redox event occurs, *i.e.*, that the four tungsten centres oxidise independently with little discernible coupling. This may be understood in terms of the oxidation occurring from the HOMO of the carbyne unit(s) which, as has been noted previously^{1c,4b,19} is primarily d_{xy} in nature (z as the W-carbyne axis) and associated with metal-carbonyl retrodonation. It has δ -symmetry with respect to the orthogonal carbyne axis and accordingly is non-bonding with the carbyne ligand orbitals accounting for negligible electronic coupling of the metal redox sites.

Figure 5. Cyclic voltammogram of **2** in dichloromethane ($[\text{t}^{\text{Bu}}\text{N}]\text{PF}_6$, 25 °C, 200 mVs^{-1} , Scale shown is relative to $E^\circ(\text{Cp}_2\text{Fe}) = 0.460 \text{ V}$ *cf.* Ag/AgCl).

Conclusions

The peripheral appending of carbyne substituents to a porphyrin scaffold demonstrates the versatility of the $\text{Pd}^0/\text{Au}^{\text{I}}$

transmetallation shuttle for the multiple introduction of carbyne units into complex architectures under comparatively mild conditions. The distal nature of these groups with respect to the central porphyrin unit, however, has little impact on the spectroscopic features of the central chromophore. Extraneous metals may be post-synthetically introduced to either the central tetrapyrrolic chelate (Zn^{II}) or across the metal-carbon multiple bonds (Au^{I}). The rapid and efficient synthesis of complexes such as **2** and **3** illustrates that carbyne functionality may be introduced late in a synthetic sequence, in contrast to previous methods.

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Conflicts of interest

There are no conflicts to declare.

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 (^1H at 400.1 MHz, ^{13}C at 100.6 MHz), a Bruker Avance 600 (^1H at 600.0 MHz, ^{13}C at 150.9 MHz) or a Bruker Avance 700 (^1H 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 peaks. 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 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, but to the level of accuracy that is reportable (*i.e.* 2 decimal places for ^1H NMR, 1 decimal place for ^{13}C NMR) they are reported as having the same chemical shift. The abbreviation ‘pz’ is used to refer to the pyrazolyl rings on the hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp^*) ligand. The abbreviation ‘pyr’ is used to refer to the pyrrole rings of the central porphyrin unit. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The ^1H NMR spectra of new compounds reported here include resonances in the region $4 < \delta_{\text{H}} < 5$ ppm due to the BH hydrogen of the Tp^* ligands which are broad due to the quadrupolar nature of $^{10}/^{11}\text{B}$ 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 although they are listed.

Infrared spectra were obtained using a PerkinElmer Spectrum One FT-IR 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). Electronic spectra were obtained on a Shimadzu UV-2450 spectrophotometer. Elemental microanalytical data were provided by the London Metropolitan University or Macquarie 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 SuperNova CCD diffractometer using Cu-K α radiation (λ = 1.54184 Å) and the CrysAlisPRO 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($\equiv$ CSnⁿBu₃)(CO)₂(Tp*)] (**2**)^{3a} has been described previously. The compounds *meso*-5,10,15,20-tetrakis(4'-bromophenyl)porphine,²³ tetrakis(3'-bromophenyl)porphine,²⁴ [Pd(PPh₃)₄]²⁵ and [AuCl(SMe₂)]²⁶ were prepared according to the literature methods. Yields for carbyne installations are based on the porphyrin precursor.

Synthesis of 'metalloporphyrin' 2. A solution of [W($\equiv$ CSnⁿBu₃)(CO)₂(Tp*)] (**1**: 500 mg, 0.596 mmol), *meso*-5,10,15,20-tetrakis(4'-bromophenyl)porphyrin (138 mg, 0.148 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (30 mL) was heated under reflux for 14 h. The solvent was then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing the polarity to 50% v/v CH₂Cl₂/petroleum ether. A dark red/purple band was collected and the volatiles were removed under reduced pressure to give a dark purple solid of **2** (358 mg, 0.128 mmol, 86%). IR (CH₂Cl₂, cm⁻¹): 1974s, 1883s ν_{CO} . UV-Vis λ_{max} (CH₂Cl₂/nm): 433, 522, 562, 653 (ϵ /L mol⁻¹ cm⁻¹ 455000, 24400, 26200, 11400). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ_H = -2.73 (br s, 2H, NH), 2.40 (s, 12H, pzCH₃), 2.44 (s, 24H, pzCH₃), 2.56 (s, 12H, pzCH₃), 2.77 (s, 24H, pzCH₃), *ca* 4.7 (br. 4 H, BH), 5.85 (s, 4H, pzCH), 6.00 (s, 8H, pzCH), 7.84 (d, ³J_{HH} = 7.9, 8H, C₆H₄), 8.15 (d, ³J_{HH} = 7.9, 8H, C₆H₄), 8.82 (s, 8H, pyr{CH}). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C = 12.8, 12.9, 15.5, 17.0 (pzCH₃), 106.7, 106.9 (pzCH), 120.3 (*C_{meso}*), 127.6, 134.8 (C₆H₄{CH}), 141.2 (C₆H₄{C_q}), 144.7, 145.3 (pzCCH₃), 149.6 (WCC, ²J_{CW} = 44), 152.3, 152.6 (pzCCH₃), 224.4 (WCO, ¹J_{CW} = 164), 278.2 (W $\equiv$ C). Two expected resonances associated with the pyrrole carbons, which are typically weak and broad in non-metallated porphyrins due to NH fluxionality,²⁷ were not located. Anal. Found: C, 49.68; H, 3.99; N, 13.89. Calcd for C₁₁₆H₁₁₄B₄N₂₈O₈W₄: C, 49.64; H, 4.09; N, 13.97%.

Crystals of a heptane solvate suitable for diffraction were grown by slow evaporation of a CHCl₃/*n*-heptane solvent mixture and proved to be an *n*-heptane hexasolvate (3 per asymmetric unit), although one of those in the asymmetric unit was found to be highly disordered and had to be excluded from the refinement using a solvent mask. *Crystal data for*

C₁₄₄H₁₇₈B₄N₂₈O₈W₄ (M_w = 3207.77 g mol⁻¹): monoclinic, space group $P2_1/n$ (no. 14), a = 10.5844(3), b = 27.3756(8), c = 28.6573(7) Å, β = 99.505(2)°, V = 8189.6(4) Å³, Z = 2, T = 150.0(1) K, μ (Cu K α) = 5.512 mm⁻¹, D_{calc} = 1.301 Mg m⁻³, 24386 reflections measured ($7.176^\circ \leq 2\theta \leq 133.2^\circ$), 14399 unique (R_{int} = 0.0311, R_{sigma} = 0.0571) which were used in all calculations. The final R_1 was 0.0458 ($I > 2\sigma(I)$) and wR_2 was 0.1228 (all data) for 871 refined parameters with 152 restraints. CCDC 2008529.

Synthesis of 'metalloporphyrin' 3. A solution of [W($\equiv$ CSnⁿBu₃)(CO)₂(Tp*)] (**1**: 250 mg, 0.298 mmol), *meso*-5,10,15,20-tetrakis(3'-bromophenyl)porphyrin (69 mg, 0.074 mmol), [Pd(PPh₃)₄] (35 mg, 0.030 mmol) and [AuCl(SMe₂)] (9 mg, 0.03 mmol) in toluene (30 mL) was heated under reflux for 14 h. The solvent was then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) and gradually increasing the polarity to 50% v/v CH₂Cl₂/petroleum ether. A dark red band was collected and the volatiles were removed under reduced pressure to give a dark red-purple solid of **3** (84 mg, 0.030 mmol, 40%). IR (CH₂Cl₂, cm⁻¹): 1974s, 1883s ν_{CO} . UV-Vis λ_{max} (CH₂Cl₂/nm): 421, 516, 551, 591, 645 (ϵ /L mol⁻¹ cm⁻¹ 340000, 10000, 7200, 4200, 3200). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ_H = -2.80 (br s, 2H, NH), 2.35 (s, 24H, pzCH₃), 2.36 (s, 12H, pzCH₃), 2.48 (s, 12H, pzCH₃), 2.68 (s, 12H, pzCH₃), 2.69 (s, 12H, pzCH₃), *ca* 4.7 (br. 4 H, BH), 5.79 (s, 4H, pzCH), 5.86 (s, 4H, pzCH), 5.89 (s, 4H, pzCH), 7.70 (s.br, 4H, C₆H₄), 7.90 (d, ³J_{HH} = 7.8, 4H, C₆H₄), 8.15 (m, 4H, C₆H₄), 8.33 (m, 4H x 2, C₆H₄), 8.91, 8.92 (s, 4H, pyr{CH}). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C = 12.7, 12.8, 15.4, 16.8 (pzCH₃), 106.6, 106.6, 106.7 (pzCH), 119.6 (*C_{meso}*), 126.7, 128.8 (C₆H₄{CH}), 131.1 (br, pyrCH), 134.1, 134.9 (C₆H₄{CH}), 142.1 (C₆H₄{C_q}), 144.5, 144.5, 145.2 (pzCCH₃), 148.6 (WCC, ²J_{CW} = 44), 152.1, 152.2, 152.5 (pzCCH₃), 224.1 (WCO, ¹J_{CW} = 164), 224.2 (WCO, ¹J_{CW} = 164), 278.0 (W $\equiv$ C, ¹J_{CW} = 187). An expected resonance associated with the pyrrole carbons, which are typically weak and broad in non-metallated porphyrins due to NH fluxionality,²⁷ was not identified. Anal. Found: C, 49.59; H, 3.96; N, 13.59. Calcd for C₁₁₆H₁₁₄B₄N₂₈O₈W₄: C, 49.64; H, 4.09; N, 13.97%.

Synthesis of the 'zinc(II) metalloporphyrin' 4. A solution of **2** (50 mg, 0.018 mmol) and Zn(OAc)₂·2H₂O (17 mg, 0.077 mmol) in CHCl₃ (5 mL) and methanol (5 mL) was heated under reflux for 1 h, during which time the solution turned green-brown. After this time, the volatiles were removed under reduced pressure and the residue was extracted with CH₂Cl₂ and filtered through diatomaceous earth. To the filtrate was added *n*-hexane and the CH₂Cl₂ was removed under reduced pressure. The resulting precipitate was collected by filtration and washed with *n*-pentane to give a green solid of **4** (36 mg, 0.013 mmol, 70%). IR (CH₂Cl₂, cm⁻¹): 1973s, 1883s ν_{CO} . UV-Vis λ_{max} (CH₂Cl₂/nm): 437, 510, 558, 601 (ϵ /L mol⁻¹ cm⁻¹ 230000, 4700, 13000, 9500). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.40 (s, 12H, pzCH₃), 2.44 (s, 24H, pzCH₃), 2.56 (s, 12H, pzCH₃), 2.78 (s, 24H, pzCH₃), *ca* 4.7 (br. 4 H, BH), 5.85 (s, 4H, pzCH), 5.99 (s, 8H, pzCH), 7.83 (d, ³J_{HH} = 7.9, 8H, C₆H₄), 8.15 (d, ³J_{HH} = 7.9, 8H, C₆H₄), 9.02 (s, 8H, pyr{CH}). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.8, 12.9, 15.5, 17.0 (pzCH₃), 106.7, 106.8 (pzCH), 121.3 (*C_{meso}*), 127.5 (C₆H₄{CH}), 132.3 (pyr{CH}), 134.6 (C₆H₄{CH}), 141.9

(C₆H₄{C_q}), 144.7, 145.3 (pzCCH₃), 149.5 (WCC, ¹J_{CW} = 44), 150.0 (pyr{C_q}), 152.3, 152.6 (pzCCH₃), 224.4 (WCO, ¹J_{CW} = 165), 278.5 (W≡C). Anal. Found: C, 47.57; H, 3.98; N, 12.91. Calcd for C₁₁₆H₁₁₂B₄N₂₈O₈W₄Zn·CH₂Cl₂: C, 47.55; H, 3.89; N, 13.27%.

A crystal suitable for structure determination was grown by slow evaporation of a dichloromethane and ethanol mixture. Regions of highly disordered solvent were found to be present which could not be adequately modelled through disordered components and so were removed from the refinement using a solvent mask. The calculation found there to be 337 electrons in the solvent accessible void, which is in good agreement with eight molecules of dichloromethane of solvation (336 electrons). *Crystal data for* C₁₁₆H₁₁₂B₄N₂₈O₈W₄Zn (*M_w* = 2870.34 g mol⁻¹): triclinic, space group *P*-1 (no. 2), *a* = 12.0635(12), *b* = 14.5979(11), *c* = 24.2222(12) Å, *α* = 80.549(5)°, *β* = 83.197(6)°, *γ* = 73.876(8)°, *V* = 4030.2(6) Å³, *Z* = 1, *T* = 150.0(1) K, *μ*(Cu Kα) = 5.693 mm⁻¹, *D_{calc}* = 1.183 Mg m⁻³, 22059 reflections measured (7.652° ≤ 2θ ≤ 133.194°), 14091 unique (*R_{int}* = 0.0625, *R_{sigma}* = 0.1137) which were used in all calculations. The final *R₁* was 0.0777 (*I* > 2σ(*I*)) and *wR₂* was 0.2276 (all data) for 705 refined parameters with 3 restraints. CCDC 2008530.

Synthesis of the ‘zinc(II) metalloporphyrin’ 5. A solution of **3** (50 mg, 0.018 mmol) and Zn(OAc)₂·2H₂O (17 mg, 0.077 mmol) in CHCl₃ (5 mL) and methanol (5 mL) was heated under reflux for 1 h, during which time the solution turned bright red. After this time, the volatiles were removed under reduced pressure, the residue was extracted with CH₂Cl₂ and filtered through diatomaceous earth. To the filtrate was added *n*-hexane and the CH₂Cl₂ was removed under reduced pressure. The resulting precipitate was collected by filtration and washed with *n*-pentane to give a bright red solid of **5** (40 mg, 0.014 mmol, 78%). IR (CH₂Cl₂, cm⁻¹): 1974s, 1883s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 428, 514, 554, 595 (ε/L mol⁻¹ cm⁻¹ 420000, 4100, 14000, 4500). The spectrum has a remarkably weak Q-band which we attribute to the alternant symmetry due to the meta-carbyne substitution (i.e., these orient above and below the porphyrin plane). For alternant symmetry, transition from the ground-state 1A_g (the Q-band) is parity-forbidden.²⁸ ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.33 (s, 24H, pzCH₃), 2.34 (s, 12H, pzCH₃), 2.46 (s, 12H, pzCH₃), 2.67 (s, 12H, pzCH₃), 2.68 (s, 12H, pzCH₃), *ca* 4.7 (br. 4 H, BH), 5.78 (s, 4H, pzCH), 5.84, 5.84, 5.87, 5.87 (s, 2H x 4, pzCH), 7.67 (m, 4H, C₆H₄), 7.88 (d, ³J_{HH} = 7.8, 4H, C₆H₄), 8.14 (m, 4H, C₆H₄), 8.33 (m, 4H, C₆H₄), 8.99, 9.00 (s, 4H x 2, pyr{CH}). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.7, 12.8, 15.4, 16.8 (pzCH₃), 106.6, 106.6, 106.7 (pzCH), 120.6 (*C_{meso}*), 126.5, 128.6 (C₆H₄{CH}), 132.2 (pyr{CH}), 134.0, 134.9 (C₆H₄{CH}), 142.7 (C₆H₄{C_q}), 144.5, 144.5, 145.1 (pzCCH₃), 148.5 (WCC), 150.3 (pyr{C_q}), 152.1, 152.2, 152.5 (pzCCH₃), 224.2 (several overlapping s, WCO), 278.5 (W≡C). Satisfactory elemental microanalytical data were not acquired.

Synthesis of the ‘tetraaurated metalloporphyrin’ 6. To a flask containing **2** (25 mg, 0.0089 mmol) and [AuCl(SMe₂)] (11 mg, 0.037 mmol) was added CH₂Cl₂ (4 mL) and the mixture was stirred at RT for 10 min, causing the solution to turn dark orange. After this time the solution was filtered through diatomaceous earth (washed with CH₂Cl₂ until the washings ran

clear). To the filtrate was added *n*-hexane (10 mL) and the CH₂Cl₂ was removed under reduced pressure. The resulting precipitate was collected by filtration and washed with *n*-pentane (3 x 10 mL) to give a dark orange solid of **6** (30 mg, 0.0080 mmol, 90%). IR (CH₂Cl₂, cm⁻¹): 2005s, 1923s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 436, 485, 561, 654, 703 (ε/L mol⁻¹ cm⁻¹ 320000, 59000, 16000, 11000, 19000). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ_H = -2.68 (br s, 2H, NH), 2.43 (s, 12H, pzCH₃), 2.47 (s, 24H, pzCH₃), 2.68 (s, 24H, pzCH₃), 2.71 (s, 12H, pzCH₃), *ca* 4.7 (br. 4 H, BH), 6.02 (s, 4H, pzCH), 6.05 (s, 8H, pzCH), 8.26–8.38 (m, 16H, C₆H₄), 8.99 (s, 8H, pyr{CH}). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.9, 13.2, 16.2, 17.9 (pzCH₃), 108.0, 108.4 (pzCH), 119.8 (*C_{meso}*), 129.3, 135.1, 144.0 (C₆H₄), 145.9, 146.3 (pzCCH₃), 148.7 (WCC, ²J_{CW} = 44), 152.7, 153.6 (pzCCH₃), 217.5 (WCO, ¹J_{CW} = 155), 262.6 (W≡C, ¹J_{CW} = 94). Decomposition over the *ca.* 12h acquisition led to emergence of small amounts of unidentified impurities in this spectrum. Two resonances associated with the pyrrole carbons, which are typically weak and broad due to NH fluxionality,²⁷ were not located. Anal. Found: C, 35.02; H, 2.75; N, 9.41. Calcd for C₁₁₆H₁₁₄Au₄B₄Cl₄N₂₈O₈W₄·3CHCl₃: C, 34.91; H, 2.88; N, 9.58%.

Single crystals of **6** were grown by slow evaporation of a chloroform/*n*-heptane/toluene solvent mixture. These were unfortunately found to have extremely weak outer data and only a low-precision dataset could be obtained which required liberal application of restraints. It is therefore included only as evidence of connectivity and caution should be exercised in interpretation. *Crystal data for* C₁₁₆H₁₁₄Au₄B₄Cl₄N₂₈O₈W₄ (*M_w* = 3736.65 g mol⁻¹): triclinic, space group *P*-1 (no. 2), *a* = 15.2352(12), *b* = 15.6101(10), *c* = 16.9339(15) Å, *α* = 86.793(6)°, *β* = 67.571(8)°, *γ* = 80.675(6)°, *V* = 3673.4(5) Å³, *Z* = 1, *T* = 150.01(10) K, *μ*(Cu Kα) = 14.039 mm⁻¹, *D_{calc}* = 1.689 Mg m⁻³, 9229 reflections measured (7.886° ≤ 2θ ≤ 80.44°), 4364 unique (*R_{int}* = 0.0641, *R_{sigma}* = 0.0864) which were used in all calculations. The final *R₁* was 0.0608 (*I* > 2σ(*I*)) and *wR₂* was 0.1704 (all data) for 762 refined parameters with 779 restraints. CCDC 2008531.

Coordination of 4-dimethylaminopyridine to ‘zinc(II) metalloporphyrin’ 4 to give a solution of 7. A solution of 4-DMAP in CDCl₃ was added dropwise to a solution of **4** in CDCl₃ until the mixture had changed from dark red-purple to bright, lime green. IR (CH₂Cl₂, cm⁻¹): 1973s, 1883s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 444, 526, 571, 615 (ε/L mol⁻¹ cm⁻¹ 480000, 5000, 11000, 14000). ¹H NMR (700 MHz, CDCl₃, 20 °C): 2.40 (s, 12H, pzCH₃), 2.44 (s, 24H, pzCH₃), 2.56 (s, 12H, pzCH₃), 2.77 (s, 24H, pzCH₃), *ca.* 2.90 (br, NMe₂), 5.85 (s, 4H, pzCH), 5.99 (s, 8H, pzCH), 7.81 (d, ³J_{HH} = 8.0, 8H, C₆H₄), 8.13 (d, ³J_{HH} = 8.0, 8H, C₆H₄), 8.94 (s, 8H, pyr{CH}). ¹H NMR (700 MHz, CDCl₃, -60 °C): 2.39 (s, 12H, pzCH₃), 2.42 (s, 24H, pzCH₃), 2.54 (s, 12H, pzCH₃), 2.74 (s, 24H, pzCH₃), *ca.* 3.05 (br m, NMe₂) 5.87 (s, 4H, pzCH), 6.02 (s, 8H, pzCH), 7.81 (br, 8H, C₆H₄), 8.17 (br, 8H, C₆H₄), 8.96 (br, 8H, pyr{CH}). Resonances associated with the 4-dimethylaminopyridine aromatic protons were too broad to pinpoint. ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 13.0, 13.1, 15.5, 17.1 (pzCH₃), 39.7 (br, NMe₂), 106.6, 106.7 (pzCH), 120.5 (br, *C_{meso}*), 127.3 (br, C₆H₄{CH}), 131.7 (br, pyr{CH}), 135.0 (br, C₆H₄{CH}), 144.8, 145.3 (pzCCH₃), 147.6, 148.5, 149.4 (br, WCC,

pyr{C_q} & C₆H₄{C_q}), 152.1, 152.3 (pzCCH₃), 224.2 (WCO). W≡C not observed.

Coordination of 4-dimethylaminopyridine to 'zinc(II) metalloporphyrin' 5 to give a solution of 8. A solution of 4-DMAP in CDCl₃ was added dropwise to a solution of **5** in CDCl₃ until the initially bright red solution had substantially darkened in colour. IR (CH₂Cl₂, cm⁻¹): 1974s, 1885s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 436, 567, 607 (ε/L mol⁻¹ cm⁻¹ 450000, 15000, 9200). ¹H NMR (700 MHz, CDCl₃, 25 °C): 2.34 (several s overlapping, 36 H, pzCH₃), 2.45 (s, 9H, pzCH₃), 2.46–2.71 (several s overlapping, 27 H, pzCH₃), ca 4.7 (br. 4 H, BH), 5.77 (s, 4 H, pzCH), 5.83–5.89 (m, 8H, pzCH), 7.36 (m, 4H, C₆H₄), 7.84 (br d, ³J_{HH} = 7.9, 4H, C₆H₄), 8.11 (m, 4H, C₆H₄), 8.29 (m, 4H, C₆H₄), 8.87, 8.88 (s, 4H, pyr{CH}). Other resonances associated with 4-dimethylaminopyridine were too broad to pinpoint. ¹³C{¹H} NMR (176 MHz, CDCl₃, -60 °C): δ_C = 12.9 (2 C, coincidental), 15.4, 16.9 (pzCH₃), 39.6 (NMe₂), 106.4, 106.5 (pzCH), 119.4 (br, C_{meso}), 126.2, 128.3, 131.5, 134.6, 142.1, 143.3, 144.5, 145.2, 147.6, 149.6, 151.8, 152.1, 152.2 (br m, C₆H₄, pzCCH₃, pyr), 223.9 (br m, CO). Limited data and assignments are available as most resonances were very broad with the appearance of multiplets, presumably due to the rapid fluxional behaviour even at low temperature.

Synthesis of [NC₅H₄{C≡W(CO)₂(Tp*)}-3] (9**).** A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (**1**: 500 mg, 0.596 mmol), 3-bromopyridine (60 μL, 0.6 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (30 mL) was heated under reflux for 14 h. The solvent was then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with 50% v/v petroleum ether (40–60 °C)/dichloromethane followed thereafter by 100% CH₂Cl₂. A slow-moving, orange-red band was collected and the volatiles were removed under reduced pressure to give an orange-red solid of **9** (268 mg, 0.427 mmol, 72%). IR (CH₂Cl₂, cm⁻¹): 1979s, 1888s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 503br (ε/L mol⁻¹ cm⁻¹ 300). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ_H = 2.36 (s, 3H, pzCH₃), 2.40 (s, 6H, pzCH₃), 2.47 (s, 3H, pzCH₃), 2.51 (s, 6H, pzCH₃), ca 4.7 (br, 1 H, BH), 5.81 (s, 1H, pzCH), 5.93 (s, 2H, pzCH), 7.22 (dd, ³J_{HH} = 7.6, 6.6, 1H, C₅H₄N), 7.74 (dt', ³J_{HH} = 7.6, ⁴J_{HH} = 1.8, 1H, C₅H₄N), 8.52 (d, ³J_{HH} = 4.9, 1H, C₅H₄N), 8.71 (s, 1H, C₅H₄N). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C = 12.7, 12.7, 15.3, 16.7 (pzCH₃), 106.7, 106.9 (pzCH), 123.2, 136.2 (C₅H₄N), 144.7, 145.4 (pzCCH₃), 146.3 (W≡CC, ²J_{CW} = 44), 146.7, 149.8 (C₅H₄N), 151.9, 152.5 (pzCCH₃), 223.8 (WCO, ¹J_{CW} = 164), 271.9 (W≡C, ¹J_{CW} = 190). MS (ESI, *m/z*): Found: 628.1841. Calcd for C₂₃H₂₇¹¹B₂N₁₃O₄¹⁸⁴W [M+H]⁺: 628.1835. Anal. Found: C, 43.96; H, 4.22; N, 15.20. Calcd for C₂₃H₂₆BN₇O₂W: C, 44.05; H, 4.18; N, 15.63%.

The crystal used for X-ray crystallography was grown by slow evaporation of a CDCl₃ solution in an NMR tube. The structure was found to contain two molecules per asymmetric unit, one of which exhibited full molecule disorder and each component was refined isotropically. The crystal was further complicated by inversion twinning. The bond distances and angles given are for the molecule which did not exhibit disorder and should be interpreted with caution. *Crystal data for* C₂₃H₂₆BN₇O₂W (*M*_w = 627.17 g mol⁻¹): orthorhombic, space group *Pna*2₁ (no. 33), *a* =

31.9296(6), *b* = 8.15350(10), *c* = 18.8459(3) Å, *V* = 4906.30(13) Å³, *Z* = 8, *T* = 150.0(1) K, μ(Cu Kα) = 9.008 mm⁻¹, *D*_{calc} = 1.698 Mg m⁻³, 27305 reflections measured (7.256° ≤ 2θ ≤ 141.74°), 8918 unique (*R*_{int} = 0.0381, *R*_{sigma} = 0.0445) which were used in all calculations. The final *R*₁ was 0.0515 (*I* > 2σ(*I*)) and *wR*₂ was 0.1226 (all data) for 610 refined parameters with 12 restraints. CCDC 2008532.

Synthesis of [NC₅H₃{C≡W(CO)₂(Tp*)}-2-3,5] (10**).** A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (**1**: 1.00 g, 1.19 mmol), 3,5-dibromopyridine (141 mg, 0.595 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (30 mL) was heated under reflux for 14 h. The solvent was then removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with 50% v/v petroleum ether (40–60 °C)/dichloromethane followed thereafter by 100% CH₂Cl₂. A slow-moving, bright red band was collected and the volatiles were removed under reduced pressure to give an orange-red solid of **10** (441 mg, 0.375 mmol, 63%). IR (CH₂Cl₂, cm⁻¹): 1980s, 1891s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 516br (ε/L mol⁻¹ cm⁻¹ 670). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.35 (s, 6H, pzCH₃), 2.39 (s, 12H, pzCH₃), 2.48 (s, 6H, pzCH₃), 2.51 (s, 12H, pzCH₃), ca 4.7 (br, 2 H, BH), 5.80 (s, 2H, pzCH), 5.92 (s, 4H, pzCH), 7.72 (s, 1H, C₆H₃N), 8.59 (d, ⁴J_{HH} = 1.9, 2H, C₆H₃N). ¹³C{¹H} NMR (176 MHz, CDCl₃, 25 °C): δ_C = 12.8, 12.8, 15.4, 16.8 (pzCH₃), 106.7, 106.9 (pzCH), 135.7 (br, C₅H₄N), 144.8, 145.4 (pzCCH₃), 145.7 (br, W≡CC), 146.5 (br, C₅H₄N), 152.0, 152.6 (pzCCH₃), 223.7 (WCO, ¹J_{CW} = 164), W≡C not observed. The pyridyl and carbyne carbon resonances were found to be unexpectedly broad in the ¹³C{¹H} NMR spectrum. MS (ESI, *m/z*): Found: 1176.3170. Calcd for C₄₁H₄₈¹¹B₂N₁₃O₄¹⁸⁴W₂ [M+H]⁺: 1176.3157. Anal. Found: C, 42.05; H, 4.17; N, 15.20. Calcd for C₄₁H₄₇B₂N₁₃O₄W₂: C, 41.90; H, 4.03; N, 15.49%.

Synthesis of [NC₅H₄{C≡W(CO)₂(Tp*)}-4] (11**).** A solution of [W(≡CSnⁿBu₃)(CO)₂(Tp*)] (**1**: 500 mg, 0.596 mmol), 4-bromopyridinium chloride (120 mg, 0.617 mmol), [Pd(PPh₃)₄] (69 mg, 0.060 mmol) and [AuCl(SMe₂)] (17 mg, 0.058 mmol) in toluene (30 mL) and triethylamine (1 mL) was heated under reflux for 14 h. The solvent was then removed under reduced pressure, the residue was extracted with *n*-hexane and subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C), followed by 50% v/v dichloromethane/petrol and finally with 100% CH₂Cl₂. A slow-moving, red-purple band was collected and the volatiles were removed under reduced pressure to give a purple solid of **11** (32 mg, 0.051 mmol, 9%). As only a very small amount was isolated, only limited characterisation data could be obtained. IR (CH₂Cl₂, cm⁻¹): 1983s, 1892s ν_{CO}. UV-Vis λ_{max} (CH₂Cl₂/nm): 521br (ε/L mol⁻¹ cm⁻¹ 360). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.35 (s, 3H, pzCH₃), 2.40 (s, 6H, pzCH₃), 2.45 (s, 3H, pzCH₃), 2.46 (s, 6H, pzCH₃), ca 4.7 (br, 1 H, BH), 5.80 (s, 1H, pzCH), 5.92 (s, 2H, pzCH), 7.22 (d, ³J_{HH} = 5.4, 2H, C₅H₄N), 8.54 (d, ³J_{HH} = 5.4, 2H, C₅H₄N). ¹³C{¹H} NMR (151 MHz, CDCl₃, 25 °C): δ_C = 12.8 (2C, coincident), 15.4, 16.7 (pzCH₃), 106.7, 107.0 (pzCH), 122.8 (C₅H₄N), 144.9, 145.6 (pzCCH₃), 149.2 (C₅H₄N), 152.0, 152.6 (pzCCH₃), 156.3 (W≡CC, ²J_{CW} = 44), 223.8 (WCO, ¹J_{CW} = 164), 271.3 (W≡C, ¹J_{CW} = 191). MS (ESI, *m/z*): Found: 628.1839. Calcd for C₂₃H₂₇¹¹B₂N₁₃O₄¹⁸⁴W [M+H]⁺: 628.1835. Anal.

Found: C, 43.85; H, 4.26; N, 15.30. Calcd for C₂₃H₂₆BN₇O₂W: C, 44.05; H, 4.18; N, 15.63%.

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