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Alkynylselenolatoalkylidynes ( $L_nM\equiv C-Se-C\equiv CR$ ) as building blocks for mixed metal/main-group extended frameworksBenjamin J. Frogley,<sup>a</sup> Tobias L. Genet,<sup>a</sup> Anthony F. Hill<sup>\*a</sup> and Chee S. Onn<sup>a</sup>Received 00th January 20xx,  
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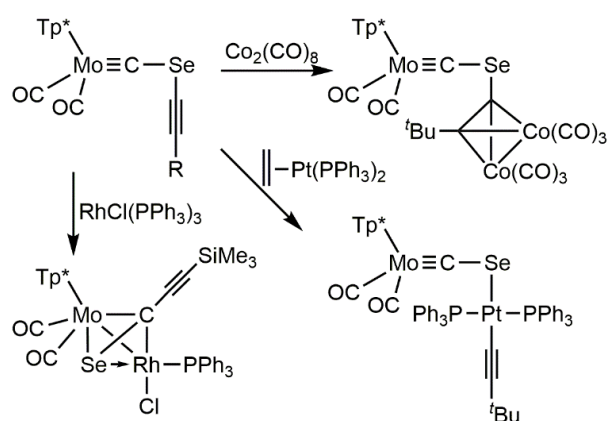
The reactions of  $[W(\equiv CBr)(CO)_2(Tp^*)]$  ( $Tp^*$  = hydrotris(3,5-dimethylpyrazol-1-yl)borate) with lithium alkynylselenolates  $LiSeC\equiv CR$  ( $R = SiMe_3, Si^iPr_3, ^nBu, ^tBu, Ph, p\text{-tolyl}$ ) afford the alkynylselenolatoalkylidyne complexes  $[W(\equiv CSeC\equiv CR)(CO)_2(Tp^*)]$ . Desilylation of the  $SiMe_3$  complex furnishes the parent  $[W(\equiv CSeC\equiv CH)(CO)_2(Tp^*)]$ , which may be further derivatised by deprotonation and treatment with triphenylcarbenium or triphenylmetal chlorides to give mixed-heteroatom products  $[W(\equiv CSeC\equiv CEPPh_3)(CO)_2(Tp^*)]$  ( $E = C, Si, Ge, Sn, Pb$ ). This procedure extends to dichlorosilanes, whereby the unusual bimetallic complexes  $[(Tp^*)(CO)_2W\equiv CSeC\equiv CSiRR'C\equiv CSeC\equiv W(CO)_2(Tp^*)]$  ( $R, R' = Ph, CH_3$ ) are obtained, bridged by unsaturated units interrupted by two different main-group heteroatoms. Finally, the trimetallic analogues,  $[(Tp^*)(CO)_2W(\equiv CSeC\equiv C)]_3SiR$  ( $R = Ph, Et$ ), may be prepared in the same manner from appropriate organotrchlorosilanes.

## Introduction

Selenium has historically enjoyed far less attention than its lighter congeners, most notably in an organometallic context where, for example, carbonyl and thiocarbonyl ligands are encountered routinely but selenocarbonyls remain scarce.<sup>1</sup> We might however anticipate something of a renaissance as the important chemical and biological properties of selenium compounds are increasingly realised, including the development of bioactive and stimuli-responsive polymers.<sup>2</sup>

Our own interests in both organometallic and main-group chemistries have repeatedly led us to complexes which address the disparities between these traditionally distinct regimes. These studies have included the synthesis of the first examples of alkynylselenolatoalkylidyne complexes,  $L_nMo\equiv CSeC\equiv CR$ , which contain a classical alkyne and a transition-metal alkylidyne both directly bonded to a single selenoether. The molybdenum complexes  $[Mo(\equiv CSeC\equiv CR)(CO)_2(Tp^*)]$ , ( $R = CMe_3, SiMe_3, p\text{-tolyl}$ ;  $Tp^*$  = hydrotris(3,5-dimethylpyrazol-1-yl)borate), remain the only such examples and were prepared by the reaction of the molybdenum chlorocarbene complex  $[Mo(\equiv CCl)(CO)_2(Tp^*)]$  with the respective lithium alkynylselenolate,  $LiSeC\equiv CR$ .<sup>3</sup> The many potential sites for reactivity — alkynyl and alkylidynyl triple bonds and weak C–Se single bonds — endow alkynylselenolatoalkylidynes with a potentially diverse range of synthetic utility. This was briefly explored with several metal complexes:  $[Co_2(CO)_8]$  unexpectedly adds across the C=C rather than  $Mo\equiv C$  bond (Scheme 1),<sup>3</sup> whereas with  $[Pt(\eta^2-CH_2CH_2)(PPh_3)_2]$  the platinum initially coordinates to the alkynyl C=C before inserting into the

Se–C bond to give the first isoselenocarbonyl complex,<sup>4</sup> further examples of which followed from alternative strategies.<sup>5</sup> Finally, Wilkinson's catalyst  $[RhCl(PPh_3)_3]$  forms a heterodinuclear selenoacyl complex, presumably through a mechanism involving a sequence of C–Se bond rupture and formation steps.<sup>6</sup>

Scheme 1. Reactions of molybdenum alkynylselenolatoalkylidynes.<sup>3,4,6</sup>

Herein we report an extension of this prior work, whereby treatment of the tungsten bromocarbene  $[W(\equiv CBr)(CO)_2(Tp^*)]$  (**1**) with a range of lithium alkynylselenolates furnishes a suite of stable alkynylselenolatoalkylidynes. One of these, bearing a terminal trimethylsilyl group, can be further derivatised by formal substitution (achieved *via* initial desilylation followed by addition of an electrophile) at the terminal alkynyl carbon with main-group elements to give a complete set of Group 14-substituted derivatives. Finally, we report that this strategy can be extended to afford bi- or even trimetallic frameworks.

## Results and discussion

The tungsten bromocarbene,  $[W(\equiv CBr)(CO)_2(Tp^*)]$  (**1**),<sup>7</sup> undergoes nucleophilic substitution at the carbene carbon with

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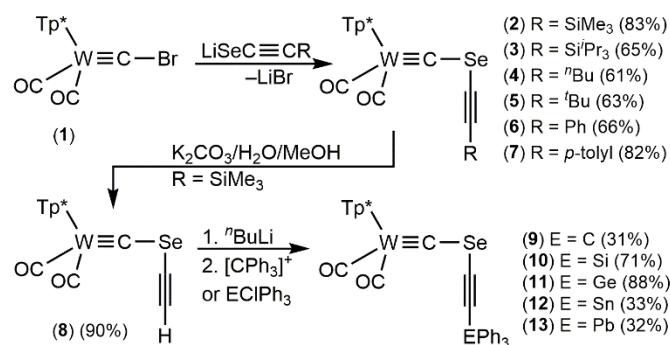
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Electronic Supplementary Information (ESI) available: Selected NMR spectra (PDF). See DOI: 10.1039/x0xx00000x. CCDC 1907302–1907306 contain the supplementary crystallographic data for this paper, and are available free of charge from The Cambridge Crystallographic Data Centre.

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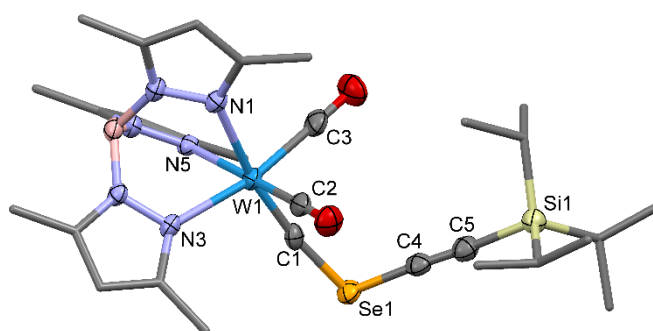
lithium alkynylselenolates,  $\text{LiSeC}\equiv\text{CR}$ , (themselves prepared by successive treatment of the respective terminal alkyne with  $^n\text{BuLi}$  and grey selenium) to furnish alkynylselenolatoalkylidynes  $[\text{W}(\equiv\text{CSeC}\equiv\text{CR})(\text{CO})_2(\text{Tp}^*)]$  ( $\text{R} = \text{SiMe}_3$  **2**;  $\text{Si}^i\text{Pr}_3$  **3**;  $^n\text{Bu}$  **4**;  $^t\text{Bu}$  **5**;  $\text{Ph}$  **6**;  $p$ -tolyl **7**) (Scheme 2), which were isolated as orange microcrystalline solids in good yield following chromatographic purification.

Selected spectroscopic and structural data for **2–7** are presented in Table 1. The  $^1\text{H}$  NMR spectra of **2–7** are reassuringly simple and exclusively populated by resonances relating to the alkynyl substituent and  $\text{Tp}^*$  ligand. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, low-field resonances for the  $\text{W}\equiv\text{C}$  carbyne carbons are located in the narrow range 235.3–240.1 ppm with the chemical shift being somewhat unresponsive to variations in alkynyl substituent. Lone singlets were observed in the  $^{77}\text{Se}\{^1\text{H}\}$  NMR spectra from 496–513 ppm with  $^2J_{\text{WSe}}$  couplings in the range 30–34 Hz. The narrow ranges of these chemical shifts and infrared  $\nu_{\text{CO}}$  absorbances (see Table 1) indicates that these ‘reporter’ data are insensitive to variation of the terminal R group which has only a minor influence on the electronic environment at tungsten. Furthermore, comparison, *e.g.*, of infrared data for the phenyl derivative **6** [ $\text{CH}_2\text{Cl}_2$ :  $\nu_{\text{CO}} = 1986$ ,  $1896\text{ cm}^{-1}$ ;  $k_{\text{Ck}} = 15.21\text{ Ncm}^{-1}$ ] with those for the simple alkylselenolate  $[\text{Mo}(\equiv\text{CSeMe})(\text{CO})_2(\text{Tp}^*)]$  (THF:  $\nu_{\text{CO}} = 1987$ ,  $1905\text{ cm}^{-1}$ ;  $k_{\text{CH}} = 15.28\text{ Ncm}^{-1}$ )<sup>5c,7b,8,9</sup> again suggests that variation in the selenoether substituent does not significantly impact upon the  $\pi$ -basicity of the metal centre.



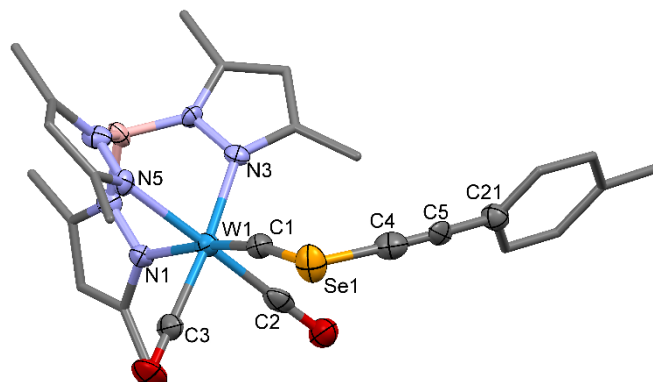
**Scheme 2.** Synthesis of alkynylselenolatoalkylidynes of tungsten and installation of  $\text{EPh}_3$  ( $\text{E} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) alkynyl substituents.

The formulations of **3** and **7** were further confirmed by single crystal X-ray crystallography; the molecular geometries are shown in Figures 1 and 2, respectively. The bond distances along the  $\text{W}\equiv\text{CSeC}\equiv\text{CR}$  spine are well within their typical ranges although the angles about the  $sp$ -hybridised carbons are not as substantially contracted as those for the related angles in the molybdenum analogue,  $[\text{Mo}(\equiv\text{CSeC}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{Tp}^*)]$  (*e.g.*, **3**:  $\text{W1}-\text{C1}-\text{Se1}$   $170.5(2)$ ,  $\text{Se1}-\text{C4}-\text{C5}$   $176.8(4)$ ,  $\text{C4}-\text{C5}-\text{Si1}$   $174.9(4)^\circ$ , *cf.*  $162.8(8)$ ,  $171.6(15)$ ,  $166.8(11)^\circ$ , respectively, for the Mo complex). Similarly, the angles about Se in **3** ( $99.78(19)^\circ$ )



**Figure 1.** Molecular structure of **3** showing 50% thermal probability ellipsoids. Pyrazolyl and isopropyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances (Å) and angles ( $^\circ$ ):  $\text{W1}-\text{C1}$   $1.810(4)$ ,  $\text{C1}-\text{Se1}$   $1.880(4)$ ,  $\text{Se1}-\text{C4}$   $1.832(5)$ ,  $\text{C4}-\text{C5}$   $1.204(6)$ ,  $\text{C5}-\text{Si1}$   $1.854(5)$ ,  $\text{W1}-\text{C1}-\text{Se1}$   $170.5(2)$ ,  $\text{C1}-\text{Se1}-\text{C4}$   $99.78(19)$ ,  $\text{Se1}-\text{C4}-\text{C5}$   $176.8(4)$ ,  $\text{C4}-\text{C5}-\text{Si1}$   $174.9(4)$ .

and **7** ( $97.0(5)^\circ$ ) are somewhat less contracted than in the molybdenum analogue ( $93.4(6)^\circ$ )<sup>3</sup>, being much closer to the  $98$ – $101^\circ$  range typically observed for acyclic alkynylselenoethers  $\text{RC}\equiv\text{CSeR}'$ .<sup>10</sup> Given their otherwise close structural similarity, these deviations presumably result from solid state packing effects, a feature commonly encountered for alkylidynes ligated by bulky poly(pyrazolyl)borates such as  $\text{Tp}^*$ .<sup>9</sup>



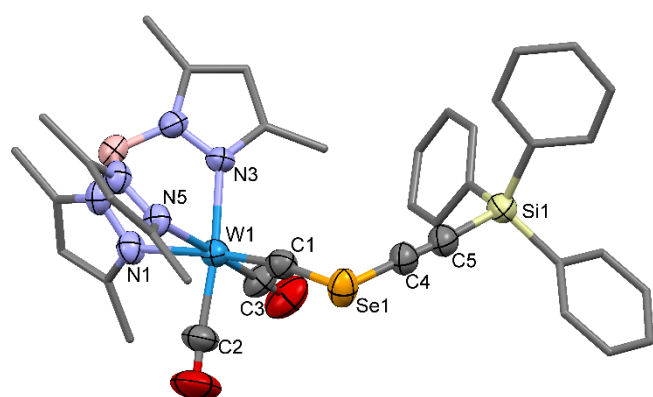
**Figure 2.** Molecular structure of **7** showing 50% thermal probability ellipsoids. Pyrazolyl and  $p$ -tolyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances (Å) and angles ( $^\circ$ ):  $\text{W1}-\text{C1}$   $1.822(10)$ ,  $\text{C1}-\text{Se1}$   $1.881(10)$ ,  $\text{Se1}-\text{C4}$   $1.843(12)$ ,  $\text{C4}-\text{C5}$   $1.206(14)$ ,  $\text{C5}-\text{C21}$   $1.417(14)$ ,  $\text{W1}-\text{C1}-\text{Se1}$   $169.6(5)$ ,  $\text{C1}-\text{Se1}-\text{C4}$   $97.0(5)$ ,  $\text{Se1}-\text{C4}-\text{C5}$   $174.6(11)$ ,  $\text{C4}-\text{C5}-\text{C21}$   $175.1(12)$ .

Although the synthesis of alkynylselenolatoalkylidynes from lithium alkynylselenolates proceeds reasonably cleanly and in high yields, the method is limited by the required inertness of the alkyne termini towards  $^n\text{BuLi}$  and grey Se. However, the good yields and apparent stability of **2–7** inspired us to consider whether further derivatisation could be achieved by chemical modification of the pre-formed complexes. In particular, incorporation of additional main-group heteroatoms is of interest as these can serve to introduce further functionality and downstream synthetic utility. Thus, the trimethylsilyl complex **2** was subjected to  $\text{K}_2\text{CO}_3/\text{H}_2\text{O}/\text{MeOH}$  and, following extraction with dichloromethane and chromatographic purification, the desilylated parent complex,  $[\text{W}(\equiv\text{CSeC}\equiv\text{CH})(\text{CO})_2(\text{Tp}^*)]$  (**8**) was isolated as an orange solid in

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encouragingly high 90% yield (Scheme 2). The spectroscopic data for this species are nearly identical to those of **2–7** and confirm that the  $W\equiv CSe\equiv C$  spine has remained intact despite the rather hostile desilylation conditions. The only distinguishing feature that is notable is a resonance at 3.24 ppm in the  $^1H$  NMR spectrum attributable to the acetylenic proton.

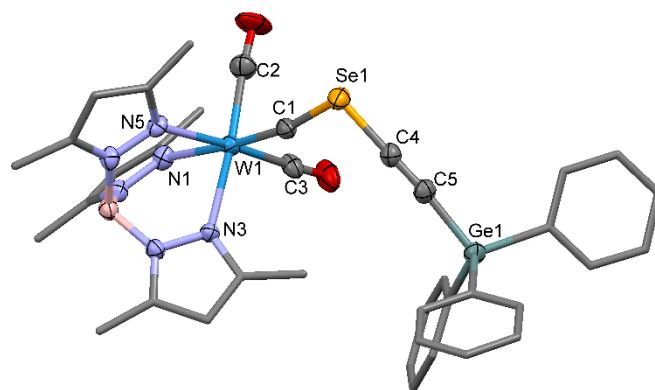
The acetylenic proton in **8** is weakly acidic and can be deprotonated *in situ* with *n*-butyllithium to generate an unisolated acetylide intermediate,  $[W(\equiv CSe\equiv C)(CO)_2(Tp^*)]Li$ , which should be susceptible to attack by electrophiles. Notably, this is an isomer of the previously reported selenoxopropadienyliene salt  $[W(\equiv CC\equiv CSe)(CO)_2(Tp^*)]Li$ . Treatment of a THF solution of **8** with  $^nBuLi$  followed shortly thereafter by triphenylcarbenium hexafluorophosphate  $[CPh_3][PF_6]$  provided the new derivative  $[W(\equiv CSe\equiv CPh_3)(CO)_2(Tp^*)]$  (**9**) as an orange microcrystalline solid in modest yield following chromatographic purification. This procedure is not limited to carbon and can be extended to the entire set of Group 14 derivatives. Thus, treatment of **8** with  $^nBuLi$  followed by  $ECIPh_3$  furnishes  $[W(\equiv CSe\equiv CEPh_3)(CO)_2(Tp^*)]$  (E = Si **10**; E = Ge **11**; E = Sn **12**; E = Pb **13**), each of which was isolated as orange or orange-brown solids. While complexes **9–11** could be purified by silica gel column chromatography and isolated in good yields, the alkynyl C–Sn and C–Pb bonds in **12** and **13** proved too hydrolytically sensitive for chromatography, being almost immediately cleaved to reform the parent complex, **8**, which could be recovered in near stoichiometric amounts. In these latter two cases, reasonable purity could be attained through successive recrystallizations from dichloromethane and ethanol (which also resulted in the diminished yield compared to the Si and Ge species), although invariably a small amount of residual  $SnClPh_3$  or  $PbClPh_3$  remained.



**Figure 3.** Molecular structure of **10** showing 50% thermal probability ellipsoids. Pyrazolyl and phenyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances (Å) and angles ( $^\circ$ ): W1–C1 1.838(5), C1–Se1 1.846(5), Se1–C4 1.848(5), C4–C5 1.182(8), C5–Si1 1.834(6), W1–C1–Se1 170.1(3), C1–Se1–C4 99.9(2), Se1–C4–C5 179.2(5), C4–C5–Si1 176.5(5).

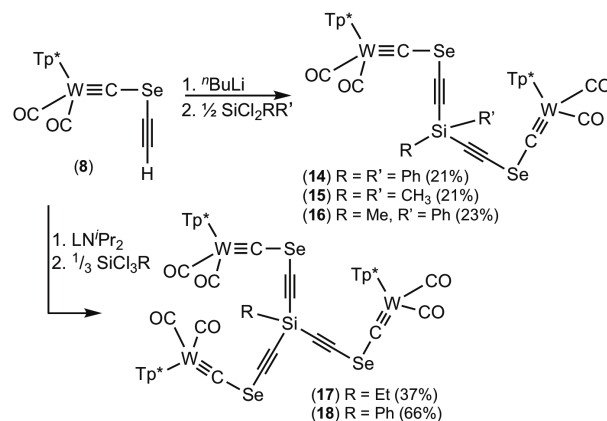
The interrupting selenium again prevents the  $EPh_3$  (E = C, Si, Ge, Sn, Pb) substituents from exerting any significant influence on the remote environment about tungsten. The  $W\equiv C$  resonances in the  $^{13}C\{^1H\}$  spectra are located between 235.3 (for Pb) and 238.8 ppm (for C) and there is no significant

difference in infrared carbonyl stretching frequencies as the group 14 element changes. The selenium resonances in the  $^{77}Se\{^1H\}$  NMR spectra do, however, shift very slightly downfield when descending Group 14, from 494 ppm in **9** to 525 ppm in **13**, thus indicating that there is at least a small degree of electronic influence being transmitted across the alkyne. The molecular structures of **10** and **11** have been determined and the geometries are shown in Figures 3 and 4, respectively. The group 14 substituents do not, within error, have any significant influence on the geometry of the  $W\equiv CSe\equiv C$  spine and the structural parameters are essentially indistinguishable from those of **3** and **7**.



**Figure 4.** Molecular structure of **11** showing 50% thermal probability ellipsoids. Pyrazolyl and phenyl groups are simplified and hydrogen atoms are not shown for clarity. Selected distances (Å) and angles ( $^\circ$ ): W–C1 1.844(4), C1–Se1 1.851(4), Se1–C4 1.840(4), C4–C5 1.194(6), C5–Ge1 1.914(5), W1–C1–Se1 169.6(3), C1–Se1–C4 99.46(19), C4–C5–Ge1 175.0(4).

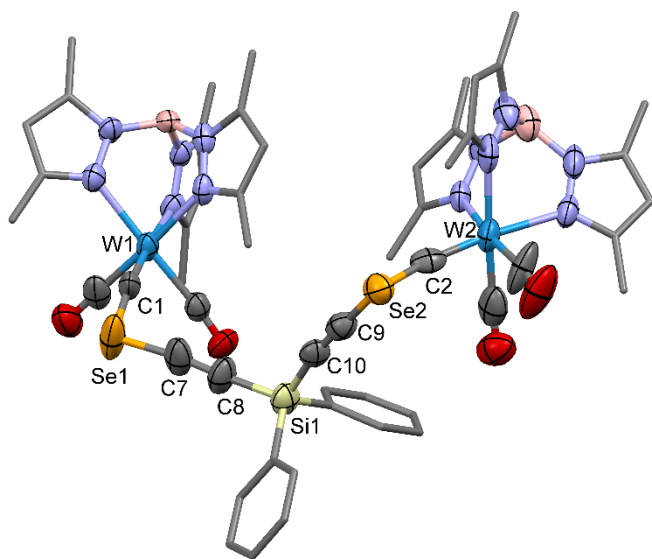
With the viability of the proposed strategy for derivatisation of alkynylselenolatoalkylidynes with main-group heteroatoms demonstrated, we considered their potential for introduction into interrupted molecular wires or even larger extended frameworks. In an initial foray into such chemistry, treatment of **8** with  $^nBuLi$  followed by half an equivalent of dichlorosilane  $SiCl_2RR'$  results in the formation of the bimetallic complexes  $\{[(Tp^*)(CO)_2W\equiv CSe\equiv C]_2SiRR'\}$  (R = R' = Ph **14**; R = R' = Me **15**; R = Ph, R' = Me **16**), each of which were isolated as orange solids in low yield (21–23%) following chromatographic purification (Scheme 3).



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**Scheme 3.** Synthesis of bi- and trimetallic complexes where the metals are bridged by  $\equiv\text{CSeC}\equiv\text{CSi}(\text{RR}')\text{C}\equiv\text{CSeC}\equiv$  units.

The complexes **14** – **16** contain two tungsten metal centers bridged by an unusual 9-atom  $\equiv\text{CSeC}\equiv\text{CSi}(\text{RR}')\text{C}\equiv\text{CSeC}\equiv$  unit, a molecular wire with two different heteroatomic elements interrupting the unsaturated units. The two ends of the complexes are, as expected, chemically equivalent on the NMR timescale and give rise to a single set of signals in the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{77}\text{Se}\{^1\text{H}\}$  NMR spectra. These are nearly identical to those for the monometallic analogue **10**, the only major distinction being the change in relative integrals between the  $\text{Tp}^*$  and  $\text{SiR}_2$  protons. The molecular structure of **14** has been crystallographically determined and the geometry is depicted in Figure 5. The poor quality of acquired data precludes detailed comparisons of structural parameters with those more precisely determined for the mononuclear examples above, but nonetheless confirm the formulation as the desired ditungsten complex where the two metal centers are bridged by a  $\equiv\text{CSeC}\equiv\text{CSiPh}_2\text{C}\equiv\text{CSeC}\equiv$  moiety. In the solid state the two ends of the “wire” are crystallographically inequivalent and the  $(\text{Tp}^*)(\text{CO})_2\text{W}$  fragments appear to be oriented adjacent to each other. With this arrangement, the shortest intramolecular  $\text{H}\cdots\text{H}$  distance is a little over 2.5 Å and indicates a mild but not prohibitive steric clash between the bulky  $\text{Tp}^*$  ligands. The single set of solution IR and NMR signals indicate that this geometry is not rigidly maintained in solution.

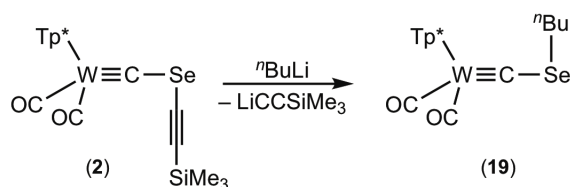


**Figure 5.** Molecular structure of **14** showing 50% thermal probability ellipsoids. Pyrazolyl and phenyl groups are simplified, hydrogen atoms and minor disorder components are not shown for clarity. Selected distances (Å) and angles ( $^\circ$ ): W1–C1 1.824(15), C1–Se1 1.851(15), Se1–C7 1.812(13), C7–C8 1.241(17), C8–Si1 1.825(12), Si1–C10 1.792(15), C10–C9 1.223(17), C9–Se2 1.849(15), Se2–C2 1.827(13), C2–W2 1.852(13), W1–C1–Se1 168.0(9), C1–Se1–C7 99.3(5), C8–Si1–C10 112.5(7), C9–Se2–C2 97.5(5), Se2–C2–W2 167.0(7).

In light of the good yields obtained from the reaction with  $\text{SiClPh}_3$ , the disappointing yields of **14**–**16** are presumed to arise from the increasing steric barrier which must be overcome to generate the bimetallic species. We have not yet been able to

identify or isolate a monometallic species arising from substitution of just one  $\text{Si}-\text{Cl}$  although this is not necessarily surprising given that these would presumably be highly reactive and decompose readily under the workup conditions used. We suspect that the slowed reaction rate gives more opportunity for conversion into undesired side or decomposition products, although thus far we have only been able to isolate small quantities (<5%) of unreacted **8** and the ditungsten octatetrayne,  $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\equiv\text{C}\equiv\text{C}\equiv\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)]$ .<sup>12</sup> Selenium extrusion was also noted for the molybdenum alkynylselenolatoalkynylidynes<sup>3</sup> and, although undesirable in the present context, this indicates that  $\text{C}-\text{Se}$  bond cleavage is viable and may be synthetically exploitable if it can be controlled selectively.

These problems are exacerbated when the same reactions are conducted with trichlorosilanes, and only traces (*ca.* 5%) of the desired trimetallic derivatives were observed when *n*-butyllithium was employed as the base. Notably, these reactions were also accompanied by the formation of variable amounts of the *n*-butyl selenoether  $[\text{W}(\equiv\text{CSe}^n\text{Bu})(\text{CO})_2(\text{Tp}^*)]$  (**19**, Scheme 4), consistent with alkynyl substitution at selenium by nucleophilic  $^n\text{BuLi}$ . The tellurium analogue of **19** has recently been described via an alternative strategy.<sup>13</sup>



**Scheme 4.** Nucleophilic  $\text{Se}-\text{C}$  cleavage of an alkynylselenolatoalkynylidyne.

The same product can be prepared in high yield (83%) by subjecting **2** to *n*-butyllithium at room temperature for several hours. Accordingly, we turned to a milder, non-nucleophilic base. Treatment of **8** with lithium diisopropylamide (LDA) followed shortly thereafter by one-third an equivalent of ethyltrichlorosilane  $\text{SiCl}_3\text{Et}$  gave the trimetallic derivative,  $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{CSeC}\equiv\text{C}_3\text{SiEt}]$  (**17**), in a reasonable 37% yield (Scheme 3). The same reaction with  $\text{SiCl}_3\text{Ph}$  furnished  $[(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{CSeC}\equiv\text{C}_3\text{SiPh}]$  (**18**) in a more respectable 66% yield. As found for the bimetallic complexes, all three metal centers are equivalent by NMR and give rise to a single set of resonances that are near identical to those for other complexes reported in this paper. Our attempts to form the tetrametallic derivative with  $\text{SiCl}_4$  have, however, not been met with success and we suspect a new strategy will be needed to overcome the steric barrier such a complex would pose.

**Table 1.** Selected crystallographic,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{77}\text{Se}\{^1\text{H}\}$  NMR and IR data for complexes reported in this paper;  $[\text{LW}(\equiv\text{CSeC}\equiv\text{CR})]$  (**2**–**13**),  $[\{\text{LW}(\equiv\text{CSeC}\equiv\text{C})_2\text{R}\}]$  (**14**–**16**) or  $[\{\text{LW}(\equiv\text{CSeC}\equiv\text{C})_3\text{R}\}]$  (**17**–**18**) ( $\text{L} = (\text{Tp}^*)(\text{CO})_2\text{W}$ ).

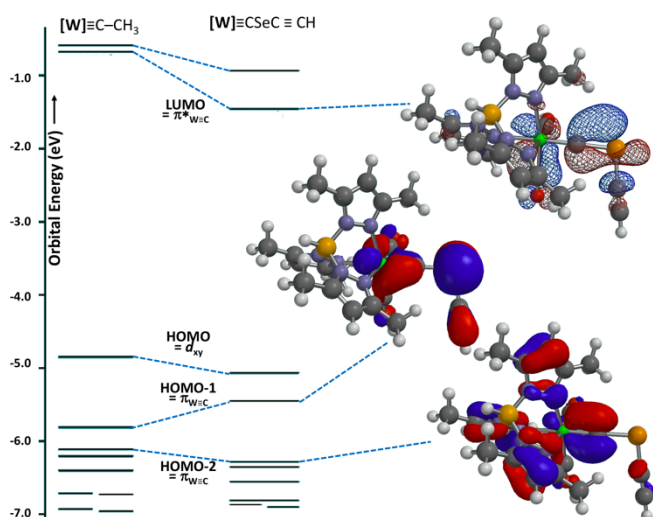
| R        | $\delta_{\text{C}}^a$ | $^1J_{\text{CW}}^b$ | $\delta_{\text{Se}}^a$ | $r_{\text{W=C}}(\text{Å})$ | $\nu_{\text{CO}}^c$    |
|----------|-----------------------|---------------------|------------------------|----------------------------|------------------------|
| <b>2</b> | TMS                   | 235.3               | 227                    | 513                        | 1988, 1897             |
| <b>3</b> | TIPS                  | 236.5               | 227                    | 510                        | 1.810(4)<br>1987, 1895 |
| <b>4</b> | $^n\text{Bu}$         | 239.9               | 225                    | 496                        | 1985, 1894             |

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|----|-------------------|-------|-----|-----|------------------------|------------|--|
| 5  | <sup>t</sup> Bu   | 240.1 | 225 | 496 |                        | 1985, 1893 |  |
| 6  | Ph                | 236.3 | 227 | 500 |                        | 1986, 1896 |  |
| 7  | <i>p</i> -tolyl   | 237.0 | 227 | 500 | 1.822(10)              | 1986, 1894 |  |
| 8  | H                 | 233.6 | 227 | 494 |                        | 1989, 1898 |  |
| 9  | CPh <sub>3</sub>  | 238.8 | 225 | 497 |                        | 1986, 1894 |  |
| 10 | SiPh <sub>3</sub> | 234.0 | 223 | 515 | 1.838(5)               | 1988, 1898 |  |
| 11 | GePh <sub>3</sub> | 235.4 | 227 | 517 | 1.844(4)               | 1987, 1896 |  |
| 12 | SnPh <sub>3</sub> | 235.7 | 228 | 522 |                        | 1985, 1893 |  |
| 13 | PbPh <sub>3</sub> | 235.3 | 227 | 525 |                        | 1988, 1900 |  |
| 14 | SiPh <sub>2</sub> | 233.3 | 227 | 516 | 1.824(15)<br>1.852(13) | 1989, 1897 |  |
| 15 | SiMe <sub>2</sub> | 233.9 | 227 | 515 |                        | 1988, 1895 |  |
| 16 | SiMePh            | 233.5 | 231 | 516 |                        | 1988, 1897 |  |
| 17 | SiEt              | 233.1 | 227 | 517 |                        | 1989, 1898 |  |
| 18 | SiPh              | 232.6 | 223 | 518 |                        | 1991, 1898 |  |

<sup>a</sup> Measured in CDCl<sub>3</sub> (ppm). <sup>b</sup> Measured in CDCl<sub>3</sub> (Hz). <sup>c</sup> Measured in Dichloromethane (cm<sup>-1</sup>).

Although structural data have been presented above for a number of alkynylselenolatoalkylidyne complexes, less than ideal geometries were often encountered along the WCSeCC spines due, no doubt, to crystal packing effects for these irregularly shaped molecules. Furthermore, crystallographic grade crystals of the parent derivative **8** were not forthcoming. Accordingly, the molecular geometry of **8** was interrogated with recourse to computational methods (DFT: B3LYP-6-31G(LANL2DZ)). The optimised geometry is shown in Figure 6 which also depicts selected frontier orbitals of interest.



**Figure 6.** Optimised geometry and selected frontier molecular orbitals of interest for the alkylidyne complexes  $[W(=CR)(CO)_2(Tp^*)]$  ( $R = Me$ ,  $SeC\equiv CH$  **8**;  $[W] = W(CO)_2(Tp^*)$ ).

In the absence of significant inter- or intra-molecular interactions, the  $W\equiv C-Se$  is close to, but not exactly, linear ( $173.7^\circ$ ) whilst the angle at selenium ( $99.0^\circ$  cf.  $97.0(5)^\circ$  for **7**) reflects the general tendency towards substituent orthogonality for compounds of the heavier *p*-block elements (so-called  $p^3$  hybridisation with reduced *s*-character). The calculated  $C-Se-C$  bond angle and the  $W\equiv C$  and  $C-Se$  bond lengths are not significantly different from those values

experimentally determined above ( $r_{WC} = 1.828 \text{ \AA}$  cf.  $1.822(10) \text{ \AA}$  for **7**). Notably, the alkylidynyl and alkynyl  $C-Se$  bond lengths are rather similar ( $2.058$  and  $2.037 \text{ \AA}$ , respectively) indicating comparable conjugation in both cases. In comparison to the benchmark ethylidyne complex  $[W(\equiv CMe)(CO)_2(Tp^*)]$  (KBr:  $\nu_{CO} = 1968, 1867 \text{ cm}^{-1}$ ;  $k_{CK} = 14.84 \text{ Ncm}^{-1}$ ),<sup>14</sup> the  $CSeC\equiv CH$  carbyne ligand is a stronger net  $\pi$ -acceptor, as reflected in the infrared data associated with carbonyl co-ligands ( $CH_2Cl_2$  **8**:  $\nu_{CO} = 1989, 1898 \text{ cm}^{-1}$ ;  $k_{CK} = 15.24 \text{ Ncm}^{-1}$ ). Whilst the two acceptor orbitals of the ethylidyne ligand are essentially degenerate, those for the ethynylselenolatoalkylidyne are not, due to different degrees of conjugation with the selenolate substituent, leading to orientational preferences. Thus the HOMO-1 which is delocalised along the  $WCSeCC$  spine is  $W-C$  and  $C-C$   $\pi$ -bonding in character but  $WC-Se$  and  $Se-CC$   $\pi$ -antibonding. In contrast the second component to the  $WC$  triple bond, primarily HOMO-2, has negligible contribution from the  $SeCCH$  substituent orbitals. For the gas-phase optimised structure, one carbonyl ligand approaches co-planarity with the  $WCSeCC$  group (dihedral  $OC-W-Se-CC$   $22.1^\circ$ ), however a range of  $OC-WSe-C$  dihedral angles are observed in the experimentally determined structures discussed above. The  $(Tp^*)(CO)_2W$  fragment presents to a carbyne ligand two orbitals of  $\pi$ -symmetry suitable for retrodonation.<sup>15</sup> These are degenerate and thus the energy differences between various orientational conformations are small and comparable to crystal packing effects. Similar arguments have been provided to describe rotational preferences for phosphinocarbyne complexes,<sup>16</sup> which also bear positively mesomeric heteroatom substituents.

The topology of the LUMO is of interest in that it is  $C-Se$   $\sigma$ -antibonding in character and protrudes significantly from the selenium. This therefore accounts for the preferred use of a *non-nucleophilic* base ( $LiN^iPr_2$ ) for the deprotonation of **8** since  $nBuLi$  can competitively act as a nucleophile ( $S_N2$ ) towards selenium, with alkynyl displacement to provide **19**. In some respects this mimics the common use of arylselenocyanates ( $Ar-SeCN$ ) for the electrophilic installation of arylselenolate substituents *via* cyanide displacement by nucleophiles.

The key issue of interest for alkynylselenolatoalkylidyne, other than their potential reactivity, is the extent to which the introduction of heteroatoms (in this case selenium) into an organometallic wire perturbs electronic communication along the chain. In this respect it is noteworthy that beyond the unremarkable  $\sigma$ -framework, selenium atomic orbitals do indeed participate in  $\pi$ -bonding along the chain, as evident *inter alia* for HOMO-1 (shown). It also stands to reason that the "lone" pairs on selenium are available for coordination to extraneous electrophiles and that this will moderate their participation in such delocalised bonding, a feature of potential interest for chemical switching processes.

## Conclusions

A suite of alkynylselenolatoalkylidyne have been prepared *via* nucleophilic substitution of a bromocarbyne with the respective lithium alkynylselenolate ( $LiSeC\equiv CR$ ). When  $R = SiMe_3$ , subsequent desilylation gives the parent

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ethynylselenolatoalkylidyne which may be derivatised further by deprotonation and subsequent treatment with an appropriate electrophile. This method allowed the complete set of group 14 element derivatives,  $[W(\equiv CSeC\equiv CEP_h_3)(CO)_2(Tp^*)]$  ( $E = C, Si, Ge, Sn, Pb$ ), to be prepared using  $[CPh_3][PF_6]$  ( $E = C$ ) or  $ECIPh_3$  ( $E \neq C$ ). A simple extension of this strategy allowed three examples of bimetallic complexes and two examples of trimetallic complexes to be prepared from dichloro- or trichlorosilanes, respectively, which possess unusual  $\equiv CSeC\equiv CSiR_2C\equiv CSeC\equiv$  bridges with two different heteroatoms connecting the unsaturated units. The synthetic strategies used to prepare these complexes can foreseeably be extended to give a wide range of main-group element interrupted molecular wires<sup>17</sup> or even extended frameworks comprised of selenolatoalkylidyne building blocks — a matter we are presently exploring.

## Experimental

### General Considerations

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 at 25 °C on a Bruker Avance 400 (<sup>1</sup>H at 400.1 MHz, <sup>13</sup>C at 100.6 MHz, <sup>31</sup>P at 162.0 MHz), a Bruker Avance 600 (<sup>1</sup>H at 600.0 MHz, <sup>13</sup>C at 150.9 MHz) or a Bruker Avance 700 (<sup>1</sup>H at 700.0 MHz, <sup>13</sup>C at 176.1 MHz) spectrometers. Chemical shifts ( $\delta$ ) are reported in ppm and referenced to the residual solvent peak (<sup>1</sup>H, <sup>13</sup>C) or externally referenced (85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, (PhSe)<sub>2</sub> for <sup>77</sup>Se, SnMe<sub>4</sub> for <sup>127</sup>Sn, PbMe<sub>4</sub> for <sup>207</sup>Pb with coupling constants given in Hz. 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 <sup>183</sup>W satellites. In some cases, distinct peaks were observed in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, but to the level of accuracy that is reportable (*i.e.*, 2 decimal places for <sup>1</sup>H NMR, 1 decimal place for <sup>13</sup>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.

Infrared spectra were obtained using a Perkin-Elmer 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). 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 CCD diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) or an Agilent SuperNova CCD diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å) using the CrysAlis PRO software.<sup>18</sup>

Data for **14** was collected at the Australian Synchrotron using the MX1 beamline using silicon double crystal monochromated synchrotron radiation at 100 K. Raw frame data were collected using BluIce<sup>19</sup> and data reduction, interframe scaling, unit cell refinement and absorption corrections were processed using XDS.<sup>20</sup> The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on  $F^2$  using the SHELXL programs<sup>21</sup> and the WinGX<sup>22</sup> or Olex2 software.<sup>23</sup> Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.<sup>24</sup> Calculations were performed at the DFT:B3LYP-LANL2DZ level of theory for gas phase molecules employing the SPARTAN-18<sup>®</sup> suite of programs.<sup>25</sup>

The complex  $[W(\equiv CBr)(CO)_2(Tp^*)]$  (**1**) has been described previously.<sup>7</sup>

**Synthesis of  $[W(\equiv CSeC\equiv CSiMe_3)(CO)_2(Tp^*)]$  (**2**).** To a solution of ethynyltrimethylsilane (450  $\mu$ L, 3.18 mmol) in THF (10 mL) at  $-78$  °C was added <sup>n</sup>BuLi (2.0 mL, 1.6 M in hexanes, 3.2 mmol). The mixture was warmed to room temperature and stirring was continued for 30 min. Grey selenium (0.251 g, 3.18 mg.atom) was then added and the mixture stirred for 1 h, during which time the solution turned clear. The mixture was again cooled to  $-78$  °C and transferred *via* cannula to a similarly cooled solution of **1** (2.00 g, 3.18 mmol) in THF (10 mL). The mixture was gradually warmed to room temperature and stirring was continued overnight, during which time the mixture turned orange-brown. Volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **3** (1.91 g, 2.63 mmol, 83 %). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2092s  $\nu_{C\equiv C}$ , 1988s, 1897s  $\nu_{CO}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_H = 0.21$  (s, 9 H, SiCH<sub>3</sub>), 2.32 (s, 3 H, pzCH<sub>3</sub>), 2.36 (s, 6 H, pzCH<sub>3</sub>), 2.41 (s, 3 H, pzCH<sub>3</sub>), 2.55 (s, 6 H, pzCH<sub>3</sub>), 5.77 (s, 1 H, pzH), 5.90 (s, 2 H, pzH). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_C = 0.2$  (SiCH<sub>3</sub>), 12.9, 13.0, 15.6, 17.2 (pzCH<sub>3</sub>), 78.2 (SeC $\equiv$ C), 106.9, 107.2 (pzCH), 112.1 (SeC $\equiv$ C), 144.8, 145.7, 152.4, 153.1 (pzCCH<sub>3</sub>), 223.3 (CO, <sup>1</sup>J<sub>WC</sub> = 164), 235.3 (W $\equiv$ C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{Se} = 513$ , <sup>2</sup>J<sub>WSe</sub> = 36 Hz. MS (ESI, *m/z*): Found: 727.1114. Calcd for C<sub>23</sub>H<sub>32</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>28</sup>Si<sup>184</sup>W [M + H]<sup>+</sup>: 727.1118. Anal. Found: C, 38.26; H, 4.42; N, 11.51%. Calcd for C<sub>23</sub>H<sub>31</sub>BN<sub>6</sub>O<sub>2</sub>SeSiW: C, 38.09; H, 4.31; N, 11.59%.

**Synthesis of  $[W(\equiv CSeC\equiv CTIPS)(CO)_2(Tp^*)]$  (**3**).** A solution of ethynyltriisopropylsilane (37  $\mu$ L, 0.17 mmol) in THF (5 mL) at  $-78$  °C was treated with <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol). The mixture was warmed to room temperature and stirring was continued for 30 min. Grey selenium (0.013 g, 0.16 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to  $-78$  °C and transferred *via* cannula into a similarly cooled solution of **1** (0.100 g, 0.159 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred

overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **3** (0.0840 g, 0.104 mmol, 65%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1987s, 1895s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 1.10 (2 x overlapping s, 21 H, SiCHCH<sub>3</sub>), 2.34 (s, 3 H, pzCH<sub>3</sub>), 2.38 (s, 6 H, pzCH<sub>3</sub>), 2.42 (s, 3 H, pzCH<sub>3</sub>), 2.57 (s, 6 H, pzCH<sub>3</sub>), 5.78 (s, 1 H, pzH), 5.91 (s, 2 H, pzH). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 11.7 (SiCH), 12.9, 13.0, 15.6, 17.2 (pzCH<sub>3</sub>), 18.9 (SiCHCH<sub>3</sub>), 79.4 (SeC≡C), 106.8, 107.1 (pzCH), 108.6 (SeC≡C), 144.7, 145.7, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.5 (CO, <sup>1</sup>J<sub>WC</sub> = 165), 236.5 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 510, <sup>2</sup>J<sub>WSe</sub> = 34 Hz. MS (ESI, *m/z*): Found: 833.1884. Calcd for C<sub>29</sub>H<sub>43</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>28</sup>Si<sup>184</sup>WNa [M + Na]<sup>+</sup>: 833.1874. Anal. Found: C, 42.95; H, 5.20; N, 10.26%. Calcd for C<sub>29</sub>H<sub>43</sub>BN<sub>6</sub>O<sub>2</sub>SeSiW: C, 43.03; H, 5.36; N, 10.38%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a Dichloromethane/ethanol mixture. *Crystal data* for C<sub>29</sub>H<sub>43</sub>BN<sub>6</sub>O<sub>2</sub>SeSiW: *M*<sub>w</sub> = 809.40 g mol<sup>-1</sup>, triclinic, space group *P*-1 (no. 2), *a* = 10.5392(4), *b* = 10.7394(4), *c* = 15.4228(8) Å,  $\alpha$  = 83.797(4)°,  $\beta$  = 86.323(4)°,  $\gamma$  = 74.083(3)°, *V* = 1667.78(13) Å<sup>3</sup>, *Z* = 2, *T* = 150.0(1) K,  $\mu(\text{Mo K}\alpha)$  = 4.625 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.612 Mg m<sup>-3</sup>, 11072 reflections measured (6.552° ≤ 2 $\theta$  ≤ 57.246°), 7046 unique (*R*<sub>int</sub> = 0.0382, *R*<sub>sigma</sub> = 0.0727) which were used in all calculations. The final *R*<sub>1</sub> was 0.0373 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.0709 (all data) for 382 refined parameters with 0 restraints. CCDC 1907302.

**Synthesis of [W(≡CSeC≡C<sup>n</sup>Bu)(CO)<sub>2</sub>(Tp\*)] (4).** To a solution of 1-hexyne (20  $\mu$ L, 0.17 mmol) in THF (5 mL) at –78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol). The mixture was brought to room temperature and stirred for 30 min. Grey selenium (0.013 g, 0.159 mg.atom) was then added and stirring was continued for 1 h, during which time the solution became clear. The mixture was again cooled to –78 °C and transferred *via* cannula into a similarly cooled solution of **1** (0.100 g, 0.159 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight, during which time the mixture turned orange-brown. The volatiles were then removed *in vacuo* the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 7:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **4** (0.069 g, 0.097 mmol, 61%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1985s, 1894s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 0.91 (t, <sup>3</sup>J<sub>HH</sub> = 7.7, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.44 (m, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 1.53 (m, 2 H, ≡CCH<sub>2</sub>CH<sub>2</sub>), 2.31 (s, 3 H, pzCH<sub>3</sub>), 2.36 (s, 6 H, pzCH<sub>3</sub>), 2.40 (s, 3 H, pzCH<sub>3</sub>), 2.43 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 2 H, ≡CCH<sub>2</sub>), 2.56 (s, 6 H, pzCH<sub>3</sub>), 5.76 (s, 1 H, pzCH), 5.89 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 13.0 (pzCH<sub>3</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>), 15.7, 17.0 (pzCH<sub>3</sub>), 22.3 (CH<sub>2</sub>CH<sub>3</sub>), 20.5 (≡CCH<sub>2</sub>), 31.0 (≡CCH<sub>2</sub>CH<sub>2</sub>), 52.4

(SeC≡C), 105.3 (SeC≡C), 106.9, 107.1 (pzCH), 144.8, 145.6, 152.5, 153.0 (pzCCH<sub>3</sub>), 223.6 (CO, <sup>1</sup>J<sub>WC</sub> = 165), 239.9 (W≡C, <sup>1</sup>J<sub>WC</sub> = 225 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 496. MS (ESI, *m/z*): Found: 733.1174. Calcd for C<sub>24</sub>H<sub>31</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>WNa [M + Na]<sup>+</sup>: 733.1192. Anal. Found: C, 40.48; H, 4.57; N, 11.91%. Calcd for C<sub>24</sub>H<sub>31</sub>BN<sub>6</sub>O<sub>2</sub>SeW: C, 40.65; H, 4.41; N, 11.85%.

**Synthesis of [W(≡CSeC≡C<sup>n</sup>Bu)(CO)<sub>2</sub>(Tp\*)] (5).** A solution of 3,3-dimethyl-1-butyne (20  $\mu$ L, 0.162 mmol) in THF (5 mL) at –78 °C was treated with <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol). The mixture was warmed to room temperature and stirred for 30 min. Grey selenium (0.013 g, 0.16 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to –78 °C and transferred *via* cannula into a similarly cooled solution of **1** (0.100 g, 0.159 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **5** (0.0710 g, 0.100 mmol, 63%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1985s, 1893s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 1.29 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.33 (s, 3 H, pzCH<sub>3</sub>), 2.38 (s, 6 H, pzCH<sub>3</sub>), 2.43 (s, 3 H, pzCH<sub>3</sub>), 2.58 (s, 6 H, pzCH<sub>3</sub>), 5.78 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0, 15.6, 17.2 (pzCH<sub>3</sub>), 31.2 (C(CH<sub>3</sub>)<sub>3</sub>), 51.0 (C(CH<sub>3</sub>)<sub>3</sub>), 77.6 (SeC≡C), 106.8, 107.1 (pzCH), 113.0 (SeC≡C), 144.7, 145.6, 152.3, 153.0 (pzCCH<sub>3</sub>), 223.6 (CO, <sup>1</sup>J<sub>WC</sub> = 166), 240.1 (W≡C, <sup>1</sup>J<sub>WC</sub> = 225 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 496, <sup>2</sup>J<sub>WSe</sub> = 32 Hz. MS (ESI, *m/z*): Found: 710.1310. Calcd for C<sub>24</sub>H<sub>31</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>W [M]<sup>+</sup>: 710.1268. Anal. Found: C, 40.48; H, 4.57; N, 11.91%. Calcd for C<sub>24</sub>H<sub>31</sub>BN<sub>6</sub>O<sub>2</sub>SeW: C, 40.65; H, 4.41; N, 11.85%.

**Synthesis of [W(≡CSeC≡CPh)(CO)<sub>2</sub>(Tp\*)] (6).** A solution of ethynylbenzene (18  $\mu$ L, 0.159 mmol) in THF (5 mL) at –78 °C was treated with <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol). The mixture was warmed to room temperature and stirred for 30 min. Grey selenium (0.013 g, 0.16 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to –78 °C and transferred *via* cannula into a similarly cooled solution of **1** (0.100 g, 0.159 mmol) in THF (10 mL). The mixture was warmed slowly to RT and stirred overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **6** (0.077 g, 0.106 mmol, 66%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1986s, 1896s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.29 (s, 3 H, pzCH<sub>3</sub>), 2.34 (s, 6 H, pzCH<sub>3</sub>), 2.39 (s, 3 H, pzCH<sub>3</sub>), 2.57 (s, 6 H, pzCH<sub>3</sub>), 5.74 (s, 1 H, pzCH), 5.87 (s, 2

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H, pzCH), 7.27 (m, 3 H, overlapping *o*- & *p*-C<sub>6</sub>H<sub>5</sub>), 7.42 (m, 2 H, *m*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>c</sub> = 12.9, 13.0, 15.6, 17.0 (pzCH<sub>3</sub>), 64.1 (SeC≡C), 104.0 (SeC≡C), 106.9, 107.2 (pzCH), 123.5 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.6 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.6 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 131.7 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.8, 145.7, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.5 (CO, <sup>1</sup>J<sub>WC</sub> = 166), 236.3 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>se</sub> = 500, <sup>2</sup>J<sub>WSe</sub> = 30 Hz. MS (ESI, *m/z*): Found: 730.0983. Calcd for C<sub>26</sub>H<sub>27</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>W [M]<sup>+</sup>: 730.0955. Anal. Found: C, 42.96; H, 3.85; N, 11.49%. Calcd for C<sub>26</sub>H<sub>27</sub>BN<sub>6</sub>O<sub>2</sub>SeW: C, 42.83; H, 3.73; N, 11.53%.

**Synthesis of [W(≡CSeC≡CTol)(CO)<sub>2</sub>(Tp\*)] (7).** A solution of 4-ethynyltoluene (21 μL, 0.166 mmol) in THF (5 mL) at −78 °C was treated with <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol). The mixture was warmed to room temperature and stirred for 30 min. Grey selenium (0.013 g, 0.16 mg.atom) was then added and stirring continued for 1 h, during which time the solution became clear. The mixture was again cooled to −78 °C and transferred *via* cannula into a similarly cooled solution of **1** (0.100 g, 0.159 mmol) in THF (10 mL). The mixture was warmed slowly to room temperature and stirring continued overnight. After this time, the volatiles were removed *in vacuo* and the residue was extracted with the minimum dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting first with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and the volatiles were removed under reduced pressure to give an orange solid of pure **7** (0.097 g, 0.131 mmol, 82%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1986s, 1894s ν<sub>CO</sub>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>H</sub> = 2.36 (s, 3 H, pzCH<sub>3</sub>), 2.38 (s, 3 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 2.40 (s, 6 H, pzCH<sub>3</sub>), 2.45 (s, 3 H, pzCH<sub>3</sub>), 2.63 (s, 6 H, pzCH<sub>3</sub>), 5.80 (s, 1 H, pzCH), 5.93 (s, 2 H, pzCH), 7.15, 7.39 (d x 2, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2 H x 2, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>c</sub> = 12.9, 13.0, 15.6, 17.0 (pzCH<sub>3</sub>), 21.8 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 63.1 (SeC≡C), 104.1 (SeC≡C), 106.9, 107.2 (pzCH), 120.5 [C<sup>1</sup>(C<sub>6</sub>H<sub>4</sub>)], 129.3 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>4</sub>)], 131.8 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>4</sub>)], 138.8 [C<sup>4</sup>(C<sub>6</sub>H<sub>4</sub>)], 144.8, 145.7, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.5 (CO, <sup>1</sup>J<sub>WC</sub> = 163), 237.0 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>se</sub> = 500, <sup>2</sup>J<sub>WSe</sub> = 31 Hz. MS (ESI, *m/z*): Found: 744.1134. Calcd for C<sub>27</sub>H<sub>29</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>W [M]<sup>+</sup>: 744.1112. Anal. Found: C, 43.71; H, 4.05; N, 11.26%. Calcd for C<sub>27</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>2</sub>SeW: C, 43.64; H, 3.93; N, 11.31%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/ethanol solution. *Crystal data* for C<sub>27</sub>H<sub>29</sub>BN<sub>6</sub>O<sub>2</sub>SeW: *M*<sub>w</sub> = 743.18 gmol<sup>-1</sup>, monoclinic, space group *P*2<sub>1</sub>/*n* (no. 14), *a* = 10.0844(7), *b* = 13.1954(16), *c* = 21.8026(14) Å, β = 101.803(6)°, *V* = 2839.9(4) Å<sup>3</sup>, *Z* = 4, *T* = 150.0(1) K, μ(Mo Kα) = 5.384 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.738 Mgm<sup>-3</sup>, 16511 reflections measured (6.9° ≤ 2θ ≤ 50.052°), 4994 unique (*R*<sub>int</sub> = 0.0926, *R*<sub>sigma</sub> = 0.1069) which were used in all calculations. The final *R*<sub>1</sub> was 0.0604 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.1190 (all data) for 350 refined parameters with 0 restraints. CCDC 1907303.

**Synthesis of [W(≡CSeC≡CH)(CO)<sub>2</sub>(Tp\*)] (8).** To a stirred solution of **2** (1.00 g, 1.38 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.300 g, 2.17 mmol) in THF (8 mL) and MeOH (3 mL) was added deionised H<sub>2</sub>O (3 mL). Stirring was continued for 30 min, after which time the

mixture was extracted with dichloromethane. The organic phase was collected and volatiles removed under reduced pressure. The residue was subjected to column chromatography (20 x 4 cm silica gel column), eluting with 3:1 v/v petroleum spirits (40–60 °C)/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and removal of the solvents under reduced pressure gave an orange-brown solid of pure **8** (0.813 g, 1.24 mmol, 90 %). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1989s, 1898s ν<sub>CO</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>H</sub> = 2.33 (s, 3 H, pzCH<sub>3</sub>), 2.37 (s, 6 H, pzCH<sub>3</sub>), 2.42 (s, 3 H, pzCH<sub>3</sub>), 2.56 (s, 6 H, pzCH<sub>3</sub>), 3.24 (s, 1 H, C≡CH), 5.78 (s, 1 H, pzCH), 5.92 (s, 2 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>c</sub> = 12.9, 13.0, 15.6, 17.0 (pzCH<sub>3</sub>), 58.9 (SeC≡C), 92.4 (SeC≡C), 106.9, 107.2 (pzCH), 144.9, 145.8, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.3 (CO, <sup>1</sup>J<sub>WC</sub> = 164), 233.6 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>se</sub> = 494, <sup>2</sup>J<sub>WSe</sub> = 37 Hz. MS (ESI, *m/z*): Found: 655.0726. Calcd for C<sub>20</sub>H<sub>24</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>W [M + H]<sup>+</sup>: 655.0723. Anal. Found: C, 36.84; H, 3.57; N, 12.73%. Calcd for C<sub>20</sub>H<sub>23</sub>BN<sub>6</sub>O<sub>2</sub>SeW: C, 36.78; H, 3.55; N, 12.87%.

**Synthesis of [W(≡CSeC≡CPh<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (9).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at −78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol) and the resulting mixture stirred for 1 h. After this time, [CPh<sub>3</sub>]PF<sub>6</sub> (0.051 g, 0.15 mmol) was added, the mixture was warmed to RT and stirring continued overnight. The volatiles were removed *in vacuo* and the residue was then extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **9** (0.042 g, 0.047 mmol, 31%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1986s, 1894s ν<sub>CO</sub>. <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>H</sub> = 2.31 (s, 3 H, pzCH<sub>3</sub>), 2.35 (s, 6 H, pzCH<sub>3</sub>), 2.38 (s, 3 H, pzCH<sub>3</sub>), 2.40 (s, 6 H, pzCH<sub>3</sub>), 5.76 (s, 1 H, pzCH), 5.82 (s, 2 H, pzCH), 7.24–7.26 (broad s, 15 H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>c</sub> = 12.9, 13.0, 15.6, 17.0 (pzCH<sub>3</sub>), 57.6 (CPh<sub>3</sub>), 59.5 (SeC≡C), 106.9, 107.1 (pzCH), 109.7 (SeC≡C), 127.1 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.3, 129.6 [C<sup>2,3,5,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.7 (pzCCH<sub>3</sub>), 145.2 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 145.7, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.8 (CO, <sup>1</sup>J<sub>WC</sub> = 164), 238.8 (W≡C, <sup>1</sup>J<sub>WC</sub> = 225 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K): δ<sub>se</sub> = 497, <sup>2</sup>J<sub>WSe</sub> = 32 Hz. MS (ESI, *m/z*): Found: 896.1749. Calcd for C<sub>39</sub>H<sub>37</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>W [M]<sup>+</sup>: 896.1763. Integrated <sup>1</sup>H NMR spectroscopy indicated that the sample used for elemental analysis contained approximately one equivalent of dichloromethane of solvation. Anal. Found: C, 48.63; H, 3.62; N, 8.45%. Calcd for C<sub>39</sub>H<sub>37</sub>BN<sub>6</sub>O<sub>2</sub>SeW·CH<sub>2</sub>Cl<sub>2</sub>: C, 49.01; H, 4.01; N, 8.57%.

**Synthesis of [W(≡CSeC≡CSiPh<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (10).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at −78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol) and the resulting mixture stirred for 1 h. After this time, chlorotriphenylsilane (0.046 g, 0.156 mmol) was added. The mixture was warmed to RT and stirred overnight. After this time, the volatiles were removed *in vacuo*, and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially



with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. An orange band was collected and freed of solvents under reduced pressure to give an orange solid of pure **10** (0.099 g, 0.11 mmol, 71%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1988s, 1898s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.32 (s, 3 H, pzCH<sub>3</sub>), 2.36 (s, 6 H, pzCH<sub>3</sub>), 2.41 (s, 3 H, pzCH<sub>3</sub>), 2.44 (s, 6 H, pzCH<sub>3</sub>), 5.77 (s, 1 H, pzCH), 5.84 (s, 2 H, pzCH), 7.33 (t, <sup>3</sup>J<sub>HH</sub> = 7.0, 6 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.43 (t, <sup>3</sup>J<sub>HH</sub> = 7.7, 3 H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.68 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 6 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0, 15.6, 17.1 (pzCH<sub>3</sub>), 84.7 (SeC≡C), 106.9 (pzCH), 107.0 (SeC≡C), 107.2 (pzCH), 128.2 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 130.2 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 133.6 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 136.0 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.7, 145.7, 152.5, 153.1 (pzCCH<sub>3</sub>), 223.5 (CO, <sup>1</sup>J<sub>WC</sub> = 165), 234.0 (W≡C, <sup>1</sup>J<sub>WC</sub> = 223 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 515, <sup>2</sup>J<sub>WSe</sub> = 33 Hz. MS (ESI, *m/z*): Found: 912.1592. Calcd for C<sub>38</sub>H<sub>37</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>28</sup>Si<sup>184</sup>W [M]<sup>+</sup>: 912.1621. Found: 935.1438. Calcd for C<sub>38</sub>H<sub>37</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>28</sup>Si<sup>184</sup>WNa [M+Na]<sup>+</sup>: 935.1434. Anal. Found: C, 49.97; H, 4.15; N, 9.10%. Calcd for C<sub>38</sub>H<sub>37</sub>BN<sub>6</sub>O<sub>2</sub>SeSiW: C, 50.08; H, 4.09; N, 9.22%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/ethanol mixture. *Crystal data for* C<sub>38</sub>H<sub>37</sub>BN<sub>6</sub>O<sub>2</sub>SeSiW: *M<sub>w</sub>* = 911.44 gmol<sup>-1</sup>, triclinic, space group *P*-1 (no. 2), *a* = 10.1346(3), *b* = 11.8723(3), *c* = 18.7804(5) Å,  $\alpha$  = 107.522(2)°,  $\beta$  = 99.643(2)°,  $\gamma$  = 95.782(2)°, *V* = 2096.74(10) Å<sup>3</sup>, *Z* = 2, *T* = 150.0(1) K,  $\mu$ (Cu K $\alpha$ ) = 6.667 mm<sup>-1</sup>, *D*<sub>calc.</sub> = 1.444 Mgm<sup>-3</sup>, 13026 reflections measured (7.886° ≤ 2 $\theta$  ≤ 147.714°), 8184 unique (*R*<sub>int</sub> = 0.0398, *R*<sub>sigma</sub> = 0.0554) which were used in all calculations. The final *R*<sub>1</sub> was 0.0432 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.1140 (all data) for 457 refined parameters with 0 restraints. CCDC 1907304.

**Synthesis of [W(CO)<sub>2</sub>(Tp\*)](≡CSeC≡CGePh<sub>3</sub>) (11).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at –78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol) and the resulting mixture was stirred for 1 h. After this time, chlorotriphenylgermane (0.052 g, 0.15 mmol) was added, the mixture was warmed to room temperature and stirred overnight. After this time, the volatiles were removed under reduced pressure and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **11** (0.128 g, 0.134 mmol, 88%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1987s, 1896s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.36 (s, 3 H, pzCH<sub>3</sub>), 2.40 (s, 6 H, pzCH<sub>3</sub>), 2.41 (s, 3 H, pzCH<sub>3</sub>), 2.50 (s, 6 H, pzCH<sub>3</sub>), 5.80 (s, 1 H, pzCH), 5.87 (s, 2 H, pzCH), 7.40–7.42 (m, 6 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.44 (d, <sup>3</sup>J<sub>HH</sub> = 7.0, 3 H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.69 (d, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 6 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0, 15.6, 17.1 (pzCH<sub>3</sub>), 81.4 (SeC≡C), 106.2 (SeC≡C), 106.9, 107.2 (pzCH), 128.7 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 129.8 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 134.9 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 135.3 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.7, 145.7, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.5 (CO, <sup>1</sup>J<sub>WC</sub> = 164), 235.4 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 517, <sup>2</sup>J<sub>WSe</sub> = 32 Hz. MS (ESI, *m/z*): Found: 957.1027. Calcd for C<sub>38</sub>H<sub>38</sub><sup>11</sup>B<sup>72</sup>GeN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>184</sup>W [M+H]<sup>+</sup>: 957.1029. Anal. Found: C, 47.59; H, 3.97; N, 8.67%. Calcd for

C<sub>38</sub>H<sub>37</sub>BGeN<sub>6</sub>O<sub>2</sub>SeW: C, 47.74; H, 3.90; N, 8.79%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/ethanol solution. *Crystal data for* C<sub>38</sub>H<sub>37</sub>BGeN<sub>6</sub>O<sub>2</sub>SeW: *M<sub>w</sub>* = 955.94 gmol<sup>-1</sup>, triclinic, space group *P*-1 (no. 2), *a* = 10.0743(4), *b* = 11.6156(6), *c* = 18.7728(8) Å,  $\alpha$  = 107.189(4)°,  $\beta$  = 99.578(3)°,  $\gamma$  = 96.105(4)°, *V* = 2041.00(17) Å<sup>3</sup>, *Z* = 2, *T* = 150.0(1) K,  $\mu$ (Cu K $\alpha$ ) = 7.361 mm<sup>-1</sup>, *D*<sub>calc.</sub> = 1.555 Mgm<sup>-3</sup>, 11845 reflections measured (8.04° ≤ 2 $\theta$  ≤ 133.156°), 7154 unique (*R*<sub>int</sub> = 0.0247, *R*<sub>sigma</sub> = 0.0377) which were used in all calculations. The final *R*<sub>1</sub> was 0.0386 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.1047 (all data) for 457 refined parameters with 0 restraints. CCDC 1907304.

**Synthesis of [W(≡CSeC≡CSnPh<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (12).** To a solution of **8** (0.050 g, 0.077 mmol) in THF (10 mL) at –78 °C was added <sup>n</sup>BuLi (0.05 mL, 1.6 M in hexane, 0.08 mmol) and the resulting mixture was stirred for 1 h. After this time, chlorotriphenylstannane (0.030 g, 0.078 mmol) was added and the mixture was warmed to RT and stirred overnight. After this time, the volatiles were removed under reduced pressure and the residue was extracted with the minimum of dichloromethane. Ethanol (20 mL) was then added and the solution concentrated under reduced pressure to precipitate an orange-brown solid which was collected by filtration and washed with ethanol (3 x 5 mL) and *n*-pentane (3 x 5 mL) to give an orange-brown solid of **12** (0.025 g, 0.025 mmol, 33%). A small amount of residual chlorotriphenylstannane persisted in the product despite repeated washings. The compound was not amenable to further chromatographic purification. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1985s, 1893s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.30 (s, 3 H, pzCH<sub>3</sub>), 2.34 (s, 6 H, pzCH<sub>3</sub>), 2.38 (s, 3 H, pzCH<sub>3</sub>), 2.46 (s, 6 H, pzCH<sub>3</sub>), 5.75 (s, 1 H, pzCH), 5.82 (s, 2 H, pzCH), 7.38 (d, <sup>3</sup>J<sub>HH</sub> = 3.6, 3 H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.39 (d, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, 6 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.64–7.66 (m, 6 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0, 15.6, 17.1 (pzCH<sub>3</sub>), 83.7 (SeC≡C), 106.9, 107.2 (pzCH), 107.7 (SeC≡C), 129.1 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 129.8 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 137.1 [C<sup>1,2,6</sup>(C<sub>6</sub>H<sub>5</sub>), overlapping], 144.7, 145.7, 152.5, 153.0 (pzCCH<sub>3</sub>), 223.4 (CO, <sup>1</sup>J<sub>WC</sub> = 165), 235.7 (W≡C, <sup>1</sup>J<sub>WC</sub> = 228 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 522. <sup>119</sup>Sn NMR (149 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Sn}}$  = –172. MS (ESI, *m/z*): Found: 1005.0825. Calcd for C<sub>38</sub>H<sub>38</sub><sup>11</sup>BN<sub>6</sub>O<sub>2</sub><sup>80</sup>Se<sup>120</sup>Sn<sup>184</sup>W [M + H]<sup>+</sup>: 1005.0872. Satisfactory elemental microanalytical data were not acquired to difficulties in removing residual traces of chlorotriphenylstannane.

**Synthesis of [W(≡CSeC≡CPbPh<sub>3</sub>)(CO)<sub>2</sub>(Tp\*)] (13).** To a solution of **8** (0.050 g, 0.077 mmol) in THF (10 mL) at –78 °C was added <sup>n</sup>BuLi (0.05 mL, 1.6 M in hexane, 0.08 mmol) and the resulting mixture was stirred for 1 h. After this time, chlorotriphenylplumbane (0.037 g, 0.078 mmol) was added and the mixture was warmed to RT and stirred overnight. After this time, the volatiles were removed under reduced pressure and the residue was extracted with the minimum of dichloromethane. Ethanol (20 mL) was then added and the solution concentrated under reduced pressure to precipitate an orange-brown solid which was collected by filtration and washed with ethanol (3 x 5 mL) and *n*-pentane (3 x 5 mL) to give an orange-brown solid of **12** (0.027 g, 0.025 mmol, 32%). A small

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quantity of residual chlorotriphenylplumbane remained in the product despite repeated washings. The compound was not amenable to further chromatographic purification. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1988s, 1900s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.33 (s, 3 H, pzCH<sub>3</sub>), 2.37 (s, 6 H, pzCH<sub>3</sub>), 2.42 (s, 3 H, pzCH<sub>3</sub>), 2.56 (s, 6 H, pzCH<sub>3</sub>), 5.77 (s, 1 H, pzCH), 5.91 (s, 2 H, pzCH), 7.35 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 3 H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.43 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 6 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.69 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0, 15.6, 17.2 (pzCH<sub>3</sub>), 78.2 (SeC≡C), 106.9, 107.2 (pzCH), 112.1 (SeC≡C), 129.5 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 129.9 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 131.9 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 134.7 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.8, 145.7, 152.4, 153.0 (pzCCH<sub>3</sub>), 223.0 (CO, <sup>1</sup>J<sub>WC</sub> = 164), 235.3 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 525. <sup>207</sup>Pb NMR (84 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Pb}}$  = -263. MS (ESI, *m/z*): Found: 1115.1389. Calcd for C<sub>38</sub>H<sub>37</sub><sup>11</sup>Bn<sub>6</sub>O<sub>2</sub><sup>208</sup>Pb<sup>80</sup>Se<sup>184</sup>WNa [M+Na]<sup>+</sup>: 1115.1429. Anal. Found: C, 40.48; H, 3.19; N, 7.42%. Calcd for C<sub>38</sub>H<sub>37</sub>Bn<sub>6</sub>O<sub>2</sub>PbSeW: C, 41.85; H, 3.42; N, 7.71%. Satisfactory elemental microanalytical data were not acquired to difficulties in removing residual traces of chlorotriphenylplumbane.

**Synthesis of [({Tp\*})(CO)<sub>2</sub>W(≡CSeC≡C)<sub>2</sub>SiPh<sub>2</sub>] (14).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at -78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol) and the resulting mixture stirred for 1 h. After this time, dichlorodiphenylsilane (0.017 mL, 0.081 mmol) was added and the mixture was warmed slowly to RT and stirred overnight. The volatiles were then removed under reduced pressure, and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **14** (0.048 g, 0.032 mmol, 21%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1989s, 1897s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 2.31 (s, 6 H, pzCH<sub>3</sub>), 2.35 (s, 12 H, pzCH<sub>3</sub>), 2.39 (s, 6 H, pzCH<sub>3</sub>), 2.45 (s, 12 H, pzCH<sub>3</sub>), 5.75 (s, 2 H, pzCH), 5.84 (s, 4 H, pzCH), 7.33 (t, <sup>3</sup>J<sub>HH</sub> = 7.7, 4 H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.40 (t, <sup>3</sup>J<sub>HH</sub> = 7.7, 2 H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.76 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 4 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 12.9, 13.0, 15.6, 17.1 (pzCH<sub>3</sub>), 84.7 (SeC≡C), 105.2 (SeC≡C), 106.9, 107.2 (pzCH), 128.3 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 130.5 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 132.6 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 135.4 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.7, 145.7, 152.5, 153.1 (pzCCH<sub>3</sub>), 223.4 (CO, <sup>1</sup>J<sub>WC</sub> = 165), 233.3 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 516. MS (ESI, *m/z*): Found: 1488.1792. Calcd for C<sub>52</sub>H<sub>55</sub><sup>11</sup>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub><sup>80</sup>Se<sub>2</sub><sup>28</sup>Si<sup>184</sup>W<sub>2</sub> [M+H]<sup>+</sup>: 1488.1819. Anal. Found: C, 41.85; H, 3.71; N, 11.17%. Calcd for C<sub>52</sub>H<sub>54</sub>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub>Se<sub>2</sub>SiW<sub>2</sub>: C, 42.02; H, 3.66; N, 11.31%. Single crystals suitable for X-ray structure diffraction were grown by slow evaporation of a dichloromethane/ethanol solution. The precision of this structure was unfortunately compromised by disorder characteristics which necessitated liberal use of restraints. *Crystal data for* C<sub>52</sub>H<sub>54</sub>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub>Se<sub>2</sub>SiW<sub>2</sub>: *M<sub>w</sub>* = 1486.40 gmol<sup>-1</sup>, triclinic, space group *P*-1 (no. 2), *a* = 14.611(8), *b* = 15.247(3), *c* = 15.864(3) Å,  $\alpha$  = 74.469(3)°,  $\beta$  = 65.540(15)°,  $\gamma$  = 89.467(10)°, *V* = 3078.6(18) Å<sup>3</sup>, *Z* = 2, *T* = 100(2) K,  $\mu$ (Mo *K* $\alpha$ ; synchrotron) = 4.985 mm<sup>-1</sup>, *D<sub>calc.</sub>* = 1.603 Mgm<sup>-3</sup>, 31610 reflections measured (2.792° ≤ 2 $\theta$  ≤ 63.478°), 14746 unique

(*R*<sub>int</sub> = 0.1192, *R*<sub>sigma</sub> = 0.1659) which were used in all calculations. The final *R*<sub>1</sub> was 0.0623 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.1757 (all data) for 734 refined parameters with 140 restraints. CCDC 1907306.

**Synthesis of [({Tp\*})(CO)<sub>2</sub>W(≡CSeC≡C)<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>] (15).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at -78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol) and the resulting mixture stirred for 1 h. After this time, dichlorodimethylsilane (0.010 mL, 0.083 mmol) was added and the mixture was warmed slowly to RT and stirred overnight. After this time, the volatiles were removed under reduced pressure and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **15** (0.044 g, 0.032 mmol, 21%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1988s, 1895s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 0.39 (s, 6 H, SiCH<sub>3</sub>), 2.31 (s, 6 H, pzCH<sub>3</sub>), 2.36 (s, 12 H, pzCH<sub>3</sub>), 2.40 (s, 6 H, pzCH<sub>3</sub>), 2.55 (s, 12 H, pzCH<sub>3</sub>), 5.76 (s, 2 H, pzCH), 5.89 (s, 4 H, pzCH). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{C}}$  = 0.6 (SiCH<sub>3</sub>), 12.9, 13.0, 15.6, 17.2 (pzCH<sub>3</sub>), 80.5 (SeC≡C), 106.9, 107.2 (pzCH), 108.1 (SeC≡C), 144.8, 145.7, 152.5, 153.1 (pzCCH<sub>3</sub>), 223.3 (CO, <sup>1</sup>J<sub>WC</sub> = 164), 233.9 (W≡C, <sup>1</sup>J<sub>WC</sub> = 227 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 515. MS (ESI, *m/z*): Found: 1363.1487. Calcd for C<sub>42</sub>H<sub>51</sub><sup>11</sup>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub><sup>80</sup>Se<sub>2</sub><sup>28</sup>Si<sup>184</sup>W<sub>2</sub> [M+H]<sup>+</sup>: 1363.1492. Anal. Found: C, 37.18; H, 3.68; N, 12.19%. Calcd for C<sub>42</sub>H<sub>50</sub>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub>Se<sub>2</sub>SiW<sub>2</sub>: C, 37.03; H, 3.70; N, 12.34%.

**Synthesis of [({Tp\*})(CO)<sub>2</sub>W(≡CSeC≡C)<sub>2</sub>SiPhCH<sub>3</sub>] (16).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at -78 °C was added <sup>n</sup>BuLi (0.10 mL, 1.6 M in hexane, 0.16 mmol) and the resulting mixture stirred for 1 h. After this time, dichloromethylphenylsilane (0.013 mL, 0.080 mmol) was added and the mixture was warmed slowly to RT and stirred overnight. The volatiles were then removed under reduced pressure and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 3:1 v/v petrol/CH<sub>2</sub>Cl<sub>2</sub>. A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **16** (0.051 g, 0.036 mmol, 23%). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1988s, 1897s  $\nu_{\text{CO}}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 0.61 (s, 3 H, SiCH<sub>3</sub>), 2.31 (s, 6 H, pzCH<sub>3</sub>), 2.35 (s, 12 H, pzCH<sub>3</sub>), 2.40 (s, 6 H, pzCH<sub>3</sub>), 2.49 (s, 6 H, pzCH<sub>3</sub>), 2.51 (s, 6 H, pzCH<sub>3</sub>), 5.76 (s, 2 H, pzCH), 5.87 (s, 4 H, pzCH), 7.33–7.41 (m, 3 H, overlapping *m*- & *p*-C<sub>6</sub>H<sub>5</sub>), 7.74 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{H}}$  = 0.2 (SiCH<sub>3</sub>), 13.0, 15.6, 17.1, 17.2 (pzCH<sub>3</sub>), 82.6 (SeC≡C), 106.5 (SeC≡C), 106.9, 107.2 (pzCH), 128.3 [C<sup>3,5</sup>(C<sub>6</sub>H<sub>5</sub>)], 130.3 [C<sup>4</sup>(C<sub>6</sub>H<sub>5</sub>)], 133.8 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 134.6 [C<sup>2,6</sup>(C<sub>6</sub>H<sub>5</sub>)], 144.7, 145.7, 152.5, 153.1 (pzCCH<sub>3</sub>), 223.3 (CO, <sup>1</sup>J<sub>WC</sub> = 163), 233.5 (W≡C, <sup>1</sup>J<sub>WC</sub> = 231 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>, 298 K):  $\delta_{\text{Se}}$  = 516. MS (ESI, *m/z*): Found: 1425.1616. Calcd for C<sub>47</sub>H<sub>52</sub><sup>11</sup>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub><sup>80</sup>Se<sub>2</sub><sup>28</sup>Si<sup>184</sup>W<sub>2</sub> [M]<sup>+</sup>: 1425.1583. Anal. Found: C,

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39.79; H, 3.82; N, 11.57%. Calcd for  $C_{47}H_{52}B_2N_{12}O_4Se_2SiW_2$ : C, 39.63; H, 3.68; N, 11.80%.

**Synthesis of  $[(Tp^*)(CO)_2W(\equiv CSeC\equiv C)]_3SiEt$  (**17**).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at  $-78^\circ C$  was added lithium diisopropylamide (0.10 mL, 2.0 M in THF, 0.20 mmol) and the resulting mixture was stirred for 1 h. After this time, trichloroethylsilane (0.007 mL, 0.05 mmol) was added and the mixture was warmed slowly to RT and stirred overnight. After this time, the volatiles were removed under reduced pressure and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 2:1 v/v petrol/ $CH_2Cl_2$ . A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **17** (0.038 g, 0.019 mmol, 37%). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 1989s, 1897s  $\nu_{CO}$ .  $^1H$  NMR (700 MHz,  $CDCl_3$ , 298 K):  $\delta_H = 0.87$  (q,  $^3J_{HH} = 7.0$ , 2 H,  $CH_2CH_3$ ), 1.08 (t,  $^3J_{HH} = 7.7$  Hz, 2 H,  $SiCH_2$ ), 2.31 (s, 9 H,  $pzCH_3$ ), 2.34 (s, 18 H,  $pzCH_3$ ), 2.39 (s, 9 H,  $pzCH_3$ ), 2.55 (s, 18 H,  $pzCH_3$ ), 5.75 (s, 3 H,  $pzCH$ ), 5.87 (s, 6 H,  $pzCH$ ).  $^{13}C\{^1H\}$  NMR (176 MHz,  $CDCl_3$ , 298 K):  $\delta_C = 6.8$  ( $CH_2CH_3$ ), 9.1 ( $SiCH_2$ ), 12.9, 13.0, 15.6, 17.2 ( $pzCH_3$ ), 82.7 ( $SeC\equiv C$ ), 104.2 ( $SeC\equiv C$ ), 107.0, 107.2 ( $pzCH$ ), 144.7, 145.6, 152.6, 153.1 ( $pzCCH_3$ ), 223.3 (CO,  $^1J_{WC} = 164$ ), 233.1 ( $W\equiv C$ ,  $^1J_{WC} = 227$  Hz).  $^{77}Se\{^1H\}$  NMR (76 MHz,  $CDCl_3$ , 298 K):  $\delta_{Se} = 517$ . MS (ESI,  $m/z$ ): Found: 2015.2018. Calcd for  $C_{62}H_{72}^{11}B_3N_{18}O_6^{80}Se_3^{28}Si^{184}W_3 [M+H]^+$ : 2015.2015. Satisfactory elemental microanalytical data not obtained. Anal. Found: C, 35.50; H, 3.87; N, 10.52%. Calcd for  $C_{62}H_{71}B_3N_{18}O_6Se_3SiW_3$ : C, 36.99; H, 3.55; N, 12.52%.

**Synthesis of  $[(Tp^*)(CO)_2W(\equiv CSeC\equiv C)]_3SiPh$  (**18**).** To a solution of **8** (0.100 g, 0.153 mmol) in THF (10 mL) at  $-78^\circ C$  was added lithium diisopropylamide (0.10 mL, 2.0 M in THF, 0.20 mmol) and the resulting mixture was stirred for 1 h. After this time, trichlorophenylsilane (0.01 mL, 0.062 mmol) was added, and the mixture was warmed slowly to RT and stirred overnight. The volatiles were then removed under reduced pressure and the residue was extracted with dichloromethane and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 2:1 v/v petrol/ $CH_2Cl_2$ . A bright orange band was collected and solvents removed under reduced pressure to give an orange solid of pure **18** (0.069 g, 0.033 mmol, 66%). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 1991s, 1898s  $\nu_{CO}$ .  $^1H$  NMR (700 MHz,  $CDCl_3$ , 298 K):  $\delta_H = 2.32$  (s, 9 H,  $pzCH_3$ ), 2.35 (s, 18 H,  $pzCH_3$ ), 2.39 (s, 9 H,  $pzCH_3$ ), 2.50 (s, 18 H,  $pzCH_3$ ), 5.76 (s, 3 H,  $pzCH$ ), 5.86 (s, 6 H,  $pzCH$ ), 7.32 (t,  $^3J_{HH} = 7.6$ , 2 H,  $m-C_6H_5$ ), 7.39 (t,  $^3J_{HH} = 6.8$ , 1 H,  $p-C_6H_5$ ), 7.82 (d,  $^3J_{HH} = 6.3$  Hz, 2 H,  $o-C_6H_5$ ).  $^{13}C\{^1H\}$  NMR (176 MHz,  $CDCl_3$ , 298 K):  $\delta_C = 12.9$ , 13.0, 15.6, 17.2 ( $pzCH_3$ ), 84.5 ( $SeC\equiv C$ ), 103.8 ( $SeC\equiv C$ ), 107.0, 107.2 ( $pzCH$ ), 128.3 [ $C^{3,5}(C_6H_5)$ ], 130.7 [ $C^4(C_6H_5)$ ], 131.1 [ $C^1(C_6H_5)$ ], 135.1 [ $C^{2,6}(C_6H_5)$ ], 144.7, 145.6, 152.6, 153.0 ( $pzCCH_3$ ), 223.4 (CO,  $^1J_{WC} = 164$ ), 232.6 ( $W\equiv C$ ,  $^1J_{WC} = 229$  Hz).  $^{77}Se\{^1H\}$  NMR (76 MHz,  $CDCl_3$ , 298 K):  $\delta_{Se} = 517$ . MS (ESI,  $m/z$ ): Found: 2062.1969. Calcd for  $C_{66}H_{72}B_3N_{18}O_6Se_3SiW_3 [M+H]^+$ : 2062.2014. Anal. Found: C,

38.32; H, 3.50; N, 12.05%. Calcd for  $C_{66}H_{71}B_3N_{18}O_6Se_3SiW_3$ : C, 38.46; H, 3.47; N, 12.23%.

**Synthesis of  $[W(\equiv CSe^nBu)(CO)_2(Tp^*)]$  (**19**).** To a solution of **2** (0.050 g, 0.069 mmol) in THF (10 mL) at  $-78^\circ C$  was added  $nBuLi$  (0.05 mL, 1.6 M in hexane, 0.08 mmol). The resulting mixture was warmed to room temperature and stirring continued for 3 h. After this time, the volatiles were removed under reduced pressure, the residue was extracted with  $CH_2Cl_2$  and subjected to column chromatography (20 x 1 cm silica gel column), eluting initially with petroleum spirits (40–60 °C) and gradually increasing the polarity to 2:1 v/v petrol/ $CH_2Cl_2$ . A bright orange band was collected and the solvents were removed under reduced pressure to give an orange solid of pure **19** (0.039 g, 0.057 mmol, 83%). IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ): 1974s, 1882s  $\nu_{CO}$ .  $^1H$  NMR (700 MHz,  $CDCl_3$ , 298 K):  $\delta_H = 0.95$  (t,  $^3J_{HH} = 7.0$ , 3 H,  $CH_2CH_3$ ), 1.45 (m,  $^3J_{HH} = 7.0$ , 2 H,  $CH_2CH_3$ ), 1.83 (m,  $^3J_{HH} = 7.0$ , 2 H,  $SeCH_2CH_2$ ), 2.31 (s, 3 H,  $pzCH_3$ ), 2.35 (s, 6 H,  $pzCH_3$ ), 2.40 (s, 3 H,  $pzCH_3$ ), 2.58 (s, 6 H,  $pzCH_3$ ), 3.17 (t,  $^3J_{HH} = 7.0$ , 2 H,  $SeCH_2$ ), 5.75 (s, 1 H,  $pzCH$ ), 5.88 (s, 2 H,  $pzCH$ ).  $^{13}C\{^1H\}$  NMR (176 MHz,  $CDCl_3$ , 298 K):  $\delta_C = 13.0$  ( $pzCH_3$ ), 13.9 ( $CH_2CH_3$ ), 15.7, 16.9 ( $pzCH_3$ ), 23.2 ( $CH_2CH_3$ ), 30.0 ( $SeCH_2$ ), 33.4 ( $SeCH_2CH_2$ ), 106.8, 107.0 ( $pzCH$ ), 144.7, 145.4, 152.3, 152.8 ( $pzCCH_3$ ), 224.9 (CO,  $^1J_{WC} = 167$ ), 258.3 ( $W\equiv C$ ,  $^1J_{WC} = 213$  Hz).  $^{77}Se\{^1H\}$  NMR (76 MHz,  $CDCl_3$ , 298 K):  $\delta_{Se} = 549$ . MS (ESI,  $m/z$ ): Found: 687.1348. Calcd for  $C_{22}H_{32}^{11}BN_6O_2^{80}Se^{184}W [M+H]^+$ : 687.1346. Anal. Calcd for  $C_{22}H_{31}BN_6O_2SeW$ : C, 38.57; H, 4.56; N, 12.27%. Found: C, 38.36; H, 4.63; N, 12.19%.

## Conflicts of interest

There are no conflicts to declare.

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