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ARTICLE

New Binding Modes for CSe: Coinage Metal Coordination to a Tungsten Selenocarbonyl Complex

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Abstract. The new tungsten selenocarbonylate $[NEt_4][W(\equiv CSe)(CO)_2(Tp^*)]$ (Tp* = hydrotris(dimethylpyrazolyl)borate) reacts with group 11 reagents to provide binuclear semi-bridging or *iso*selenocarbonyl complexes of the form $[WM(\mu\text{-}CSe)(CO)_2(PR_3)_n(Tp^*)]$ (M = Cu, Ag, Au; R = Ph, Cy; n = 1,3) depending on the phosphine stoichiometry or steric bulk. With $[Cu(NCMe)_4]PF_6$ and 1,4,7-trithiacyclononane ([9]aneS$_3$) however, the tetrametallic species $[WCu_3\{\mu\text{-}CSe)(CO)_2([9]aneS_3)_3(Tp^*)](PF_6)_2$ is obtained in which one Cu coordinates to the W≡C triple bond and two coordinate to the Se atom.

Introduction

In contrast to their lighter carbonyl congeners, transition-metal *seleno*carbonyl complexes remain exceptionally rare.[1] This largely reflects the lack of conveniently accessible "CSe" source reagents (*cf.* CO). A corollary of the very small number of known non-general synthetic routes to CSe complexes[2] is that the diverse range of binuclear bonding modes adopted by CO or CS[1,3] (**b**–**e**, Chart 1) has yet to be fully realised in CSe chemistry.

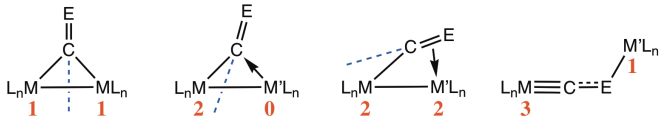

Chart 1. Possible chalcocarbonyl binuclear bonding modes (E = O, S, Se, Te) and (in red) associated valence electron contribution to each metal.

The first binuclear selenocarbonyl unexpectedly arose *via* insertion of '$Pt(PPh_3)_2$' into the Se–C bond of $[Mo(\equiv CSeC\equiv C^tBu)(CO)_2(Tp^*)]$ (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate), furnishing the *iso*selenocarbonyl (Chart 1d) complex *cis*-$[MoPt(\mu\text{-}CSe)(C\equiv C^tBu)(CO)_2(PPh_3)_2(Tp^*)]$.[4a] Similar isoselenocarbonyls have been implicated as intermediates in reactions of other metal substrates with alkynylselenolatocarbynes *en route* to more complex products,[4b-e] and a small number of molybdenum isoselenocarbonyls (Chart 1d) have arisen *via* a salt elimination strategies commencing with $[NEt_4][Mo(\equiv CSe)(CO)_2(Tp^*)]$.[4e] The only example of the symmetric μ-CSe bridging mode (Chart 1a) was recently prepared by deprotonation of a diruthenium methylidyne followed by addition of elemental selenium.[5]

Given the paucity of bimetallic CSe complexes, we considered whether binuclear selenocarbonyls might be accessible using Group 11 metals, which have demonstrated affinity for metal–carbon multiple bonds[6,7] and on one occasion a thiocarbonyl[8] complex. Herein we report a new tungsten selenocarbonylate and its reactions with coinage metal (Cu, Ag, Au) reagents, which give rise to rare isoselenocarbonyls (Chart 1d), the first examples of σ–π-bridging (Chart 1c) and semi-bridging (Chart 1b) modes and a coordination mode without precedent in thiocarbonyl chemistry.

Results and Discussion

Treating the bromocarbyne $[W(\equiv CBr)(CO)_2(Tp^*)]$ (**1**)[9] with NaSeH followed by salt metathesis furnishes the selenocarbonyl salt $[Et_4N][W(CSe)(CO)_2(Tp^*)]$ ($[Et_4N][$**2**$]$) (Scheme 1) in 90% yield. Spectroscopic and structural data for **2** (Table 1, Figure 1) are comparable to those of the molybdenum analogue[2h,4b] and, importantly, suggest that Se presents appreciable nucleophilic character and should be susceptible to electrophilic attack. The reaction of $[Et_4N]$[**2**] with $[Cu(NCMe)_4]PF_6$ and PPh_3 provided a bright orange product, $[WCu(\mu\text{-}CSe)(CO)_2(PPh_3)(Tp^*)]$ (**3**), consistent with coordination of a single '$CuPPh_3$' unit although the spectroscopic data did not unequivocally establish the CSe coordination mode. Rather, this followed from a crystallographic analysis (Figure 2) that revealed the adoption of a σ–π bridging mode (Chart 1d, Scheme 1). This coordination mode has been seen previously in one instance for a CS ligand in $[WMo(\mu\text{-}CS)(CO)_4(\eta^5\text{-}C_9H_7)(Tp)]$ (Tp = hydrotris(pyrazolyl)borate; C_9H_7 = indenyl) (W–C 1.895(5) Å; W–C–S 170.8(3)°),[3e] but not for CSe. The molecular structure of **3** (Figure 1) exhibits similar metal–carbon distances (W1–C1

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CCDC 1919338 – 1919344 contain the supplementary crystallographic data for this paper and may be obtained free of charge from The Cambridge Crystallographic Data Centre.

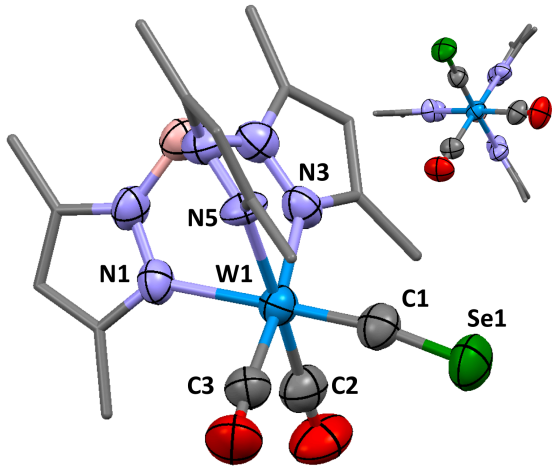


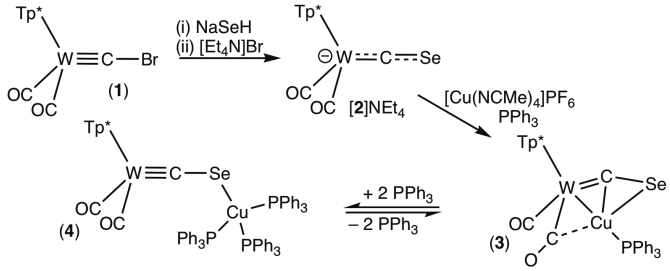
Figure 1. Molecular structure of [**2**]$^-$ in a crystal of [**2**]NEt$_4$ (50% thermal probability ellipsoids, pyrazolyl groups simplified, counter-cation and hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.872(11), W1–C2 1.967(12), W1–C3 1.983(11), W1–N1 2.293(7), W1–N3 2.247(7), W1–N5 2.252(7), C1–Se1 1.781(11), W1–C1–Se1 170.9(7). Inset – view along W1···B1 vector

1.895(14), Cu1–C1 1.913(13) Å) while the W1–C1–Se1 177.0(7) angle bends marginally *towards* Cu, confirming σ–π (4-electron) rather than semi-bridging (Chart 1c) character, which would be manifest in an obtuse Cu1–C1–Se1 angle, as seen for the genuinely semi-bridging carbonyl ligand (W1–C2–O1 166.9(8)°). These data are comparable to those of Angelici's first (and only) binuclear σ–π (4-electron) thiocarbonyl.[3e]

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

	$\delta_{\equiv C}$ [a]	$r_{W\equiv C}$ (Å)	r_{SeM} (Å)	$\angle_{WCSe}$ (°)	ν_{CO} [b]
[**2**]$^-$	311.3	1.872(11)		170.9(7)	1895, 1801
3	278.0	1.896(14)	2.5375(17)	177.1(7)	1916, 1808
4	278.6	1.850(5)	2.5019(8)	167.0(3)	1914, 1810
5					1976, 1893
6		1.864(6)	2.6959(7)	167.4(3)	1983, 1891
7	268.2	1.826(6)	2.4064(7)	170.8(4)	1951, 1859
8	266.7	1.879(9)	2.8051(9)	167.2(5)	1951, 1860
9	270.8				1949, 1857
10		1.879(3)	2.3663(7)	155.6(2)	1973, 1888

[a] Measured in CD_2Cl_2 (ppm). [b] Measured in CH_2Cl_2 (cm^{-1}).



Scheme 1. Synthesis of the tungsten selenocarbonyl [**2**]$^-$ and its reactions with copper(I) phosphines to furnish an σ–π-bridging or an isoselenocarbonyl complex.

Complex **3** is susceptible towards coordination of additional PPh_3 and in solution a fluxional process exists between (at least) two coordination modes. This is manifest in the $^{31}P\{^1H\}$ NMR

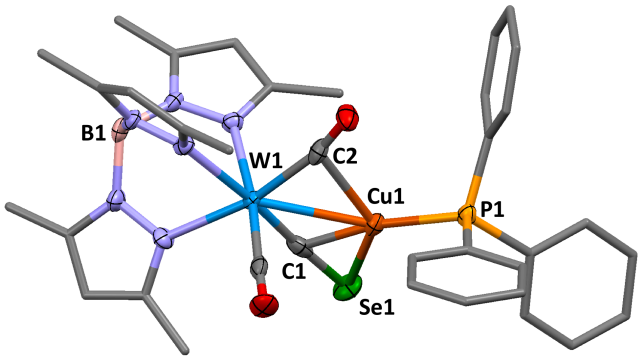


Figure 2. Molecular structure of **3** (50% thermal probability ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): W1–C1 1.895(14), C1–Se1 1.798(14), W1–Cu1 2.7273(12), C1–Cu1 1.913(12), Se1–Cu1 2.5375(16), Cu1–P1 2.207(2), Cu1–C2 2.361(10), W1–C1–Se1 177.0(7), W1–C1–Cu1 91.5(5).

approaches the chemical shift of free PPh_3 (CD_2Cl_2: δ_P = –5.5) though at no point was a distinct signal observed for the free phosphine, even when over 20 equiv. were added, i.e., exchange of free and coordinated phosphine is rapid. The remaining spectroscopic data do not, however, change as significantly and suggest that σ–π (4-electron) bridging may be retained in solution. Repeated recrystallisation (CH_2Cl_2/ethanol/*n*-hexane) serves to gradually remove excess PPh_3 such that **3** could be recovered nearly stoichiometrically.

Single crystals grown in the presence of excess PPh_3 proved to be [W{≡CSeCu(PPh_3)$_3$}(CO)$_2$(Tp*)] (**4**) (Scheme 1), an isoselenocarbonyl (Chart 1e) with a σ-*Se* coordinated copper(I) ligated by three PPh_3 ligands (Figure 3) but devoid of any direct W···Cu interaction.

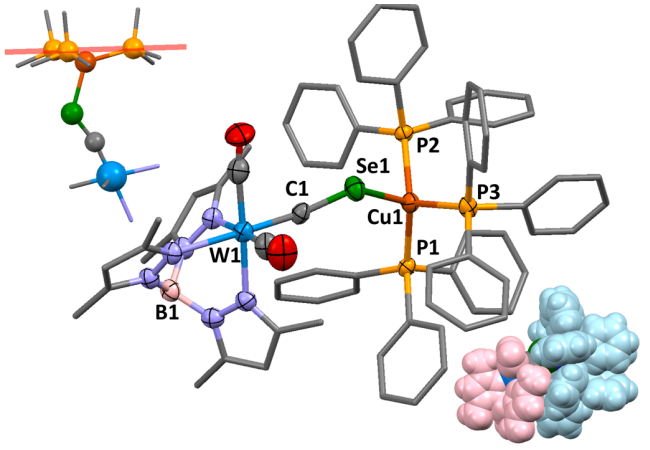


Figure 3. Molecular structure of **4** showing 50% thermal probability ellipsoids. Pyrazolyl and phenyl groups are simplified, and hydrogen atoms and a minor disorder component are not shown for clarity. Selected distances (Å) and angles (°): W1–C1 1.850(5), C1–Se1 1.798(5), Se1–Cu1 2.5019(8), Cu1–P1 2.3397(12), Cu1–P2 2.4136(11), Cu1–P3 2.3679(12), W1–C1–Se1 167.0(3), C1–Se1–Cu1 121.58(14), Se1–Cu1–P1 120.79(4), Se1–Cu1–P2 98.89(4), Se1–Cu1–P3 90.92(4), P1–Cu1–P2 116.47(4), P1–Cu1–P3 111.13(4), P2–Cu1–P3 115.88(4). Insets = inner coordination of WCSeCuP$_3$ unit with P1-P2-P3 plane shown in red and space filling representation with Cu(PPh_3)$_3$ in blue.

This complex represents a likely intermediate during the phosphine exchange inferred to occur in solution. The steric bulk of these ligands provides a steric barrier to acquiring ideal

tetrahedral geometry about Cu; the sum of P–Cu–P angles is 343.5°, midway between idealised trigonal (360°) and tetrahedral (327°) geometries. The Cu atom lies 0.56 Å out of the least-squares plane formed by the three phosphorusatoms. The simplest comparator, $[CuCl(PPh_3)_3]$[10] is nearly perfectly tetrahedral (329.5° and 0.77 Å, respectively), whilst the selenolate $[Cu(SePh)(PEt_3)_3]$[11] with more compact phosphines has a P–Cu–P angle sum (341.3°) closer to that of **4** and a conventional Cu–Se bond length of 2.4774(7) Å which is considerably shorter than found in **3** (2.5019(8) Å). We therefore consider the geometry about copper in **3** to lie between an ideal three and four-coordinate complex, suggesting a degree of Frustrated Lewis Pair character,[12] albeit involving soft anionic selenocarbonyl and cationic copper(I) partners.

The reaction with silver follows a similar route, i.e., combination of [**2**]NEt_4 with ¼$[AgCl(PPh_3)]_4$ furnishes the silver complex, $[WAg(\mu\text{-}CSePPh_3)(CO)_2(PPh_3)(Tp^*)]$ (**5**) (Scheme 2), in which one 'AgPPh$_3$' unit coordinates to the selenocarbonyl. The complex **5** was found to be more prone to decomposition and single crystals were not forthcoming. Limited spectroscopic data preclude unequivocal assignment of the selenocarbonyl coordination mode, although comparison of infrared data with other complexes reported herein suggests the isoselenocarbonyl mode is the most likely. As was the case for **3**, in the presence of additional PPh_3 a fluxional process operates involving rapid phosphine exchange such that the $^{31}P\{^1H\}$ NMR spectrum comprises a lone, broad singlet at 10.0 ppm which shifts progressively up-field on addition of PPh_3 (up to 20 equivalents), without the emergence of a discreet resonance for free phosphine (see ESI).

Crystals grown in the presence of excess PPh_3 were crystallographically confirmed to be the tris(phosphine)silver isoselenocarbonyl complex, $[W\{\equiv CSeAg(PPh_3)_3\}(CO)_2(Tp^*)]$ (**6**, Figure 4) adopting a structure analogous to **4**. As with **4**, the steric bulk of the three phosphines about Ag results in its geometry being between expectations for idealised trigonal and tetrahedral (Σ_{PAgP} = 341.3°; Ag lies *ca* 0.65 Å out of the P_3 plane). The geometry is in good agreement with $[AgCl(PPh_3)_3]$ (345.2° and 0.57 Å, respectively),[13] and the conventional selenolate complex $[Ag(SeC_5H_4N\text{-}4)(PPh_3)_3]$ (Σ_{PAgP} = 335.3°, Ag-Se = 2.6871(11) Å).[14] The tungsten-carbon (W1–C1 1.864(6) Å) and carbon-selenium (1.786(6) Å) distances are comparable to related selenolatoalkylidynes,[4,15] but the Se–Ag distance is somewhat longer (2.6959(7) Å) than would be expected for a single covalent bond.

The reaction of [**2**]NEt_4 with $[AuCl(PPh_3)]$ follows the same route but, in contrast to complex **3**, gold coordinates *terminally* to Se to give $[W\{\equiv CSeAu(PPh_3)\}(CO)_2(Tp^*)]$ (**7**) (Scheme 2), an isoselenocarbonyl complex with a two-coordinate gold. This complex is stable but remains capable of coordinating further PPh_3 to give the four-coordinate gold derivative, $[W\{\equiv CSeAu(PPh_3)_3\}(CO)_2(Tp^*)]$ (**8**), which was isolated upon crystallisation in the presence of excess PPh_3.

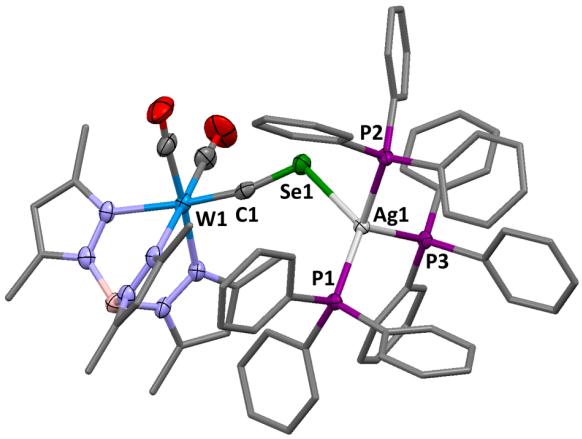
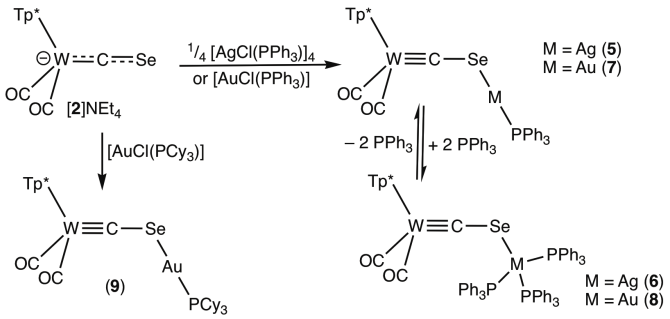


Figure 4. Molecular structure of **6** in a crystal of **6**.2CH_3CN (50% thermal probability ellipsoids, pyrazolyl and phenyl groups, simplified, hydrogen atoms and solvent molecules omited for clarity). Selected distances [Å] and angles [°]: W1–C1 1.864(6), C1–Se1 1.786(6), Se1–Ag1 2.6959(7), Ag1–P1 2.5110(13), Ag1–P2 2.5550(13), Ag1–P3 2.5940(12), W1–C1–Se1 167.4(3) , C1–Se1–Ag1 115.15(16), Se1–Ag1–P1 124.67(3), Se1–Ag1–P2 89.40(3), Se1–Ag1–P3 98.34(3), P1–Ag1–P2 112.60(4), P1–Ag1–P3 115.90(4), P2–Ag1–P3 112.79(4).



Scheme 2. Coordination of the tungsten selenocarbonylate [**2**]$^-$ to silver(I) and gold(I) triphenylphosphine complexes.

Once again, only minor differences in the spectroscopic data for **7** and **8** were observed and therefore it seems unlikely that the four-coordinate geometry predominates in solution. Crystallographic analysis (Figures 5 and 6) indicates that the Se–Au distance is significantly shorter in **7** (2.4064(7) Å) than in **8** (2.8051(9) Å), reflecting the steric pressures applied by three large PPh_3 ligands and increased coordination number of gold. Furthermore, in **8** the sum of the P–Au–P angles is 349.2° and Au lies only 0.47 Å from the P_3 plane in **8**, scarcely different to $[AuCl(PPh_3)_3]$ (352.3° and 0.39 Å, respectively) which was also considered as lying between idealised three and four-coordination.[16] Most notable, however, is that the isoselenocarbonyl connectivity is confirmed for both **7** and **8**, which is in marked contrast to the thiocarbonyl complexes $[WAu(\mu\text{-}CS)(CO)_2(PR_3)(Tp)]$ (W–C–S = 167.3° R = Me, 165.8° R = Ph) which each involve a semi-bridging thiocarbonyl ligand.[8]

The above observations point towards a dynamic situation in solution, where uncertainty prevails as to the speciation due to rapid phosphine association/dissociation. We reasoned that replacement of monodentate phosphines by a 'tetrahedral enforcer'[17] ligand, specifically 1,4,7-trithiacyclononane ([9]aneS_3), should enhance metal binding to selenium. The

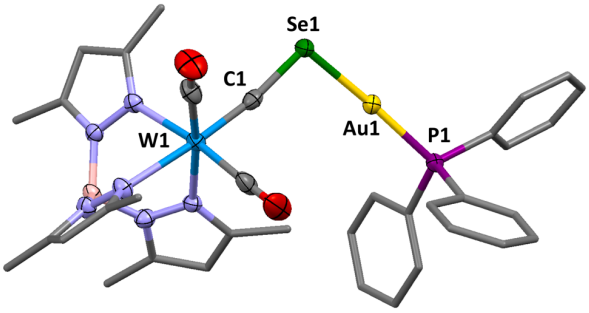


Figure 5. Molecular structure of **7** in a crystal of **7**.$(CH_2Cl_2)_{0.5}$ (50% thermal probability ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms and solvent molecules omitted for clarity, one of two crystallographically distinct molecules shown). Selected distances [Å] and angles [°]: W1–C1 1.826(6), C1–Se1 1.866(6), Se1–Au1 2.4064(7). Au1–P1 2.2633(14), W1–C1–Se1 170.8(4), C1–Se1–Au1 98.80(18), Se1–Au1–P1 174.03(4).

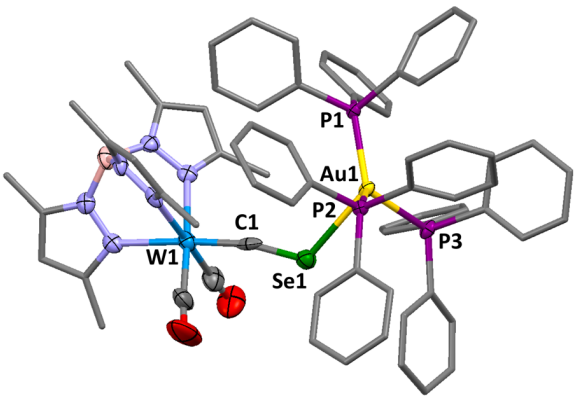
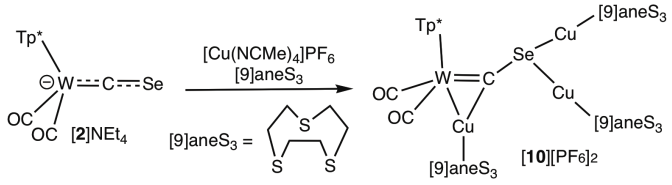


Figure 6. Molecular structure of **8** showing 50% thermal probability ellipsoids. Pyrazolyl and phenyl groups are simplified and hydrogen atoms and a minor disorder component are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.879(9), C1–Se1 1.770(9), Se1–Au1 2.8051(9), Au1–P1 2.3927(18), Au1–P2 2.4470(18), Au1–P3 2.4326(17), W1–C1–Se1 167.2(5), C1–Se1–Au1 118.6(2), Se1–Au1–P1 119.34(5), Se1–Au1–P2 95.82(5), Se1–Au1–P3 87.03(5), P1–Au1–P2 118.50(6), P1–Au1–P3 114.50(6), P2–Au1–P3 116.19(6).

reaction of $[Et_4N]$[**2**] with $[Cu(NCMe)_4]PF_6$ and [9]aneS$_3$ resulted not in the simple expected complex $[WCu(\mu\text{-}CSe)(CO)_2([9]aneS_3)(Tp^*)]$ but rather, the tetrametallic compound, $[WCu_3(\mu\text{-}CSe)(CO)_2([9]aneS_3)_3(Tp^*)][PF_6]_2$ [**10**]$[PF_6]_2$ (Scheme 3, Figure 7). Complex [**10**]$^{2+}$ features an unprecedented CSe bridging mode that combines both isoselenocarbonyl and semi-bridging selenocarbonyl components (Figure 7). The semi-bridging component recalls Angelici's thiocarbonyl species $[WAu(\mu\text{-}CS)(CO)_2(PR_3)(Tp)]$[8] whilst the $SeCu_2$ unit is similar to that observed in the dirhodium complex $[Mo_2Rh_2(\mu\text{-}CSe)_2(COD)_2(CO)_4(Tp^*)_2]$.[4c]



Scheme 3. Bridge-assisted metal-metal bond formation employing 'Cu([9]aneS$_3$)$^{+}$'.

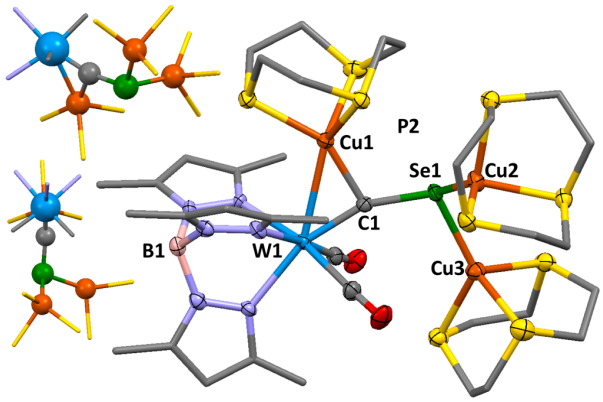


Figure 7. Molecular structure of [**10**]$^{2+}$ in a crystal of [**10**]$[PF_6]_2$ (50% thermal probability ellipsoids, pyrazolyl and ethylene groups, simplified, and hydrogen atoms and counter-anions omitted clarity). Selected distances (Å) and angles (°): W1–C1 1.879(3), C1–Se1 1.881(3), W1–Cu1 2.7560(6), C1–Cu1 1.999(3), Se1–Cu2 2.3663(7), Se1–Cu3 2.3843(7), W1–C1–Se1 155.60(19), W1–C1–Cu1 90.52(13), C1–Se1–Cu2 110.47(10), C1–Se1–Cu3 109.33(10), Cu2–Se1–Cu3 98.87(3). Insets = alternative views of $WCSeCu_3$ core.

The '([9]aneS$_3$)Cu' unit bound to the tungsten–carbon bond is manifest as a broad signal integrating for 12 H in the ^{1}H NMR spectrum of [**10**]$^{2+}$ (separating into two 6 H broad resonances at 210 K for *endo* and *exo* protons). The sulfur macrocycles ligating the Se-bound copper centres, however, undergo rapid exchange, resulting in significant broadening to the point that they are essentially unresolved, even at 210 K. The solid-state structure of [**10**]$[PF_6]_2$ has been crystallographically determined and the geometry of [**10**]$^{2+}$ is shown in Figure 7. This confirms that one Cu coordinates across the W–C bond (W1–Cu1 2.7560(6), C1–Cu1 1.999(3) Å), lying in a cleft between two pyrazolyl groups. The trigonal pyramidal ($\Sigma\angle_{Se}$ = 318.7°) Se1 is bent away from Cu1 (W1–C1–Se1 155.6(2) Å) and the two Se–Cu distances differ only marginally (Se1–Cu2 2.3663(7), Se1–Cu3 2.3843(7) Å).

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 (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, ^{31}P at 162.0 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C at 176.1 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the residual solvent peak (^{1}H, ^{13}C) or externally referenced ($CFCl_3$ for ^{19}F, 85% H_3PO_4 for ^{31}P, $(PhSe)_2$ for ^{77}Se) 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 ^{183}W satellites. In some cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (i.e. 2 decimal places for ^{1}H NMR, 1 decimal place

for ^{13}C NMR) they are reported as having the same chemical shift. The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand.

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). 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. Elemental microanalytical data were provided the London Metropolitan University. A number of complexes reported exist with a non-stoichiometric quantity of triphenylphosphine present and this unfortunately precluded acquisition of satisfactory elemental analyses.

Data for X-ray crystallography were collected with an Agilent Xcalibur CCD diffractomer using Mo-Kα radiation (λ = 0.71073 Å) or an Agilent SuperNova CCD diffractometer using Cu-Kα radiation (λ = 1.54184 Å) using the CrysAlis PRO software.[21] The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXL programs[22] and the WinGX[23] or Olex2 software.[24] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[25]

The synthesis of [W(≡CBr)(CO)$_2$(Tp*)] (**1**) has been described previously.[9b] The reagents [Cu(NCMe)$_4$]PF$_6$,26 [AgCl(PPh$_3$)]$_4$[27] and [AuCl(PPh$_3$)][28] were prepared according to literature methods. [AuCl(PCy$_3$)] was prepared by the reaction of an equimolar amount of [AuCl(THT)][29] and PCy$_3$.

Synthesis of [W(≡CSe)(CO)$_2$(Tp*)]NEt$_4$ ([2]NEt$_4$). To a suspension of **1** (3.00 g, 4.78 mmol) in degassed EtOH (60 mL) at 0 °C was added an ethanolic solution of NaSeH (prepared from grey selenium (753 mg, 9.54 mg.atom) and NaBH$_4$ (861 mg, 22.8 mmol) in EtOH (25 mL)). The mixture was warmed to RT and a second identical solution of ethanolic NaSeH was added. Stirring was continued for 67 h, after which time a separate solution of NEt$_4$Br (4.00 g, 19.1 mmol) in degassed H$_2$O (40 mL) was transferred *via* cannula into the solution, immediately forming a bright yellow precipitate. After 1 h the solvent was removed by filtration and the solid was washed with H$_2$O (3 x 50 mL) and EtOH (2 x 50 mL) to remove unreacted NaSeH then pentane (2 x 50 mL) to furnish a yellow solid of pure [**2**]NEt$_4$ (3.15 g, 4.3 mmol, 90%). IR (CH$_2$Cl$_2$, cm^{-1}): 1895s, 1801s ν_{CO}. IR (ATR, cm^{-1}): 1899s, 1808s $\nu_{CO,}$ 1030 $\nu_{Se.}$ ^{1}H NMR (600 MHz, CD$_3$CN, 298K): δ_H = 5.82 (s, 2 H, pzC*H*), 5.72 (s, 1 H, pzC*H*), 3.14 (q, $^3J_{HH}$ = 7.2, 8 H, NC*H*$_2$), 2.69 (s, 6 H, pzC*H*$_3$), 2.35 (s, 6 H, pzC*H*$_3$), 2.34 (s, 3 H, pzC*H*$_3$), 2.30 (s, 3 H, pzC*H*$_3$), 1.94 (t, $^3J_{HH}$ = 7.2 Hz, 12 H, NCH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR (150 MHz, CD$_3$CN, 298K): δ_C = 311.3 (W*C*Se), 228.2 ($^1J_{WC}$ = 177 Hz, W*C*O), 153.5, 152.4, 145.5, 144.8 (pz*C*CH$_3$), 106.5, 106.4 (pz*C*H), 53.1 (N*C*H$_2$CH$_3$), 16.2, 15.6, 12.8, 12.6 (pz*C*H$_3$), 7.7 (NCH$_2$*C*H$_3$). ^{77}Se NMR (76 MHz, CD$_3$CN, 298K): δ_{Se} = 542. MS (ESI, -ve ion, *m/z*): Found: 627.0416. Calcd. for $C_{18}H_{22}BN_6O_2Se^{184}W$ [M]$^-$: 627.0545. MS (ESI, +ve ion, *m/z*): Found: 889.3785. Calcd. for $C_{34}H_{62}{}^{11}BN_8O_2{}^{80}Se^{184}W$ [M+NEt$_4$]$^+$: 889.3752. Anal. Found: C, 41.07; H, 5.64; N, 12.86 %. Calcd for $C_{26}H_{42}BN_7O_2SeW$: C, 41.18; H, 5.58; N, 12.93%. Crystals suitable for structure determination were grown by evaporation of CH$_2$Cl$_2$ at –20 °C. *Crystal data for* $C_{26}H_{42}BN_7O_2SeW$ (*M* =758.28 g.mol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 10.0340(9), *b* = 10.0396(9), *c* = 16.8180(9) Å, *α* = 94.430(6)°, *β* = 93.666(6)°, *γ* = 113.172(9)°, *V* = 1544.6(2) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 8.549 mm^{-1}, *Dcalc* = 1.630 g.cm^{-3}, 8571 reflections measured (9.64° ≤ 2Θ ≤ 143.92°), 5810 unique (R_{int} = 0.0404, R_{sigma} = 0.0742) which were used in all calculations. The final R_1 was 0.0590 (I > 2σ(I)) and wR_2 was 0.1599 (all data) for 353 refined parameters with 0 restraints. CCDC 1919338.

Synthesis of [WCu(μ-CSe)(PPh$_3$)(CO)$_2$(Tp*)] (3). A solution of **[2]**NEt$_4$ (150 mg, 0.207 mmol), [Cu(NCMe)$_4$]PF$_6$ (154 mg, 0.414 mmol) and PPh$_3$ (326 mg, 1.24 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred for 19 hours at RT. After this time, the solution was filtered through a pad of diatomaceous earth (1 x 5 cm), which was washed with CH$_2$Cl$_2$ until the filtrate ran clear. To the filtrate was added EtOH (15 mL) and the CH$_2$Cl$_2$ was removed under reduced pressure to give an orange precipitate. The precipitate was collected by filtration, washed with EtOH (70 mL) and petroleum spirits (40–60 °C) (30 mL), and dried *in vacuo* to give an orange microcrystalline solid of pure **3** (0.084 g, 0.088 mmol, 43%). IR (CH$_2$Cl$_2$, cm^{-1}): 1916m, 1808m ν_{CO}. IR (ATR, cm^{-1}): 1952, 1909, 1869, 1853, 1804 ν_{CO}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298K): δ_H = 7.70–7.46 (m, 15 H, P*Ph$_3$*), 5.88 (s, 2 H, pzC*H*), 5.75 (s, 1 H, pzC*H*), 2.54 (s, 6 H, pzC*H*$_3$), 2.37 (s, 6 H, pzC*H*$_3$), 2.34 (s, 3 H, pzC*H*$_3$), 2.30 (s, 3 H, pzC*H*$_3$). $^{13}C\{^1H\}$ NMR (176 MHz, CD$_2$Cl$_2$, 298K): δ_C = 278.4 (W*C*Se), 229.4 (W*C*O), 153.0, 152.7, 145.5, 144.9 (pz*C*CH$_3$), 134.6 (d, $^2J_{CP}$ =14 Hz, *o*-PPh$_3$), 131.4 (s, *p*-P*Ph$_3$*), 130.3 (d, $^1J_{CP}$ = 42 Hz, *i*-P*Ph$_3$*), 129.3 (d, $^3J_{CP}$ = 9 Hz, *m*-P*Ph$_3$*), 107.1, 107.0 (pz*C*H), 17.1, 15.2, 12.8, 12.8 (pz*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD$_2$Cl$_2$, 298 K): δ_P = 15.7 (br). MS (ESI, +ve ion, *m/z*): Found: 726.9562. Calcd. for $C_{18}H_{22}{}^{11}B^{35}ClN_6O_2{}^{80}Se^{184}W$ [M–PPh$_3$+Cl]$^+$: 726.9556. Crystals suitable for structure determination were grown by evaporation from a solution of 1:1 v/v mixture of CH$_2$Cl$_2$ and ethanol. *Crystal data for* $C_{36}H_{38}BCuN_6O_2PSeW$ (*M* = 953.84 g.mol^{-1}): monoclinic, space group P2$_1$ (no. 4), *a* = 9.5204(2), *b* = 20.3906(3), *c* = 10.6522(2) Å, *β* = 115.409(2)°, *V* = 1867.85(7) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 8.148 mm^{-1}, *Dcalc* = 1.696 g.cm^{-3}, 10804 reflections measured (8.674° ≤ 2Θ ≤ 133.198°), 6190 unique (R_{int} = 0.0254, R_{sigma} = 0.0429) which were used in all calculations. The final R_1 was 0.0300 (I > 2σ(I)) and wR_2 was 0.0731 (all data) for 448 parameters with 1 restraint. CCDC 1919339.

Synthesis of [W{≡CSeCu(PPh$_3$)$_3$}(CO)$_2$(Tp*)] (4) in the presence of excess PPh$_3$. To a solution of **3** in CH$_2$Cl$_2$ was added 3 equiv. of triphenylphosphine. Removal of volatiles under reduced pressure yields a yellow solid comprised of nearly stoichiometric quantities of **4** in the presence of excess triphenylphosphine. IR (CH$_2$Cl$_2$, cm^{-1}): 1914m, 1810m ν_{CO}. IR (ATR, cm^{-1}): 1952s, 1866, 1853s ν_{CO}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298K): δ_H = 7.38 (m, 60 H, P*Ph$_3$*), 5.87 (s, 2 H, pzC*H*), 5.75 (s, 1 H, pzC*H*), 2.54 (s, 6 H, pzC*H*$_3$), 2.37 (s, 6 H, pzC*H*$_3$), 2.34 (s, 3 H, pzC*H*$_3$), 2.30 (s, 3 H, pzC*H*$_3$). $^{13}C\{^1H\}$ NMR (176 MHz, CD$_2$Cl$_2$, 298K): δ_C = 278.6 (W*C*Se), 229.4 ($^1J_{WC}$ = 163 Hz, W*C*O), 153.0, 152.7, 145.5, 144.9 (pz*C*CH$_3$), 134.2, 134.2 (d, $^2J_{PC}$ = 20 Hz, *o*-P*Ph$_3$*), 129.7 (s, *p*-P*Ph$_3$*), 129.0, 129.0 (d, $^3J_{PC}$ = 7 Hz, *m*-P*Ph$_3$*), 107.1, 107.0 (pz*C*H), 17.1, 15.2, 12.8, 12.8 (pz*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD$_2$Cl$_2$, 298 K): δ_P = 3.4 (br). Satisfactory mass spectrometry results were not obtained, presumably because

of the lability of the triphenylphosphine ligands. Crystals suitable for structure determination were grown by vapour diffusion of *n*-hexane into CH_2Cl_2 at 4 °C. *Crystal data for* $C_{72}H_{67}BCuN_6O_2P_3SeW$ (*M* =1478.38 g.mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.6422(3), *b* = 25.6817(4), *c* = 19.9094(3) Å, *β* = 102.594(2)°, *V* = 6807.5(2) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(CuKα) = 5.119 mm^{-1}, *Dcalc* = 1.442 g.cm^{-3}, 20692 reflections measured (6.884° ≤ 2Θ ≤ 133.202°), 11883 unique (R_{int} = 0.0222, R_{sigma} = 0.0382) which were used in all calculations. The final R_1 was 0.0398 (I > 2σ(I)) and wR_2 was 0.1105 (all data) for 806 refined parameters with 90 restraints. CCDC 1919340.

Synthesis of [WAg(μ-CSe)(PPh$_3$)(CO)$_2$(Tp*)] (5). A solution of **[2]**NEt_4 (150 mg, 0.207 mmol) and $AgClPPh_3$ (169 mg, 0.414 mmol) was stirred for 21 hours at RT. After this time, the solution was filtered through a pad of diatomaceous earth (1 x 5 cm), which was washed with CH_2Cl_2 until the filtrate ran clear. The volatiles were removed under reduced pressure to give a yellow solid which was then sonicated in EtOH for 10 mins. The solid was collected by filtration and washed with EtOH (50 mL) and petroleum spirits (40–60 °C, 30 mL) to give a pale yellow powder. The precipitate was dissolved in CH_2Cl_2 (30 mL), EtOH (50 mL) was added and the CH_2Cl_2 was removed under reduced pressure to give a yellow precipitate. This was collected by filtration, washed with ethanol (40 mL) and petroleum spirits (40–60 °C) (20 mL) to give a bright yellow microcrystalline solid of pure **5** (0.025 g, 0.025 mmol, 12%). IR (CH_2Cl_2, cm^{-1}): 1976s, 1940m, 1893s, 1842m. IR (ATR, cm^{-1}): 1934s, 1843s. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ_H = 7.47–7.28 (m, 15 H, P*Ph$_3$*), 5.75 (s, 2 H, pzC*H*), 5.70 (s, 1 H, pzC*H*), 2.44 (s, 6 H, pzC*H*$_3$), 2.34 (s, 3 H, pzC*H*$_3$), 2.33 (s, 6 H, pzC*H*$_3$), 2.29 (s, 3 H, pzC*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ_P = 10.0 (br s). Rapid decomposition of this species in solution precluded the acquisition of satisfactory ^{13}C{^{1}H} and ^{77}Se NMR spectra. Satisfactory mass spectrometry results were not obtained, presumably because of the sensitivity of the complex and its intolerance of ESI conditions. Anal. Found: C, 43.21; H, 3.76; N, 8.33 %. Calcd for $C_{36}H_{37}AgBN_6O_2PSeW$: C, 43.29; H, 3.74; N, 8.42%.

Generation of [W{≡CSeAg(PPh$_3$)$_3$}(CO)$_2$(Tp*)] (6) in the presence of excess PPh$_3$. To a solution of **5** in CH_2Cl_2 was added 2 equiv. of triphenylphosphine. Removal of volatiles under reduced pressure yields a yellow solid comprised of nearly stoichiometric quantities of **6** in the presence of excess triphenylphosphine. IR (CH_2Cl_2, cm^{-1}): 1983s, 1891s. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ_H = 7.38–7.30 (m, 45 H, P*Ph$_3$*), 5.74 (s, 2 H, pzC*H*), 5.70 (s, 1 H, pzC*H*), 2.45 (s, 6 H, pzC*H*$_3$), 2.35 (s, 3 H, pzC*H*$_3$), 2.33 (s, 6 H, pzC*H*$_3$), 2.29 (s, 3 H, pzC*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ_P = 2.9 (br s). Rapid decomposition of this species in solution precluded the acquisition of satisfactory ^{13}C{^{1}H} and ^{77}Se NMR spectra. Satisfactory mass spectrometry results were not obtained, presumably because of the sensitivity of the complex and its intolerance of ESI conditions. Crystals suitable for structure determination were grown by slow evaporation of an acetonitrile solution. *Crystal data for* $C_{76}H_{73}AgBN_8O_2P_3SeW$ (*M* =1604.82 g.mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.9218(3), *b* = 25.7404(5), *c* = 19.9769(4) Å, *β* = 101.064(2)°, *V* = 7025.7(3) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 2.553 mm^{-1}, *Dcalc* = 1.517 g.cm^{-3}, 26405 reflections measured (6.664° ≤ 2Θ ≤ 52.744°), 13523 unique (R_{int} = 0.0311, R_{sigma} = 0.0540) which were used in all calculations. The final R_1 was 0.0427 (I > 2σ(I)) and wR_2 was 0.1013 (all data) for 842 refined parameters with 12 restraints. CCDC 1919341.

Synthesis of [W(≡CSeAuPPh$_3$)(CO)$_2$(Tp*)] (7). A suspension of **8** (40 mg, 0.025 mmol) in EtOH (70 mL) was sonicated for 20 mins. An orange solid was collected by filtration. The yellow filtrate was collected and volatiles removed under reduced pressure to give a yellow microcrystalline powder of pure **7** (15 mg, 0.014 mmol, 55%). IR (CH_2Cl_2, cm^{-1}): 1951s, 1859s ν_{CO}. IR (ATR, cm^{-1}): 1953s, 1867s, 1856s ν_{CO}. ^{1}H NMR (700 MHz, CD_2Cl_2, 298K): δ_H = 7.60-7.46 (m, 15H, PPh_3), 5.81 (s, 2H, pz*H*), 5.76 (s, 1H, pz*H*), 2.54 (s, 6 H, pzC*H*$_3$), 2.38 (s, 3 H, pzC*H*$_3$), 2.34 (s, 6 H, pzC*H*$_3$), 2.30 (s, 3 H, pzC*H*$_3$). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2 298K): δ_C = 268.2 (W*C*Se), 224.5 (s, W*C*O), 153.0, 152.8, 145.6, 144.8 (pz*C*CH$_3$), 134.6 (d, $^2J_{PC}$ = 15, *o*-P*Ph$_3$*), 132.0 (s, *p*-P*Ph$_3$*) 130.0, 130.2 (br d, $^1J_{CP}$ = 55 Hz, *i*-PPh_3), 129.5 (d, $^3J_{CP}$ = 11, *m*-P*Ph$_3$*), 106.6, 106.5 (pz*C*H), 16.8, 15.5, 12.8, 12.7 (pz*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ_P = 36.1. MS (ESI, +ve ion, *m/z*): Found: 1088.1145. Calcd. for $C_{36}H_{37}Au^{11}BN_6O_2P^{80}Se^{184}W$ [M]$^+$: 1088.1165. Anal. Found: C, 39.86; H, 3.47; N, 7.58 %. Calcd for $C_{36}H_{37}AuBN_6O_2PSeW$: C, 39.74; H, 3.43; N, 7.73%. A crystal suitable for structure determination was grown by slow evaporation of a solution of CH_2Cl_2 at –20 ˚C and was found to contain 0.5 equivalents of CH_2Cl_2 of solvation. *Crystal data for* $C_{36.5}H_{38}AuBClN_6O_2PSeW$ (*M* =1129.73 g.mol^{-1}): monoclinic, space group $P2_1/n$ (no. 14), *a* = 9.86360(10), *b* = 24.9374(2), *c* = 31.5709(3) Å, *β* = 89.5550(10)°, *V* = 7765.34(12) Å^3, *Z* = 8, *T* = 150.0(1) K, μ(CuKα) = 14.816 mm^{-1}, *Dcalc* = 1.933 g.cm^{-3}, 41511 reflections measured (7.09° ≤ 2Θ ≤ 133.192°), 13695 unique (R_{int} = 0.0300, R_{sigma} = 0.0327) which were used in all calculations. The final R_1 was 0.0340 (I > 2σ(I)) and wR_2 was 0.0811 (all data) for 929 refined parameters with 3 restraints. CCDC 1919342.

Synthesis of [W{≡CSeAu(PPh$_3$)$_3$}(CO)$_2$(Tp*)] (8). To a solution of [**2**]NEt_4 (400 mg, 0.551 mmol) in CH_2Cl_2 (20 mL) was added $AuCl(PPh_3)$ (329 mg, 0.661 mmol) and PPh_3 (347 mg, 1.32 mmol). Stirring was continued for 1 h, after which time the resulting orange solution was filtered through a pad of diatomaceous earth (3 x 3 cm), which was washed with CH_2Cl_2 until the filtrate ran clear. The volatiles were subsequently removed under reduced pressure, the residue was dissolved in the minimum of acetonitrile (*ca.* 30 mL) and stored at –20 °C for 17 hours, during which time bright orange crystals formed. These were collected by filtration and washed with ethanol (50 mL) and petroleum ether (40–60 °C) (3 x 20 mL) to give orange crystals of pure **8** (0.51 g, 0.29 mmol, 53%). IR (CH_2Cl_2, cm^{-1}): 1951s, 1860s ν_{CO}. IR (ATR, cm^{-1}): 1912s, 1824s ν_{CO}.^{1}H NMR (600 MHz, $CDCl_3$, 298K): δ_H = 7.37–7.43 (m, 45 H, P*Ph$_3$*), 5.77 (s, 2 H, pzC*H*), 5.71 (s, 1 H, pzC*H*), 2.59 (s, 6 H, pzC*H*$_3$), 2.40 (s, 3 H, pzC*H*$_3$), 2.32 (s, 6 H, pzC*H*$_3$), 2.29 (s, 3 H, pzC*H*$_3$). ^{13}C NMR (150 MHz, CD_3CN, 298K): δ_C = 266.7 (W*C*Se, $^2J_{CW}$ = 203 Hz), 228.2 (W*C*O, $^2J_{CW}$ = 170 Hz,), 152.7, 152.4, 144.6, 143.8 (pz*C*CH$_3$), 134.2 (d, $^1J_{CP}$ = 16 Hz, *i*-P*Ph$_3$*), 134.0 (d, $^2J_{CP}$ = 16 Hz, *o*-P*Ph$_3$*), 130.0 (s, *p*-P*Ph$_3$*), 128.8 (d, $^3J_{CP}$ = 10 Hz, *m*-P*Ph$_3$*), 106.3, 106.3 (pz*C*H), 16.9, 15.6, 12.8, 12.7 (pzCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ_P = 12.0 (br s). ^{77}Se NMR (76 MHz, $CDCl_3$, 298K): δ_{Se} = 393.

MS (ESI, +ve ion, *m/z*): Found: 1089.1198. Calcd. for $C_{36}H_{38}Au^{11}BN_6O_2P^{80}Se^{184}W$ [M–2PPh$_3$+H]$^+$: 1089.1227. Anal. Found: C, 53.52; H, 4.32; N, 5.10 %. Calcd for $C_{72}H_{67}AuBN_6O_2P_3SeW$: C, 53.65; H, 4.19; N, 5.21%. Crystals suitable for structure determination were grown from an acetonitrile solution at –20 °C. *Crystal data for* $C_{72}H_{67}AuBN_6O_2P_3SeW$ (*M* =1611.81 g.mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.7862(3), *b* = 25.8754(7), *c* = 19.8758(3) Å, *β* = 101.188(2)°, *V* = 6955.4(3) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(MoKα) = 4.399 mm^{-1}, *Dcalc* = 1.539 g.cm^{-3}, 25468 reflections measured (6.8° ≤ 2Θ ≤ 52.742°), 13437 unique (R_{int} = 0.0385, R_{sigma} = 0.0704) which were used in all calculations. The final R_1 was 0.0547 (I > 2σ(I)) and wR_2 was 0.1057 (all data) for 800 parameters with 90 restraints. CCDC 1919343.

Synthesis of [W(≡CSeAuPCy$_3$)(CO)$_2$(Tp*)] (9). A solution of **[2]**NEt$_4$ (102 mg, 0.140 mmol) and AuCl(PCy$_3$) (72 mg, 0.14 mmol) in CH_2Cl_2 (10 mL) was stirred for 2 hours at RT. After this time, *n*-hexane (20 mL) was added and the CH_2Cl_2 was removed under reduced pressure to give a yellow precipitate. This was collected by filtration and washed with *n*-hexane (30 mL) before being extracted with benzene (30 mL). The solvent was again removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (10 mL) and filtered through a pad of diatomaceous earth, washed with CH_2Cl_2 until the filtrate ran clear. The volatiles were removed under reduced pressure to give a green solid of pure **9** (85 mg, 0.077 mmol, 54%). IR (CH_2Cl_2, cm^{-1}): 1949s, 1857s ν_{CO}. IR (ATR, cm^{-1}): 1941s, 1848s ν_{CO}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ_H = 5.87 (s, 2 H, pzC*H*), 5.76 (s, 1 H, pzC*H*), 2.64 (s, 6 H, pzCH_3), 2.39 (s, 3 H, pzCH_3), 2.34 (s, 6 H, pzCH_3), 2.30 (s, 3 H, pzCH_3), 1.99–1.25 (m, 33 H, PCy$_3$). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2 298K): δ_C = 270.8 (W*C*Se), 224.6 (W*C*O), 152.9, 152.7, 145.6, 144.8 (pz*C*CH$_3$), 107.5, 106.4 (pz*C*H), 33.9 (d, $^1J_{CP}$ = 30 Hz, *i*-P*C*y$_3$), 31.0 (*m*-P*C*y$_3$), 27.5 (d, $^2J_{CP}$ = 13 Hz, *o*-P*C*y$_3$), 26.3 (*p*-P*C*y$_3$), 16.7, 15.5, 12.8, 12.7 (pz*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ_P = 57.0. ^{77}Se NMR (134 MHz, CD_2Cl_2, 298 K): δ_{Se} = 488. MS (ESI, +ve ion, *m/z*): Found: 1107.2634. Calcd. for $C_{36}H_{56}Au^{11}BN_6O_2P^{80}Se^{184}W$ [M+H]$^+$: 1107.2635. Found: 1129.2450. Calcd. for $C_{36}H_{55}Au^{11}BN_6NaO_2P^{80}Se^{184}W$ [M+Na]$^+$: 1129.2455. Anal. Found: C, 38.96; H, 4.89; N, 7.61 %. Calcd for $C_{36}H_{55}AuBN_6O_2PSeW$: C, 39.08; H, 5.10; N, 7.60%.

Synthesis of [WCu([9]aneS$_3$){μ-CSe(Cu[9S$_3$])$_2$}(CO)$_2$(Tp*)](PF$_6$)$_2$ (10). A yellow solution of [Cu(NCMe)$_4$]PF$_6$ (185 mg, 0.496 mmol) and 1,4,7-trithiacyclononane ([9]aneS$_3$) (90 mg, 0.50 mmol) was heated to reflux in MeOH (10 mL) then allowed to cool to room temperature. To this solution was added **[2]**NEt$_4$ (120 mg, 0.165 mmol) and stirring continued for 10 minutes, during which time a yellow precipitate formed. The precipitate was collected by filtration and washed with EtOH (80 mL) and *n*-hexane (40 mL) then dried *in vacuo* to give pure **10** as a yellow microcrystalline solid (70 mg, 0.042 mmol, 25%). IR (CH_2Cl_2, cm^{-1}): 1973, 1888 ν_{CO}. IR (ATR, cm^{-1}): 1918s, 1835s, 1824s ν_{CO}. ^{1}H NMR (700 MHz, CD_2Cl_2, 210K): δ_H = 5.85 (s, 2H, pz*H*), 5.74 (s, 1H, pz*H*), 3.07, 3.01 (br, 6H, 9S$_3$) 2.61 (br, 6H, 9S$_3$), 2.61 (s, 6 H, pzCH_3), 2.31 (s, 3 H, pzCH_3), 2.29 (s, 6 H, pzCH_3), 2.24 (s, 3 H, pzCH_3). ^{1}H NMR (700 MHz, CD_2Cl_2, 298K): δ_H = 5.85 (s, 2H, pz*H*), 5.74 (s, 1H, pz*H*), 2.86 (br, 12 H, 9S$_3$), 2.68 (s, 6 H, pzCH_3), 2.36 (s, 3 H, pzCH_3), 2.34 (s, 6 H, pzCH_3), 2.29 (s, 3 H, pzCH_3). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2 298K): 153.1 (pz*C*CH$_3$), 107.6, 106.5 (pz*C*H) 35.4 (br), 32.0 (br), 30.1 (9S$_3${*C*H$_2$}), 16.5, 15.5, 14.5, 12.8, 12.7, 12.6 (pz*C*H$_3$). Limited ^{13}C{^{1}H} data was obtained due to the poor solubility of **10** in all common NMR solvents. ^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, 298 K): δ_F = –74.3 (d, $^1J_{FP}$ = 707, P*F$_6$*). MS (ESI, +ve ion, *m/z*): Found: 1114.9370. Calcd. for $C_{30}H_{46}{}^{11}B^{63}Cu_2N_6O_2S_6{}^{80}Se^{184}W$ [M–Cu(9S$_3$)–2(PF$_6$)]$^+$: 1114.9366. Found: 871.9975. Calcd. for $C_{24}H_{34}{}^{11}B^{63}CuN_6O_2S_3{}^{80}Se^{184}W$ [M–2Cu(9S$_3$) –2(PF$_6$)]$^+$: 871.9962. A crystal suitable for structure determination was grown by slow evaporation of an acetonitrile solution. *Crystal data for* $C_{36}H_{58}BCu_3F_{12}N_6O_2P_2S_9SeW$ (*M* =1649.60 g.mol^{-1}): triclinic, space group P-1 (no. 2), *a* = 14.3857(7), *b* = 15.1513(7), *c* = 16.9587(8) Å, *α* = 64.575(5)°, *β* = 73.129(4)°, *γ* = 62.160(5)°, *V* = 2933.3(3) Å^3, *Z* = 2, *T* = 150.0(1) K, μ(CuKα) = 9.657 mm^{-1}, *Dcalc* = 1.868 g.cm^{-3}, 21766 reflections measured (7.408° ≤ 2Θ ≤ 147.634°), 11582 unique (R_{int} = 0.0369, R_{sigma} = 0.0565) which were used in all calculations. The final R_1 was 0.0334 (I > 2σ(I)) and wR_2 was 0.0825 (all data) for 667 refined parameters with 0 restraints. CCDC 1919344.

Conclusions

The preceding discussion describes for the first time, three new bridging scenarios for the CSe molecule: (i) Semi-bridging;[20] (ii) σ-π bridging and (iii) Combined semi-bridging/bifurcated isoselenocarbonyl bridging. The latter arises from the first use of the 'Cu([9]aneS$_3$)' unit as a module for bridge-assisted metal-metal bond formation, being isolobal with the previously employed 'Cu(η-C$_5$Me$_5$)' group.[18] Together, these provide models of plausible intermediates for the bi- and polymetallic activation of CS and CSe diatomics *en route* to μ-carbido species.[4b,19]

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