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COMMUNICATION

Carbon-chalcogen Wires: Alkynyltellurolatocarbynes

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The reactions of [W(≡CBr)(CO)$_2$(Tp*)] (Tp* = tris(dimethylpyrazolyl)borate) with LiTeC≡CR (R = SiMe$_3$, Si^{i}Pr$_3$, ^{i}Pr, ^{n}Bu, ^{t}Bu, Ph, C$_6$H$_4$Me-4, methylimidazol-2-yl) afford the first alkynyltellurolatocarbynes [W(≡CTeC≡CR)(CO)$_2$(Tp*)]. Both the W≡C and C≡C multiple bonds are prone to metal addition as exemplified by treatment with [MCl(SMe$_2$)] (M = Cu, Au) to afford the hexametallic complex [W$_2$Cu$_4$(μ-CTeC≡CSi^{i}Pr$_3$)$_2$Cl$_4$(CO)$_4$(Tp*)$_2$] and [WAu(μ-CTeC≡CSiMe$_3$)Cl(CO)$_2$-(Tp*)] which evolves to the unusual hypervalent [WAu(μ-CTeCl$_4$)(SMe$_2$)(CO)$_2$(Tp*)].

Alkynylselenolatocarbynes, L$_n$M≡CSeC≡CR,[1] are of interest in that the unsaturated spine includes both metal-carbon and carbon-carbon triple bonds, each of which may be expected, alongside selenium, to be centres of reactivity. The first such complex [Mo(≡CSeC≡C^{t}Bu)(CO)$_2$(Tp*)] (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate)[1a] was shown to initially coordinate to 'Pt(PPh$_3$)$_2$' through the alkynyl C≡C bond prior to C–Se bond activation,[1b] while [Mo(≡CSeC≡CSiMe$_3$)(CO)$_2$(Tp*)] undergoes multiple C–Se bond cleavage/formation processes with [RhCl(PPh$_3$)$_3$] to ultimately afford a bridging alkynylselenoacyl complex.[1c] Desilylation of the tungsten derivative affords the parent [W(≡CSeC≡CH)(CO)$_2$(Tp*)], allowing the installation of a diverse range of alkynyl termini.[1d-f] Together, these results demonstrate the considerable synthetic utility of alkynylselenolatocarbynes for the elaboration of unsaturated carbon-selenium wire ligand systems.

While Angelici has amply demonstrated the rich synthetic chemistry of thiolatocarbynes,[2] the carbyne chemistry of heavier chalcogens, especially tellurium, is rather limited. Angelici's studies emerged from the chemical modification of the thiocarbonyl ligand in derivatives of [W(CS)(CO)$_5$] for which no tellurium analogue is known. Limited details for the first structurally characterised tellurocarbyne [Os(≡CTeMe)(CO)$_2$-(PPh$_3$)$_2$]$^+$ (Chart 1) from methylation of [Os(CTe)(CO)$_2$(PPh$_3$)$_2$], appeared in a review,[3] while all other examples are derived from the halo or lithiocarbynes [M(≡CX)(CO)$_2$(Tp*)] (M = Mo, W; X = Cl, Br, Li).[4]

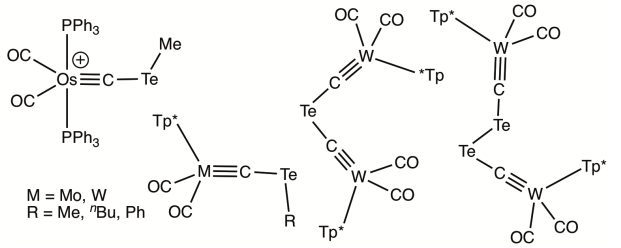

Chart 1. Known tellurium-based carbynes.[3,4]

Chemists are guided and inspired by periodicity and it might be expected that chalcogen derivatives display smooth monotonic variation in properties and reactivities on descending group 16. Chivers has however, had good cause to describe tellurium as the '*enfant terrible*' amongst chalcogens.[5] The heaviest p-block elements of any group have the greatest propensity for increased coordination numbers, hyper-valency, higher and lower (inert pair effect) oxidation states, secondary bonding, spin-orbit coupling ($\propto Z^4$) and poor pπ-pπ overlap that compromises multiple bonding. Recognising these distinctive factors, we address herein the possibility of synthesising alkynyltellurolatocarbynes, L$_n$M≡CTeC≡CR, *viz.* telluroethers that carry both C≡C and C≡M substituents.

Treatment of lithium alkynyls (LiC≡CR) with selenium affords ambident alkynylselenolate nucleophiles (LiSeC≡CR) that are useful reagents *en route* to alkynylselenoethers,[6] selenium heterocycles[7] and alkynylselenolato complexes.[8] Their reaction with halocarbyne complexes remains the only current route to alkynylselenolatocarbynes.[1] Accordingly, a similar approach was explored for tellurium. Given that alkynylthiolatocarbynes are also unknown, the protocol was first extended to sulfur. Successive treatment of ethynyltrimethylsilane with ^{n}BuLi, sulfur and [W(≡CBr)(CO)$_2$(Tp*)] (**1**) afforded [W(≡CSC≡CSiMe$_3$)(CO)$_2$(Tp*)] (**2a**, Scheme 1) in 45% yield. The reaction of **2a** with [AuCl(SMe$_2$)] results in coordination of the W≡C multiple bond to gold(I) with the alkynylthiolatocarbyne coordinating in a semi-bridging[1d,9] manner (**3a**; W1–C1–S1 = 160.5(12)°). In these respects the chemistry is entirely analogous to that of the corresponding alkynyl-selenolatocarbynes, *e.g.*, [W(≡CSeC≡C-SiMe$_3$)(CO)$_2$(Tp*)] (**2b**).[1d-f] The characterisation of **2a** and **3a** included crystallographic authentication (see ESI Figure S1).

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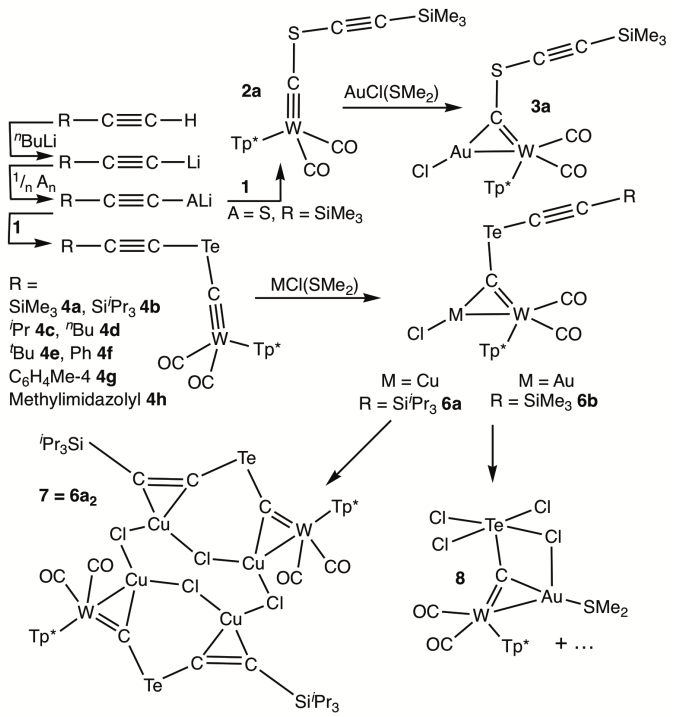

Scheme 1. Synthesis and reactivity of alkynylthiolato- and alkynyletellurolatocarbynes.

Treating a range of alkynyllithium reagents with tellurium followed by **1** afforded, following chromatography, the alkynyltellurolatocarbynes [W(≡CTeC≡CR)(CO)$_2$(Tp*)] (R = SiMe$_3$ **4a**, Si^{i}Pr$_3$ **4b**, ^{i}Pr **4c**, ^{n}Bu **4d**, ^{t}Bu **4e**, Ph **4f**, C$_6$H$_4$Me-4 **4g**, *N*-methylimidazol-4-yl **4h**), demonstrating a degree of generality to the approach. Furthermore, desilylation of **4a** (K$_2$CO$_3$/MeOH) readily afforded the parent derivative [W(≡CTeC≡CH)(CO)$_2$(Tp*)] (**4i**). The molybdenum analogue [W(≡CTeC≡CSiMe$_3$)(CO)$_2$(Tp*)] (**5a**) was similarly acquired (61% yield), however subsequent discussion will focus on the tungsten series. In contrast to the syntheses of the selenium and sulfur derivatives, the formation of **4** (and **5a**) was in most cases attended by varying amounts (0-25%) of the corresponding propargylidynes [W(≡CC≡CR)(CO)$_2$(Tp*)] (R = SiMe$_3$ **6a**, Si^{i}Pr$_3$ **6b**, ^{t}Bu **6e**, Ph **6f**, C$_6$H$_4$Me-4 **6g**). This observation is noteworthy in that the halocarbynes *do not* react with alkynyllithium reagents to afford propargylidynes, necessitating palladium catalysed cross-coupling protocols.[10] Discounting residual LiC≡CR as the source of the propargylidynes leads to the conclusion that the tellurium serves to effectively carry the alkynyl nucleophile prior to presumed tellurium extrusion under the conditions employed.

Structural characterisation of **4b**, **4f** and **4h** (Figure 1) reveals geometric features similar to those for less exotic carbyne complexes of the form [M(≡CR)(CO)$_2$(Tp*)],[11] noting however the characteristically small C–Te–C angles (95.8(3)-97.5(4)° *cf.* 102.0(8)° for **2a**). The bond lengths between tellurium and alkynyl *cf.* carbyne carbons are equivalent within precision limits. Table 1 collates data for **4a**-**4i**, all of which are essentially insensitive to variations in the remote alkynyl substituent.

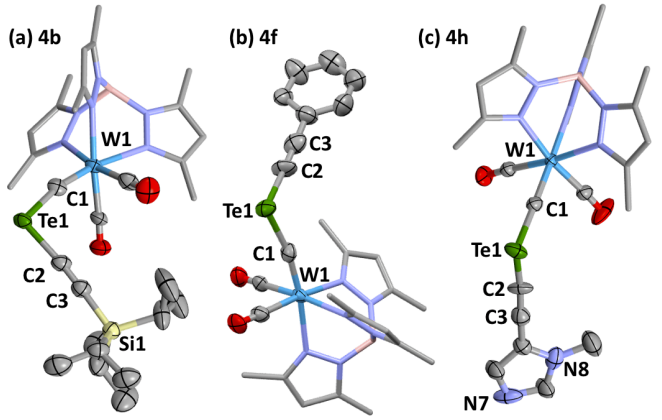

Figure 1. Molecular structures of (a) **4b,** (b) **4f** and (c) **4h** in crystals (50% displacement ellipsoids, pyrazolyl groups simplified, hydrogen atoms omitted). For selected bond lengths and angles see Table 1.

Table 1. Structural and spectroscopic data for alkynylchalcogenolatocarbynes [W(≡CAC≡CR)(CO)$_2$(Tp*) (A = S, Se, Te; R = SiMe$_3$ **4a**, Si^{i}Pr$_3$ **4b**, ^{i}Pr **4c**, ^{n}Bu **4d**, ^{t}Bu **4e**, Ph **4f**, C$_6$H$_4$Me-4 **4g**, *N*-methylimidazol-2-yl **4h**, H **4i**).

	$\delta_{W\equiv C}$ [a] (ppm)	$^1J_{C}$ (Hz)	δ_{Te} [b] (ppm)	$r_{W\equiv C}$ (Å)	$\angle_{WCA}$ (°)	ν_{CO} [c] (cm^{-1})
2a	233.5	225	–	1.842(17)	168.1(12)	1988, 1987
2b[1d]	235.0	227	*d*	–	–	1988, 1897
4a	234.5	215	771	–	–	1988, 1897
4b	235.7	215	764	1.811(10)	168.2(6)	1987, 1897
4c	237.4	214	747			1986, 1896
4d	238.4	214	747			1986, 1895
4e	238.9	211	745			1986, 1895
4f	235.5	213	759	1.822(8)	179.1(5)	1989, 1896
4g	236.2	215	758			1987, 1897
4h	234.1	214	761	1.850(17)	176.7(11)	1987, 1897
4i	232.6	*e*	762			1988, 1899

[a] Measured in $CDCl_3$. [b] Relative to $\delta_{Te}(Ph_2Te_2)$ = 422. [c]Measured in CH_2Cl_2. [d]δ_{Se} = 513. [e]Insufficient signal/noise achieved to accurately observe.

Relative to conventional alkylidynes, the carbyne resonances in the $^{13}C\{^1H\}$ NMR spectra appear to lower frequency,[11] however the almost identical chemical shifts observed for sulfur, selenium and tellurium examples requires comment. The shielding tensor reflects three factors[12] – (i) Diamagnetic shielding, for which chalcogen-dependent variations are expected to be modest; (ii) Paramagnetic deshielding, which is expected to increase for heavier chalcogens (*vide infra*) and (iii) Relativistic spin-orbit (SO) coupling which generally results in shielding.[13] It therefore appears that the heavy-atom SO-coupling contribution for **4** almost exactly cancels out the diametric paramagnetic deshielding. Similar arguments apply for haloalkanes[14] and halocarbynes.[15] The resonances associated with the tellurium-bound alkynyl carbon also appear to comparatively low frequencies, from 42.6 (**4f**) to 77.6 (**4d**) ppm. Thus while the alkynyl resonances for **2a** occur at 82.8 (S*C*≡C) and 107.3 (SC≡*C*) ppm, those for **4a** appear at 59.6 (Te*C*≡C) and 125.2 (TeC≡*C*) ppm, suggesting that the SO heavy atom effect dominates for **4a**. This might suggest that the virtual orbital with which the tellurium lone pair couples in an applied magnetic field has more W≡C than C≡C character (*vide infra*).

The ^{125}Te{^{1}H} NMR spectrum for each of the complexes **4** comprise a single resonance that appears in a very narrow range (745-771 ppm) towards the high frequency end of the range typical of organotellurium(II) species, *e.g.*, alkynyl telluroethers typically present resonances in the region of 200 ppm.[16] This substantial deshielding is most likely due to the paramagnetic contribution from the W≡C-dominated LUMO. With all but an alkynyloxycarbyne now available, it is useful to consider the bonding in the full series of alkynylchalcogenolatocarbynes. Table 2 and Figures 2 and 3 summarise computational results for the simpler model complexes [W≡CAC≡CMe)(CO)$_2$(Tp)] [A = O, S, Se, Te; Tp = tris(pyrazolyl)borato; DFT:ω97X-D/6-31G*/LANL2Dζ(W,Se,Te)].

Table 2. Computationally Derived[a] Features of [W(≡CAC≡CMe)(CO)$_2$(Tp)] including Natural charge (*Z*), Atom-condensed Fukui index (f^+),[17] Electrostatic potentials (EP) and Löwden bond orders (BO).

A	Z_W	Z_C	Z_A	f^+(A)[17]	EP_A[b]	r_{WC}	BO_{WC}	BO_{CA}	ν_{CC}[c,d]
	au	au	au	au	kJmol^{-1}	Å			cm^{-1}
O	0.88	+0.04	–0.50	0.030	–70[e]	1.811	2.39	1.29	2158
S	0.99	–0.54	+0.41	0.104	+27	1.813	2.41	1.26	2192
Se	0.97	–0.59	+0.52	0.108	+62	1.807	2.47	1.18	2183
Te	0.99	–0.73	+0.78	0.149	+111	1.807	2.50	1.13	2162

[a]DFT: ωB97X-D/6-31G(d)/LANL2Dζ(W,Se,Te)/Gas phase, charges in atomic units (=1.60 x 10^{-19} C). [b]Electrostatic potential maxima (0.002 e/au^3 isosurface, see Figure 3) at A, 115 kJmol^{-1} for Te(C≡CMe)$_2$. [c]Anharmonic scaling factor λ = 0.9297.[18] [d]Negligible IR intensity. [e]Very approximate estimation.

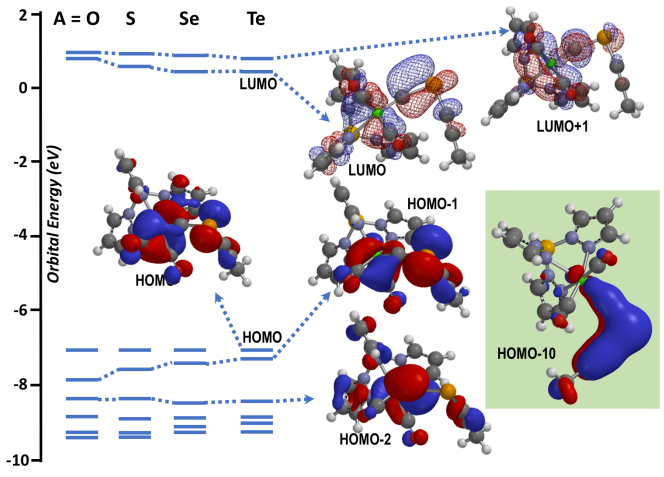

Figure 2. Molecular orbitals of interest (isovalue = 0.032 √(e.au^{-3})) for the model alkynylchalcogenolatocarbynes [W(≡CAC≡CMe)(CO)$_2$(Tp)] (A = O, S, Se, Te (shown); Tp = tris(pyrazolyl)borate), DFT: ω97X-D/6-31G*/LANL2Dζ(W,Se,Te)/gas phase.

The HOMO associated with carbonyl retrodonation is invariant across the series, accounting for the ν_{CO} values for the real compounds being insensitive to variation in chalcogen. The HOMO-1 and HOMO-2 correspond to the two π-components of the WC multiple bond, the order of which very gradually increases down the series. The HOMO-1 (but not the HOMO-2) involves a large contribution from the chalcogen 'lone' pair, as does the LUMO (maximal for A = Te), as reflected in the increase in atom-condensed Fukui function[17] for nucleophilic attack at the chalcogen. The most dramatic variation is, however the increase in charge of the chalcogen from –0.50 (A = O) to +0.78 (A = Te). This is naturally accompanied by an increase in the electrostatic potential (Figure 3), however this is seen to present two σ-holes (each opposite a Te–C bond), the localisation of which becomes increasingly pronounced for the heavier chalcogens. In the case of A = Te (111 kJmol^{-1}) this value approaches that calculated for Te(C≡CMe)$_2$ (115 kJmol^{-1}) which serves as a reference point given that alkynyl telluroethers are known to enter into supramolecular chalcogen bonding.[16,19]

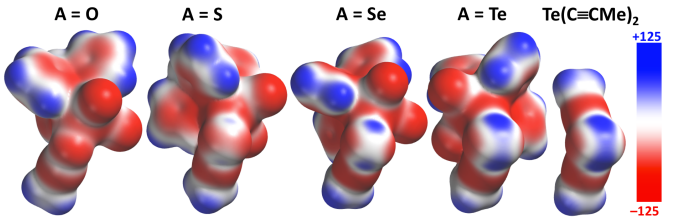

Figure 3. Electrostatic potential (EP: –125 to 125 kJ) surfaces (isovalue = 0.002 e/au^3) for [W(≡CAC≡CMe)(CO)$_2$(Tp)] (A = O, S, Se, Te) and Te(C≡CMe)$_2$ (DFT: ω97X-D/6-31G*/LANL2Dζ(W,Se,Te)/gas phase).

Group 11 metals, in particular gold(I) readily coordinate to M≡C triple bonds in much the same way as to a C≡C triple bond.[1d,9,15b,20] Treating **4b** with [CuCl(SMe$_2$)] does result in coordination of copper to the W≡C bond, however the alkyne *also* coordinates to a second 'CuCl' unit. The entire assembly dimerises *via* chloride bridges to afford a centrosymmetric Cu$_4$(μ-Cl)$_4$ metallacyclic core (**6**, Figure 4). This aggregation does not however persist in soution as indicated by ESI-mass spectrometry (ESI) which reveals the monomer [M-Cl]$^+$.

In a manner similar to the conversion of **2a** to **3a**, addition of [AuCl(SMe$_2$)] to **4a** results in the formation of the heterobimetallic bridging alkynyltellurolatocarbyne complex [WAu(μ-CTeC≡CSi^{i}Pr$_3$)Cl(CO)$_2$(Tp*)] (**6a**), the infrared spectrum of which was identical to that of **3a** (2015, 1935 cm^{-1}). In contrast to **3a**, however, **6a** proved to be unstable in solution compromising the acquisition of some data. Attempts to slowly grow crystals from the crude reaction mixture afforded crystals of a decomposition product [WAu(μ-CTeCl$_4$)(SMe$_2$)(CO)$_2$(Tp*)] (**8**, Figure 5). While the actual mechanism of its formation remains moot, the molecular structure includes curious features to justify its inclusion here. The alkynyl group has been cleaved and the tellurium oxidised to the tetravalent state. The carbido atom assumes a trigonal planar geometry between the tungsten, gold and hypervalent tellurium centres with the latter displaying a near perfect (τ_5 = 0.06) square-pyramidal arrangement as required by VSEPR (AX$_5$E$_1$) considerations.

In conclusion, alkynyltellurolatocarbynes are viable and readily accessed by a generalisable route. Although some parallels with the lighter chalcogens emerged, the alkynyl-tellurium bond is clearly fragile. An unexpected decomposition product revealed that carbynes functionalised by a hypervalent tellurium substituent (TeCl$_4^-$) are viable, however the study of such species would require useful synthetic approaches to be devised, an issue we are currently addressing.

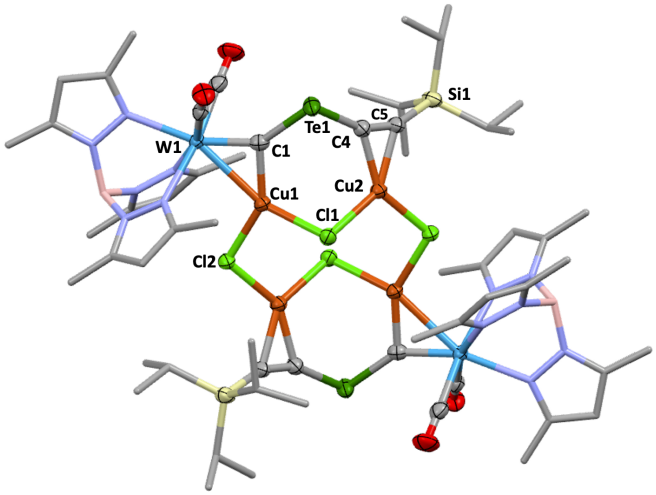

Figure 4. Molecular structure of centrosymmetric ($P2_1/n$) **6** in a crystal (50% displacement ellipsoids, pyrazolyl groups simplified and hydrogen atoms omitted).

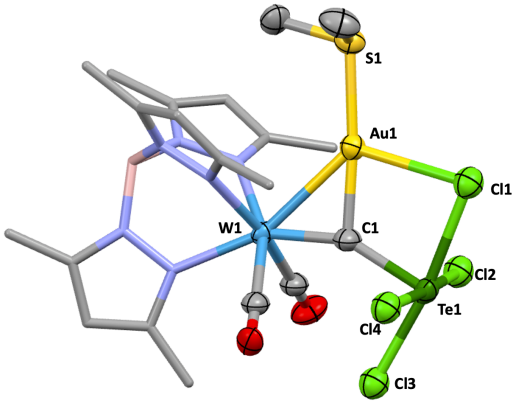

Figure 5. Molecular structure of **7** in a crystal of **7**.CH_2Cl_2 (50% displacement ellipsoids, pyrazolylborate and ^{i}Pr groups simplified, hydrogen atoms omitted).

Acknowledgements

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