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Dimetallapoly-yn-diylidynes: $L_nM{\equiv}C{-}(C{\equiv}C)_x{-}C{\equiv}ML_n$ (x = 0-4)

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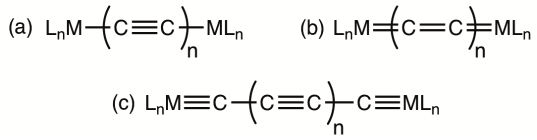
Abstract: Synthetic routes to dimetallated C_x carbon wires in which two metals are separated by a linear carbon chain involving terminal metal-carbon triple bonds are described for the complexes $[(Tp^*)(CO)_2W{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}W(CO)_2(Tp^*)]$ (Tp^* = hydrotris(dimethylpyrazolyl)borate) where n = 1, 3 or 4, joining the previously known examples with n = 0, 1 and 2 to complete the series as models for linear carbyne.

In 1885 Adolf von Baeyer famously predicted the possible existence of the one-dimensional carbon allotrope (poly)carbyne, C_∞, but also suggested that its extreme reactivity would most likely preclude its isolation.[1] In the interim it has been predicted that this elusive material would present exceptional tensile strength (arguably the strongest material 'known')[2] and electrical and thermal conductivity.[3] The promise of such properties has piqued the interest of a broad range of materials, polymer and theoretical chemists but has also naturally attracted the attention of synthetic chemists, in particular in the field of organometallic chemistry,[4] not only inspired by the fundamental synthetic challenges, but also for the possibility that molecular electronic or electro-optical applications might emerge, and the raft of spectroscopic techniques that may be brought to bear on interrogating the properties of molecular model compounds.[5] Terminating poly-yne chains with bulky end-caps has been shown to confer stability allowing discreet *sp*-carbon chains as long as Tr*-(C≡C)$_{22}$-Tr* (Tr* = tris(3,5-di-*t*-butylphenyl)methyl) to be isolated,[6] whilst in the transition metal regime, the longest chain achieved to date is found in Gladysz's complex $[Pt_2(\mu\text{-}C_{28})R_2(PR_3)_4]$ (R = C_6H_4Me-4).[7] These poly(carbyne) mimics all have in common that the chain is terminated by *single* metal-carbon bonds, *i.e.*, they may be described as poly-yn-diyls (Scheme 1a). One might however consider situations wherein the chain is bound to the metal termini by double (cumulenic poly-en-diylidene Scheme 1b) or indeed triple bonds (poly-yn-diylidyne, Scheme 1c), however these are by a significant margin far less common.



Scheme 1. (a) Poly-yn-diyl (x = 2n), (b) poly-en-diylidene (x = 2n) and (c) poly-yn-diylidyne (x = 2n+2) valence representations for $L_nMC_xML_n$ carbon wires.

The longest poly-yn-diylidynes are the dimetalla-octatetraynes $[(L)(CO)_2W{\equiv}C\text{-}(C{\equiv}C)_2\text{-}C{\equiv}W(CO)_2(L)]$ (L= Tp, Tp* **WC$_6$W**; Tp = hydrotris(pyrazolyl)borate, Tp* = hydrotris(dimethylpyrazolyl)borate)[8] which are obtained via catalytic demercuration of the mercury bis(tricarbido) complexes $[Hg\{C{\equiv}C\text{-}C{\equiv}W(CO)_2(L)\}_2]$. Prior to this, Templeton had obtained the tetracarbido analogue $[(Tp^*)(CO)_2W{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}W(CO)_2(Tp^*)]$ (**WC$_4$W**) via an elegant multiple deprotonation/oxidation sequence commencing with the ethylidyne complex $[(Tp^*)(CO)_2W(\equiv CMe)]$[9] and we have recently described the simplest 'parent' C_2 example $[(Tp^*)(CO)_2W{\equiv}C\text{-}C{\equiv}W(CO)_2(Tp^*)]$ (**WC$_2$W**).[10] The routes employed lack generality, however Berke has demonstrated a redox valence-relocalisation approach in which 4-electron oxidation of dimetallated butadi-yn-diyls may be converted to dimetallahexatriynes (butadi-yn-diylidynes),[11] whilst Tamm has identified the complex $[R_3W{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}WR_3]$ (R = $OSi(O^tBu)_3$) as being present during alkyne-diyne cross metatheses mediated by $[R_3W{\equiv}CPh]$.[12] As the chemistry of these shorter chain poly-yn-diylidynes (**MC$_x$M**) (x = 2, 4, 6) develops, the question arises as to whether longer chain examples might also be accessible, as so amply demonstrated for poly-yn-diyls.[4] We report herein that extended **MC$_8$M** and **MC$_{10}$M** bridged diylidynes are indeed viable as exemplified by the new complexes $[(Tp^*)(CO)_2W{\equiv}C\text{-}(C{\equiv}C)_3\text{-}C{\equiv}W(CO)_2(Tp^*)]$ (**WC$_8$W**) and $[(Tp^*)(CO)_2W{\equiv}C\text{-}(C{\equiv}C)_4\text{-}C{\equiv}W(CO)_2(Tp^*)]$ (**WC$_{10}$W**) in addition to providing a convenient new approach to Templeton's archetypal complex **WC$_4$W**.

We have optimized Sonogashira-type C–C cross-coupling processes for the coupling of a range of 1-alkynes (HC≡CR) with the bromocarbyne complex $[W(\equiv CBr)(CO)_2(Tp^*)]$ (**1**)[13] so as to provide a new route to variously functionalised propargylidynes $[W(\equiv CC{\equiv}CR)(CO)_2(Tp^*)]$.[14] In attempting to extend this approach to ethynyltriphenylstannane we find that the reaction does not proceed as intended. Rather, combination of **1** with $HC{\equiv}CSnPh_3$ in the presence of $[Pd(PPh_3)_4]$ and CuI affords Templeton's **WC$_4$W** in reasonable yields (44-50%) rather than the intended monometallic stannyl propargylidyne $[W(\equiv CC{\equiv}CSnPh_3)\text{-}(CO)_2(Tp^*)]$ (**2**) (Scheme 2), which is however a plausible intermediate *en route* to **WC$_4$W**. Even when an excess of the alkyne is employed, **WC$_4$W** is the sole observed new organometallic product, the implication being that the mediated cross-coupling between **1** and **2** is significantly more rapid than between **1** and the alkynylstannane. Although the longer **WC$_6$W** carbon chain readily enters into reactions involving addition of metal(s) to either the C≡C or W≡C multiple bonds, **WC$_4$W** is unreactive towards either [AuCl(THT)] (THT = tetrahydrothiophene) or $[Co_2(CO)_8]$, presumably reflecting steric congestion in the region between the bulky (Tp*)W termini.

Recently, the first example of a pentadiynylidyne complex $[W(\equiv CC{\equiv}CC{\equiv}CSiMe_3)(CO)_2(Tp^*)]$ (**3**) was shown to serve through desilylation as a precursor to pentacarbido-bridged bi- and polymetallic complexes.[15] With **3** and the previously reported propargylidyne $[W(\equiv CC{\equiv}CSiMe_3)(CO)_2(Tp^*)]$ (**4**)[16] in hand we considered the possibility of extending the dimetallapoly-yn-diylidyne class of complex to include the new complexes $[(Tp^*)(CO)_2W{\equiv}C\text{-}(C{\equiv}C)_3\text{-}C{\equiv}W(CO)_2(Tp^*)]$ (**WC$_8$W**) and $[(Tp^*)(CO)_2W{\equiv}C\text{-}(C{\equiv}C)_4\text{-}C{\equiv}W(CO)_2(Tp^*)]$ (**WC$_{10}$W**). The

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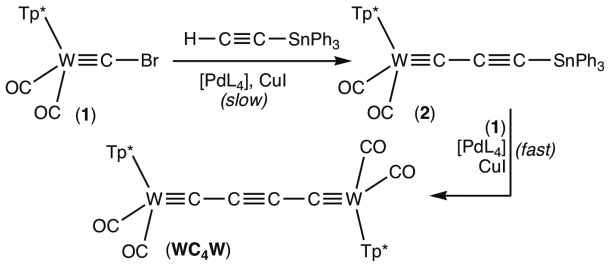
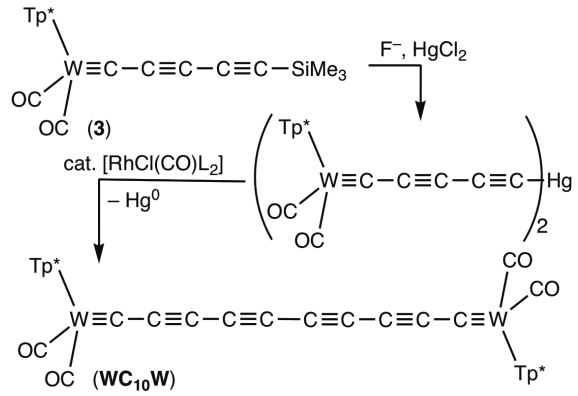


Scheme 2. Synthesis of a ditungstahexatriyne **WC₄W**.

combination of **3** with $[NBu_4]F$ and $HgCl_2$ afforded the bis(pentacarbido)mercurial $[Hg\{C{\equiv}C\text{-}C{\equiv}W(CO)_2(Tp^*)\}_2]$ (**WC₅HgC₅W**, 87%) which upon treatment with a catalytic amount of $[RhCl(CO)(PPh_3)_2]$[17] afforded **WC₁₀W** (50% yield, Scheme 3, Table 1).



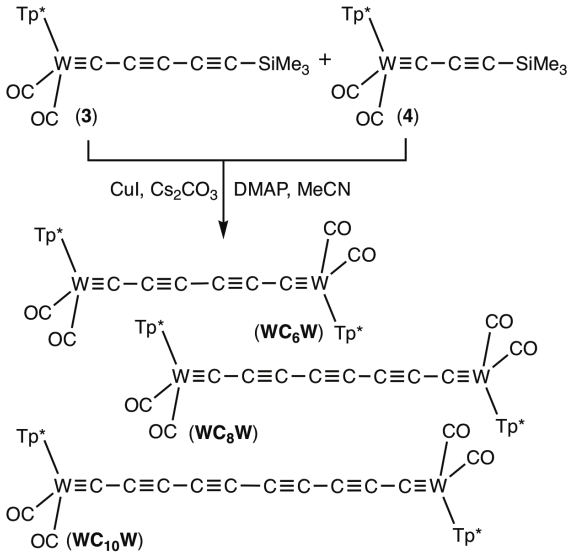
Scheme 3. Synthesis of a ditungstadodecahexayne **WC₁₀W**.

Table 1. Selected IR (CH_2Cl_2) and NMR Data ($CDCl_3$: δ_C) for **MC$_x$M** Bridged species **M** = $M(CO)_2(Tp^*)$, M = Mo, W, x = 2,4,6,8,10

	ν [cm⁻¹]	δC Cα	Cβ	Cγ	Cδ	Cε
WC₂W[10a]	1949,1933, 1876	*a*				
MoC₂Mo[10b]	2009, 1972, 1915	271.5				
WC₄W[9]	1991, 1965, 1896	243.8	88.2			
MoC₄Mo[9]	2004, 1977, 1901	248.9	107.0			
WC₆W[8]	1982, 1915, 1890	242.8	96.2	58.6		
WC₈W	1993, 1982, 1905	243.5	94.4	59.8	85.3	
WC₁₀W	1986, 1907	243.0	93.5	59.1	67.8	65.7

[a] Insufficiently soluble for ^{13}C NMR data acquisition.

The synthesis of **WC₈W** proved more problematic and, whilst achieved, we concede that there remains room for procedural improvement. Under aerobic conditions, the combination of **3**, **4**, Cs_2CO_3, CuI and 4-dimethyaminopyridine (DMAP) in acetonitrile (adapted Glaser-Hay conditions[18]) afforded a non-statistical chromatographically separable mixture of **WC₁₀W** (2%), **WC₈W** (8%) and **WC₆W** (4%), which elute in that order (silica gel, pet. spirit/CH_2Cl_2 1:1).



Scheme 4. Synthesis of dimetallapoly-yn-diylidynes **WC₆W, WC₈W** and **WC₁₀W**.

The characterisation of **WC₈W** (Table 1) included a crystallographic analysis, the results of which are summarised in Figure 1.

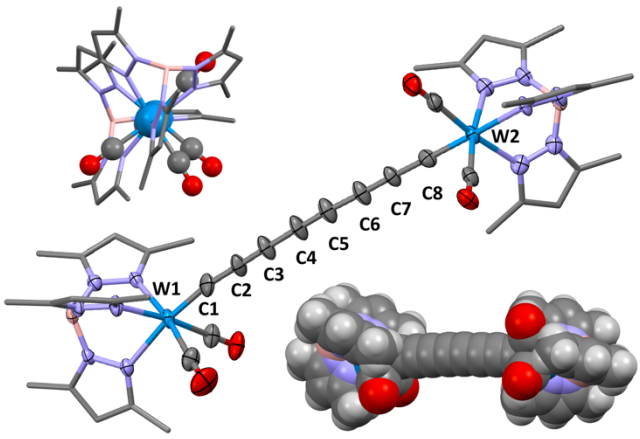


Figure 1. Molecular structure of **WC₈W** in a crystal (50% displacement ellipsoids, most hydrogens omitted and Tp* ligands simplified for clarity). Selected bond lengths (Å) and angles (°): W1–C1 1.845(8), W2–C8 1.836(7), C1–C2 1.362(10), C2–C3 1.210(10), C3–C4 1.365(10), C4–C5 1.212(11), C5–C6 1.354(10), C6–C7 1.213(10), C7–C8 1.376(9), W1–C1–C2 171.5(7), C7–C8–W2 174.0(5), C1–C2–C3 178.8(9), C2–C3–C4 177.1(8), C3–C4–C5 179.0(11), C4–C5–C6 175.7(10), C7–C6–C5 177.4(9), C6–C7–C8 178.0(9). Insets = view along W1···W2 vector and space-filling representation.

The geometric parameters associated with the essentially linear tungsten octacarbido spine of **WC₈W** are consistent with a poly-yn-diylidyne W≡C-$(C{\equiv}C)_3$-C≡W valence bond localisation. This involves short W≡C separations (1.836(7), 1.845(8) Å) that are comparable to those for more conventional carbyne complexes $[W(\equiv CR)(CO)_2(Tp^*)]$[19] and distinct from dimetallated octatetra-yn-diyls $L_nM–(C{\equiv}C)_4–ML_n$ for which copious structural data are available.[20]

Because the only variable in the homologous series is the number of carbon atoms in the chain, in principle any variation in spectroscopic properties may be directly related to this. Although infrared ν_{CO} frequencies for carbonyl co-ligands are useful in benchmarking the electronic nature of carbyne ligands,[19] in the case of the **MC$_x$M** series caution should be exercised due to the possibility of Fermi resonance with C$_x$-chain alkynyl stretching modes of appropriate symmetry, commonly encountered in acetylenic materials.[21] Whilst weak absorptions were observed (Supporting Information) that most likely relate to $\nu_{C\equiv C}$ modes, these are not identified with confidence. The UV-Vis spectra for the series (Figure 2, Table 2) are, however, of interest in that the origins of colour in carbyne complexes of the form [W(≡CR)XL$_4$] are well-understood.[15,22] In general two types of transition (with *z* as the W≡C vector) are typically observed *viz* $d_{xy}\rightarrow\pi^*_{W\equiv C}$ and, to higher energy, $\pi_{W\equiv C}\rightarrow\pi^*_{W\equiv C}$.

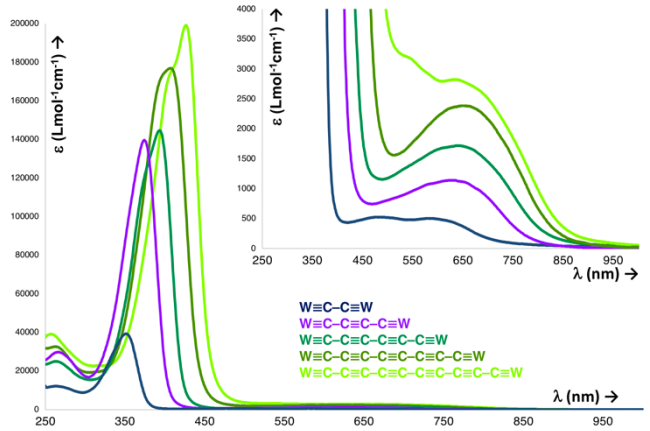


Figure 2. Ultraviolet-Visible Spectra for **WC$_x$W** (x = 2,4,6,8,10; **W** = W(CO)$_2$(Tp*)), For deconvoluted spectra see Supporting Information.

The (two) near degenerate orbitals denoted d_{xy} are primarily associated with π-retrodative carbonyl binding and are orthogonal to the **WC$_x$W** spine. The weak $d_{xy}\rightarrow\pi^*_{W\equiv C}$ absorption is (with the exception of x = 2) remarkably insensitive to variation in the length of the carbon chain and considerably lower in energy than the MLCT transitions associated with the carbonyl ligands (ca 250 nm). The insensitivity of the energy of the $d_{xy}\rightarrow\pi^*_{W\equiv C}$ absorption to variations in C$_x$ chain length contrasts with the behaviour of d^8-square planar poly-yn-diyl complexes such as [L$_3$PtC$_x$PtL$_3$] discussed by Yam (L$_3$Pt = Pt(terpy^{t}Bu$_3$)$^+$)[20] and Gladysz (L$_3$Pt = PtR(PR$_3$)$_2$; R = C$_6$H$_4$Me-4),[7] for which the HOMO comprises an intimate combination of both metal-based d$_{xz}$ and C$_x$ π-system orbitals. In contrast, the $\pi_{W\equiv C}\rightarrow\pi^*_{W\equiv C}$ absorptions are bathochromically shifted into the visible region with increasing chain length as the energy gap between $\pi_{W\equiv C}$ and $\pi^*_{W\equiv C}$ orbitals decreases with increasing conjugation. Given that λ_{max} for the $d_{xy}\rightarrow\pi^*_{W\equiv C}$ absorption is essentially independent of chain length, we might infer that the energy of $\pi^*_{W\equiv C}$ is not significantly stabilised but rather that the energy of $\pi_{W\equiv C}$ is progressively raised in energy as x increases. This is in concert with Bock's early observations on the ionisation and transition (π→π*) energies of poly-ynes Me$_3$Si-(C≡C)$_n$SiMe$_3$ (n = 1, 2, 3).[23] Notably, the molar absorptivities of both types of absorption increase monotonically with increasing chain length as has also been noted for silyl-capped poly-ynes.[6,23]

Cyclic voltammetry indicates that with the exception of **WC$_2$W** which is insufficiently soluble for study, each of the series has two oxidation events that are remarkably insensitive to the carbon chain length. This may be attributed to the essential invariance of the energy of the HOMO which is associated with metal-carbonyl bonding rather than being intimately involved with the WC$_x$W chain. The reversibility of the second oxidation decreases with increasing chain length which is most likely due to oxidative decarbonylation.[24]

Table 2. Experimental UV-Vis λ_{max} for **WC$_x$W**[a]

x	λ_{max}[b] nm	ε Lmol^{-1}cm^{-1}	λ_{max}[b] nm	ε Lmol^{-1}cm^{-1}	$E_{½}$[a] V[c]
2	485, 584	530, 510	352	39,000	*d*
4	635	1,100	374	140,000	0.59, 0.81
6	641	1,700	393	145,000	0.61, 0.80
8	652	2,400	407	177,000	0.57, 0.72
10	633	2,800	426	199,000	0.75, 0.85

[a]Measured in CH_2Cl_2.[b]Each of these peaks comprises two absorptions. For deconvoluted spectra see Supporting Information. [c]Relative to $[Fe(\eta\text{-}C_5H_5)_2]^{0/+}$ = 0.460 V *cf.* Ag/AgCl = 0. See Supporting Information for CV traces. [d]Insufficiently soluble.

Figure 3 presents the frontier orbitals of interest for the hypothetical complex "W$_2$(μ-C$_8$)(CO)$_4$(Tp)$_2$"[25] confirming a near degenerate pair of d_{xy} CO-binding orbitals as HOMO and HOMO-1 with HOMO-2 and HOMO-3 corresponding to orbitals involving both terminal W≡C π-bonding components and considerable conjugation out to the C$_8$ chain. The LUMO and LUMO+1 have distinctly WC π-antibonding character but are again significantly delocalised along the C$_8$ bridge. Similar observations and arguments have been presented for the series of complexes [W(C$_x$SiMe$_3$)(CO)$_2$(Tp)] (x = 1,3,5).[15]

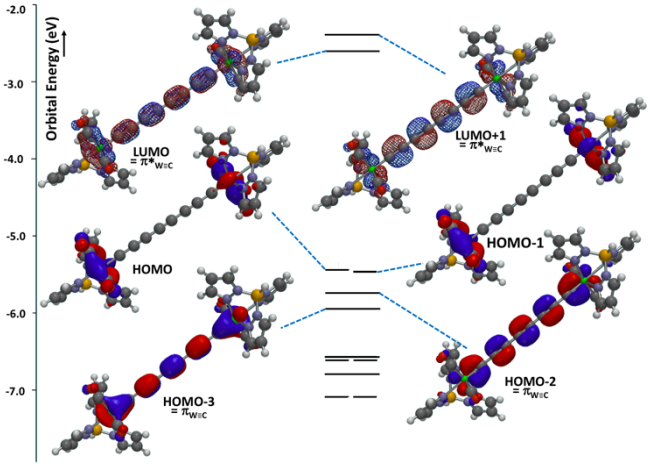


Figure 3. Frontier orbitals of interest for the hypothetical complex "W$_2$(μ-C$_8$)(CO)$_4$(Tp)$_2$" (isovalue = 0.032).[25]

In conclusion, we have shown that long-chain carbon wires are not limited to simple metal-capped poly-yndiyls but can also be constructed with metal alkylidyne termini. Interest in the

electro-optical properties of dimetallated poly-yn-diyl based carbon wires is typically associated with metal-ligand charge transfer events. Replacing rather weakly π-acidic alkynyl metal linkages with those involving strongly π-acidic metal-carbon multiple bonds should significantly enhance the facility of such events and inspire further studies.

Acknowledgements

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Keywords: Bis(carbyne) • Carbon • Tungsten • Polymetallic • Carbyne

[1] (a) A. von Baeyer, *Ber. Dtsch. Chem. Ges.*, **1885**, *18*, 674-681.(b) "*…dam es aller Wahrscheinlichkeit nach gelingen wird, noch längere Ketten von Kohlenstoffatomen aufzubauen, wenn nicht die schon bei den Diacetylenverbindungen zu Tage tretende leichte Zersetzbarkeit einen Strich durch die Rechnung machen sollte*".

[2] M. J. Liu, V. I. Artyukhov, H. Lee, F. B. Xu and B. I. Yakobson, *ACS Nano,* **2013,** *7*, 10075–10082.

[3] (a) A. La Torre, A. Botello-Mendez, W. Baaziz, J.-C. Charlier and F. Banhart, *Nat. Commun.*, **2015**, *6*, 6636, 1-7. (b) Y. Deng and S. W. Cranford, *Comp. Mater. Sci.*, **2017**, *129*, 226-230.

[4] (a) P. J. Low and M. I. Bruce, *Adv. Organomet. Chem.,* **2002**, *48*, 71-288. (b) P. J. Low and M. I. Bruce, *Adv. Organomet. Chem.,* **2004**, *50*, 179-444. (c) S. Szafert and J. A. Gladysz, *Chem. Rev.*, **2003**, *103*, 4175-4206. (d) S. Szafert and J. A. Gladysz, *Chem. Rev.*, **2003**, *106*, PR1-PR33.

[5] A. Moneo, A. González-Orive, S. Bock, M. Fenero, I. L. Herrer, D. C. Milan, M. Lorenzoni, R. J. Nichols, P. Cea, F. Perez-Murano, P. J. Low and S. Martin, *Nanoscale*, **2018**, *10*, 14128-14138.

[6] W. A. Chalifoux and R. R. Tykwinski *Nat. Chem.*, **2010**, *2*, 967-971.

[7] Q. Zheng, J. C. Bohling, T. B. Peters, A. C. Frisch, F. Hampel and J. A. Gladysz, *Chem. Eur. J.,* **2006**, *12,* 6486-6505.

[8] (a) R. D. Dewhurst, A. F. Hill and A. C. Willis, *Organometallics*, **2005**, *24*, 13, 3043-3046. (b) R. D. Dewhurst, A. F. Hill and A. C. Willis, *Chem. Commun.*, **2004**, 2826-2827

[9] (a) B. E. Woodworth, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, **1997**, *119*, 828-829.

[10] (a) B. J. Frogley and A. F. Hill, *Angew. Chem., Int. Ed.,* **2019**, 58, 8044-8048. (b) A. L. Colebatch, R. L. Cordiner, A. F. Hill, K. T. H. D. Nguyen, R. Shang and A. C. Willis, *Organometallics*, **2009**, *28*, 4394-4399.

[11] (a) S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan and H. Berke, *J. Am. Chem. Soc.*, **2010**, *132*, 3115-3127. (b) S. N. Semenov, S. F. Taghipourian, O. Blacque, T. Fox, K. Venkatesan and H. Berke, *J. Am. Chem. Soc.*, **2010**, *132*, 7584-7585. (c) Such processes may be inferred to occur in the 4-electron oxidation of diruthenated butadiynes observed electrochemically by Bruce: M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best and G. A. Heath, *J. Am. Chem. Soc.,* **2000**, *122*, 1949-1962.

[12] T. M. Schnabel, D. Melcher, K. Brandhorst, D. Bockfeld and M. Tamm, *Chem. Eur. J.*, **2018**, *24*, 9022-9032.

[13] (a) F. J. Lalor, T. J. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez and B. Ruhl, *J. Chem. Soc., Dalton Trans.*, **1995**, 1709-1726. (b) R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, **2008**, *27*, 5177-5179.

[14] (a) A. F. Hill and R. A. Manzano, *Dalton Trans.*, **2019**, *48*, 6596-6610. (b) For a review of propargylidyne chemistry see A. F. Hill and R. A. Manzano, *Adv. Organomet. Chem.*, **2019**, *72*, 1-69.

[15] A. F. Hill and R. A. Manzano, *Angew. Chem., Int. Ed.*, **2019**, *58*, 7357-7360.

[16] (a) B. Schwenzer, L. Schleu, N. Burzlaff, C. Karl and H. Fischer, *J. Organomet. Chem.*, **2002**, *641*, 134-141. (b) R. D. Dewhurst, A. F. Hill and M. K. Smith, *Angew. Chem., Int. Ed*., **2004**, *43*, 476-478.

[17] R. B. Bedford, A. F. Hill, A. R. Thompsett, A. J. P. White and D. J. Williams, *Chem. Commun.,* **1996**, 1059-1060.

[18] B. S. Navale and R. G. Bhat, *RSC Adv.*, **2013**, *3*, 5220-5226.

[19] For a review of complexes of the form $[W(\equiv CR)(CO)_2(Tp^*)]$ see L. M. Caldwell, *Adv. Organomet. Chem.*, **2008**, *56*, 1-94.

[20] Recent papers (and references therein) by contributing groups include: (a) G. R. Owen, S. Gauthier, N. Weisbach, F. Hampel, N. Bhuvanesh and J. A. Gladysz, *Dalton Trans.*, **2010**, *39*, 5260-5271. (b) N. Weisbach, Z. Baranova, S. Gauthier, J. H. Reibenspies and J. A. Gladysz *Chem. Commun.*, **2012**, *48*, 7562-7564. (c) M. Akita, Y. Tanaka, C. Naitoh, T. Ozawa, N. Hayashi, M. Takeshita, A. Inagaki and M.-C. Chung, *Organometallics*, **2006**, *25*, 5261-5275. (d) M.-C. Oerthel, D. S. Yufit, M. A. Fox, M. R. Bryce and P. J. Low, *Organometallics*, **2015**, *34*, 2395-2405. (e) M. I. Bruce, M. L. Cole, B. G. Ellis, M. Gaudio, B. K. Nicholson, C. R. Parker, B. W. Skelton and A. H. White, *Polyhedron*, **2015**, *86*, 43-56. (f) T. D. Cook, S. N. Natoli, P. E. Fanwick and T. Ren, *Organometallics*, **2016**, *35*, 1329-1338. (g) F. Coat, F. Paul, C. Lapinte, L. Toupet, K. Costuas and J.-F. Halet, *J. Organomet. Chem.*, **2003**, *683*, 368-378. (h) L.-B. Gao, J. Kan, Y. Fan, L.-Y. Zhang, S.-H. Liu and Z.-N. Chen, *Inorg. Chem.,* **2007**, *46*, 5651-5664. (i) V. W.-W. Yam, K. M.-C. Wong and N. Zhu, *Angew. Chem., Int. Ed.,* **2003**, *42*, 1400-1403.

[21] R. D. Markwell, I. S. Butler, A. K. Kakkar, M. S. Khan, Z. H. Al-Zakwani and J. Lewis *Organometallics,* **1996**, *15*, 2331-2337.

[22] (a) B. M. Lovaasen, J. V. Lockard, B. W. Cohen, S. Yang, Shujiang, X. Zhang, C. K. Simpson, L. X. Chen and M. D. Hopkins, *Inorg. Chem.,* **2012**, *51*, 5660-5670. (b) R. E. Da Re and M. D. Hopkins, *Coord. Chem. Rev.*, **2005**, *249*, 1396-1409. (c) J. Sun, S. E. Shaner, M. K. Jones, D. C. O'Hanlon, J. S. Mugridge and M. D. Hopkins, *Inorg. Chem.,* **2010,** *49*, 1687-1698.

[23] H. Bock and H. Seidl, *J. Chem. Soc., B,* **1968**, 1158-1163.

[24] Oxidative decarbonylation of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(Tp)]$ to $[W(\equiv CC_6H_3Me_2\text{-}2,6)Cl_2(Tp)]$ by $[Fe(C_5H_5)_2]Cl$ has been discussed previously, as has the chlorination of WC_6W by $[AuCl(SMe_3)]$ to afford $[(Tp^*)Cl_2W\equiv C\text{-}(C\equiv C)_2\text{-}C\equiv WCl_2(Tp^*)]$: (a) S. Anderson, D. J. Cook, A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, *Organometallics*, **2004**, *23*, 2552-2557. (b) A. R. Delaney, B. J. Frogley and A. F. Hill, *Dalton Trans.,* **2019**, in press, DOI: 10.1039/c9dt03041g.

[25] The tris(dimethylpyrazolyl)borate ligand (Tp*) was replaced with the computationally more economical but slightly less electron releasing tris(pyrazolyl)borate (Tp) ligand; DFT: B3LYP/6-31G*/LanL2DZ, gas phase, no imposed symmetry, optimisation converged to approximate centrosymmetry.

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