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Flexible Platinum(0) Coordination to a Ditungsten Ethanediylidyne

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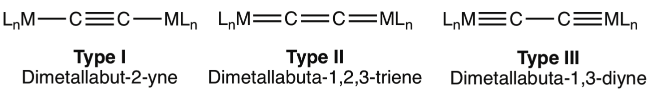
Abstract: The lithiocarbyne [W(≡CLi)$(CO)_2$(Tp*)] (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) reacts with [$PtCl_2(L_2)$] (L_2 = 1,5-cyclo-octadiene, norbornadiene) to furnish ditungsten ethanediylidyne complexes, [W_2{μ-$C_2Pt(L_2)$}$(CO)_4(Tp^*)_2$], wherein a trigonal platinum(0) center unsymmetrically ligates one W≡C bond in the solid state but rapidly "shimmies" between the two W≡C bonds in solution. The η^4-dienes are displaced by monodentate CO or isocyanide ligands to provide derivatives where *both* W≡C bonds coordinate to a single Pt^0 center, attended by significant distortion of the WCCW spine.

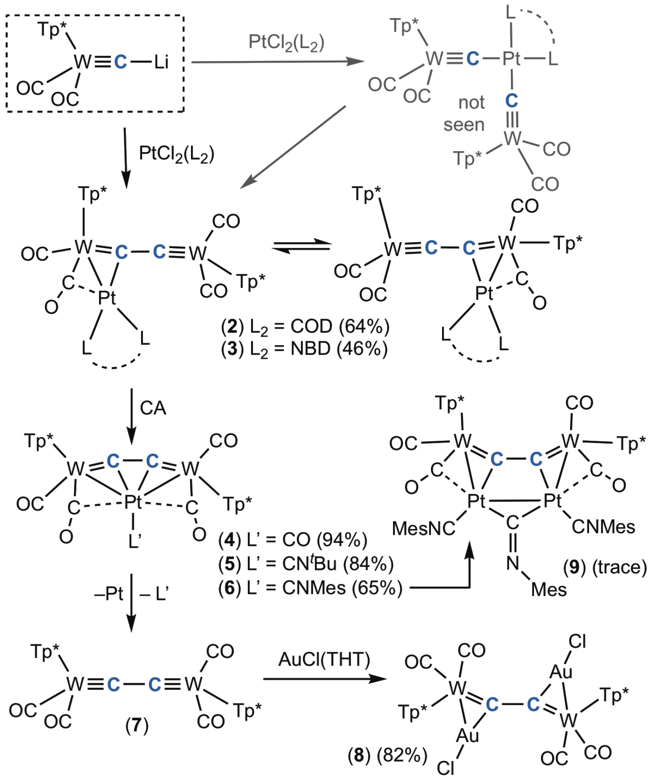
The vast majority of C_2-bridged dimetallic complexes are best described as dimetallated ethynes, often recalling their synthetic origins (Scheme 1, Type **I**).[1] A small number are better viewed as 'cumulenic' dimetallabutatrienes (Type **II**),[2] so as to satisfy the EAN requirements of the particular metal termini. Rarest of all are ethanediylidyne-bridged (biscarbyne) complexes or dimetallabutadiynes (Type **III**)[3] which have historically arisen only sporadically. Accordingly, the scope of such compounds has yet to be explored.



Scheme 1. Valence bond localization of μ-dicarbido complexes.

Schrock provided the archetypal biscarbyne complex, [W_2(μ-C_2)$(O^tBu)_6$], which arose from alkyne metathesis of 1,3-diynes by [$W_2(O^tBu)_6$],[3a] derivatives or analogues of which comprise the majority of Type **III** examples.[3c-e,3h] Templeton has constructed two Type **III** complexes *via* sequential deprotonation/oxidation of M≡C–CH_2–W (M = Mo, W) bridges,[3g] further demonstrating his elegant and more widely applicable strategies for preparing unsaturated bimetallic molecular wires.[4] Oxidation of a Type **II** dimanganese complex has been shown by Berke to result in Type **III** valence localisation.[2d] Finally, the bis(carbido)mercurial [Hg{C≡Mo$(CO)_2$(Tp*)}$_2$] (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) undergoes demercuration catalysed by [RhCl(CO)$(PPh_3)_2$] to form [Mo_2(μ-C_2)$(CO)_4(Tp^*)_2$].[3f] This method has yet to find success for the tungsten analogue because the requisite mercurial has so far eluded isolation. Implicit in this catalysis, however, is the intermediacy of a rhodium(III) bis(μ-carbido) complex [RhCl{C≡Mo$(CO)_2$(Tp*)}$_2$(CO)$(PPh_3)_2$], which was however not observed. Indeed, bis(μ-carbido) complexes remain exceedingly rare,[5] providing motivation for the present study to explore the relationship between such complexes and Type **III** biscarbynes arising from reductive elimination. Modern, isolobally related, alkynyl C–C coupling protocols reflect some 150 years of research.[6] Palladium-mediated C–C and C–P bond forming reactions of bromocarbynes[7] are presumed to proceed *via* mono μ-carbido complexes akin to, *e.g.*, [WNi(μ-C)Cl$(PEt_3)_2(CO)_2$(Tp*)][8] suggesting group 10 metals might be suitable for the isolation and study of bis(μ-carbido) complexes. Herein we report the results of our initial foray into μ-carbido coupling processes by reaction of lithiocarbynes with haloplatinum(II) complexes.

The lithiocarbyne [W(≡CLi)$(CO)_2$(Tp*)] (**1**, formed from [W(≡CBr)$(CO)_2$(Tp*)] and ^{n}BuLi[7c]) reacts with [$PtCl_2$(COD)] (COD = η^4-1,5-cyclo-octadiene) by halide metathesis to furnish the platinum-coordinated ethanediylidyne complex [W_2{μ-C_2Pt(COD)}$CO)_4(Tp^*)_2$] (**2**, Scheme 2).



Scheme 2. Ethanediylidyne synthesis and novel coordination modes.

The reaction presumably proceeds, as intended, *via* initial formation of a bis(μ-carbido)platinum(II) intermediate, [Pt{C≡W$(CO)_2$(Tp*)}$_2$(COD)], which is however followed by reductive coupling to give the ethanediylidyne fragment. The process recalls traditional alkyne coupling reactions, except that the product is not eliminated from the reduced platinum(0) center but instead remains coordinated to *one* of the W≡C bonds.[9,10] The appended Pt(0) also retains the diene ligand to achieve an

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approximately trigonal geometry which is further supported by a semi-bridging CO ligand, as usually found in Pt^0 adducts of tungsten carbynes. In a similar manner, reaction between the lithiocarbyne and $[PtCl_2(NBD)]$ (NBD = 2,5-norbornadiene) furnishes the related complex $[W_2\{\mu\text{-}C_2Pt(NBD)\}(CO)_4(Tp^*)_2]$ (**3**).

Although in the ground-state and solid state, the Pt(COD) or Pt(NBD) moieties coordinate to only one of the W≡C bonds, the energy barrier to exchange between the two in solution is relatively small and at room temperature the platinum diene fragment rapidly "shimmies" between the two carbyne bonds. This feature manifests as significant broadening of the ^1H and $^{13}C\{^1H\}$ NMR resonances at room temperature. On cooling to –30 °C these sharpen significantly as the rate of "shimmy" is vastly reduced. Variable temperature NMR experiments (See ESI) return exchange rates at 298 K of *ca* 130 s^{-1} ($\Delta G^‡$ = 59.4(12) $kJmol^{-1}$) and 3600 s^{-1} ($\Delta G^‡$ = 52.0(9) $kJmol^{-1}$) for **2** and **3**, respectively, suggesting the smaller 'Pt(NBD)' unit is more mobile. The process recalls, in isolobal terms, Rosenthal's observation of metallocene sliding along a poly-yne chain,[11a] an analogy we will build upon (*vide infra*).

The inequivalence of the two $W(CO)_2(Tp^*)$ moieties in **2** and **3** is similarly evident in the low temperature $^{13}C\{^1H\}$ NMR spectra wherein every carbon nuclei gives rise to a unique resonance. The tungsten and platinum-coordinated μ-C resonances (**2**: 299.4, **3**: 302.1 ppm) are shifted to lower frequency compared to the terminal W≡C resonances (**2**: 289.3, **3**: 289.8 ppm), being flanked by ^{195}Pt satellites ($^1J_{CPt}$ = 690 and 755 Hz for **2** and **3**, respectively). These μ-*C* chemical shifts and associated $^1J_{CPt}$ values are reassuringly similar to those of bimetallic Pt(0)-coordinated tungsten alkylidynes reported by Stone (*ca* 290–330 ppm and 690–850 Hz, respectively)[9] although the ^{195}Pt resonances for **2** (–3739 ppm) and **3** (–3914 ppm) are shifted dramatically up-field from those reported by Stone (0 – 2000 ppm).

The molecular structures of **2** (ESI) and **3** (Figure 1) confirm the presumed ground-state structures. The precision of the structural model for **2** is somewhat compromised by positional disorder of the Pt(COD) fragment over the two W≡C bonds and so discussion is focused on the more precise structural model for **3**. This presents a unique opportunity to compare the structural parameters of terminal and bridging carbynes within the same molecule. The W1–C1 bond distance (1.982(5) Å) is elongated on coordination to Pt and the W1–C1–C2 angle (152.2(4)°) is appreciably bent ('semi-bridging' character), conforming to extant structural data for heterobimetallic bridging carbynes.[8-11] The much shorter terminal W2–C2 distance (1.881(5) Å) falls towards the longer end of typical W≡C distances in monometallic alkylidynes (*ca* 1.78–1.86 Å)[10] and is far closer to linearity (W2–C2–C1 175.7(4)°). The C1–C2 distance (1.357(7) Å) is crystallographically identical to the related distance in the "free" ethanediylidyne complex $[Mo_2(\mu\text{-}C_2)(CO)_4(Tp^*)_2]$ (1.370(7) Å), for which the valence localized Mo≡C–C≡Mo description is most appropriate.[3g]

A plausible trajectory for this platinum "shimmy" in **2** and **3** might involve initial deco-ordination of one alkene bond and coordination of the second W≡C bond to Pt, forming an intermediate with a *tetrahapto* bis-carbyne. We reasoned that if

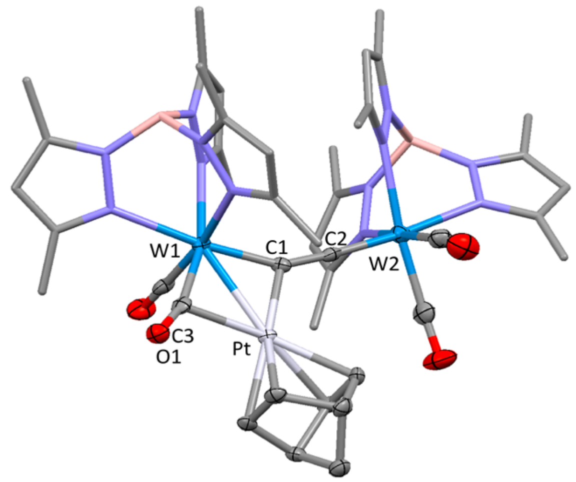

Figure 1. Molecular structure of **3** in a crystal of **3**.CH_2Cl_2 (50% displacement ellipsoids, hydrogen atoms and solvent omitted, pyrazolyl rings simplified). Selected bond lengths (Å) and angles (°): W1–C1 1.982(5), C1–C2 1.357(7), C2–W2 1.881(5), W1–Pt 2.6964(3), C1–Pt 2.031(5), Pt–C3 2.252(5), W1–C1–C2 152.2(4), C1–C2–W2 175.7(4), W1–C1–Pt 84.42(18), W1–C3–O1 162.8(4).

the η^4-diene ligands could be displaced by a monodentate ligand, the proposed bidentate association might endure. Thus, CO was bubbled through a CH_2Cl_2 solution of **2** or **3**, causing the initially dark red solutions to turn deep purple with formation of the expected product, $[W_2\{\mu\text{-}C_2Pt(CO)\}(CO)_4(Tp^*)_2]$ (**4**) (Scheme 2), which was isolated as a dark purple solid following chromatographic purification. This reaction is not limited to CO and treatment of **2** or **3** with CN^{t}Bu or CNMes (Mes = mesityl, $C_6H_2Me_3$-2,4,6) furnishes the dark purple isocyanide derivatives $[W_2\{\mu\text{-}C_2Pt(CNR)\}(CO)_4(Tp^*)_2]$ (R = ^{t}Bu **5**; R = Mes **6**).

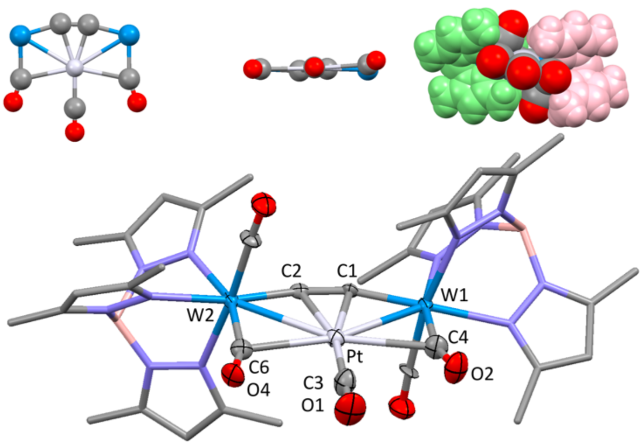

Figure 2. Molecular structure of **4** in a crystal of **4**.CH_2Cl_2 (50% displacement ellipsoids, hydrogen atoms and solvent omitted, pyrazolyl rings simplified). Insets = Views orthogonal to the platinum coordination plane, along the C3-O1 axis and space-filling representation. Selected bond lengths (Å) and angles (°): W2–Pt 2.9446(5), W1–Pt 2.9519(5), W2–C2 1.956(8), Pt–C1 2.113(7), Pt–C2 2.157(8), C1–C2 1.297(12), Pt–C6 2.559(9), Pt–C4 2.592(10), Pt–C3 1.887(11), C2–C1–W1 165.9(6), C1–C2–W2 161.0(7).

NMR data for **4** confirm a symmetrical structure with both the sharp ^{1}H and ^{13}C{^{1}H} NMR spectra indicating that the two 'W(CO)$_2$(Tp*)' termini are chemically equivalent. The μ-C nuclei resonate at 237.4, 241.7 and 240.7 ppm in **4**–**6**, respectively, moved to higher frequency from those for **2** and **3** (*ca* 300 ppm). There is also an up-field shift of *ca* 500 ppm in the ^{195}Pt NMR spectra of **4**–**6** (–4724, –4484 and –4443 ppm, respectively) compared to the precursors. The crystal structure determinations of **4** (ESI) and **4**·CH_2Cl_2 (Figure 2) confirm the symmetric molecular geometry inferred from spectroscopic data (for *C*2/c-**4** the Pt–C–O lies along a C_2 axis such that only half the molecule is crystallographically unique). The tungsten-carbon bond distance in **4** (W1–C1 1.919(8) Å) is comparable to those observed for bridging carbynes in **2**, **3** and related binuclear W(μ-C)Pt complexes.[9] The W–Pt (2.9519(5), 2.9446(5) Å) and Pt–C (2.113(7), 2.157(8) Å) distances are, however, much longer (*ca* 0.25 and 0.1 Å, respectively) than the corresponding distances in **3** and other related tungstaplatinacyclopropenes, which are invariably supported by semi-bridging CO ligands. These observations most likely result from a combination of the steric constraints imposed by accommodating the bulky Tp* ligands and the WCCW deformation required for bidentate coordination to Pt.

Although the coordination in **4** is without precedent, in isolobal terms (methyne and W(CO)$_2$(Tp*) are isolobes) some analogy might be entertained with Rosenthal's series of group 4 metallocene butadiyne adducts[11] in which the C_4 spine is severely distorted to allow all four carbons to coordinate in an η^4-manner. Indeed, Rosenthal has previously proposed that complexes such as **4** might be viable,[11f] in addition to demonstrating fluxionality between η^4 and η^2-1,3-diyne coordination modes[11g] that would be, in isolobal terms, directly analogous to the shimmy process discussed above for **2** and **3**. In this respect it is noteworthy that the W1–C1–C2 angle (165.9(6)° in **4** is less contracted than those found for the internal carbon atoms of η^4-diyne complexes (145.9 – 153.5°). That said, this analogy calls for an additional d^8-Pt(II) canonical form (**B**, Scheme 3) to be considered. Given the near linear WCO angles at C4 and C6 as well as the long Pt···C4 and Pt···C6 bond lengths, we are inclined to view these as conventional WPt semi-bridging carbonyls rather than as integral components of a seven-membered PtW_2 metallacycle.

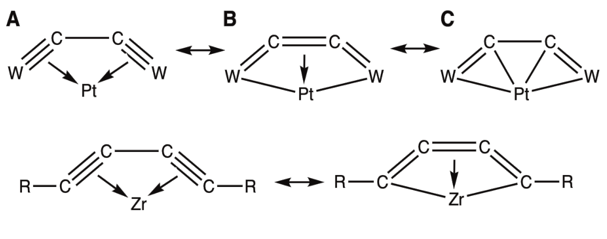

Chart 2. Canonical forms to describe **4** and an (isolobal) analogy with η^4-butadiyne coordination.

We have explored similar experiments using [$PtCl_2(PR_3)_2$] (R = Me (*cis*), Ph (*cis*), Cy (*trans*)) and in each case a complex mixture of products arises, amongst which the platinum-free species **7** eventually predominates. This process is also implicit in our catalytic formation of (free) **7** *via* reductive elimination from the putative palladium bis(carbido) [W_2Pd(μ-C)$_2$(CO)$_4$(Tp*)$_2$(PPh_3)$_n$] (n = 1,2, *vide infra*). Furthermore, careful addition of 1-2 equivalents of PPh_3 to isolated **2** or **3** results in elimination of the platinum to also afford **7**. We therefore conclude that phosphines (L) are incompatible with coordination of 'PtL$_n$' (n = 1, 2) to the W≡C-C≡W spine, perhaps (but not definitively) due to steric issues.

The shimmying of platinum between WC units appears to be a specific feature of the ditungstabutadiyne in that such a process does not occur for a ditungstaoctatetrayne [W_2(μ-C_6)(CO)$_4$(Tp*)$_2$]. Upon treatment with [Pt(nbe)$_3$]/COD, an inseparable mixture of adducts arises with either one or two 'Pt(COD)' appendages which do not, however, migrate between W≡C termini. Addition of [Pt(η-C_2H_4)(PPh_3)$_2$] to the same tetrayne results in coordination of one 'Pt(PPh_3)$_2$' unit to one C≡C bond.[12] These results further substantiate the need for simultaneous platinum coordination to both W≡C units (as in **4**) to account for its mobility in **2** and **3**.

The compounds **4**–**6** are reasonably stable in the solid state but in solution loss of the PtL' fragment occurs within hours at room temperature to give the 'free' ethanediylidyne, [W_2(μ-C_2)(CO)$_4$(Tp*)$_2$] (**7**, Scheme 1). This pale purple solid has surprisingly low solubility in all common solvents and is only very sparingly soluble in CH_2Cl_2 and $CHCl_3$. This aids in its isolation but has also precluded acquisition of satisfactory ^{13}C NMR data. A simpler and more reliable synthesis of **7** involves treatment of **1** with *half an equivalent* of ^{n}BuLi (see ESI) in the presence of a catalytic amount of [Pd(PPh_3)$_4$], a reaction with direct parallels to traditional alkyne couplings. The characterisation of **7** included a crystallographic analysis (ESI), the geometric parameters of which conform to the (crystallographically centrosymmetric) dimetallabutadiyne description (W–C1 = 1.864(5), C1–C1' = 1.377(11)Å). Although the W1–C1–C1'–W1' spine is somewhat deformed (W1–C1–C1' = 168.2(6)Å, this has no significance beyond reflecting intra-ligand steric congestion.

Further support for the bis(carbyne) description of **7** is provided by its reaction with excess [AuCl(THT)] (THT = tetrahydrothiophene). This species delivers the AuCl fragment which has a demonstrated proclivity for bridging alkylidyne bonds.[13] The resulting orange product, [W_2(μ-$C_2Au_2Cl_2$)(CO)$_4$(Tp*)$_2$] (**8**), contains two AuCl fragments transversely added across both W≡C bonds and, being much more soluble than **7**, is more amenable to complete spectral and structural characterization (Figure 3 and ESI). The few known tetra-metallated dicarbido assemblies all adhere to ethyn-di-yl[14] or ethen-tetra-yl[15] bonding descriptions that retain a degree of C–C multiple bonding. The exception, [Fe_2Ru_2(μ_4-C_2)(CO)$_8$(μ-PhCCPh)(Cp*)$_2$][16] may be described as involving Ru=C and Ru=Ru multiple bonding within a Ru_2C_2 trapezoidal dimetallacyclobutatriene with minimal C–C double bond character ($r_{C\text{-}C}$ = 1.313 Å). The crystallographically centrosymmetric molecular structure of **8** in **8**.CH_2Cl_2 has the two dimetallacyclopropene units coplanar such that some conjugation between the WAuC rings is plausible but not reflected in the long C1–C1' bond length (1.398(16)Å). Notably, rotation about this bond would allow the development of an aurophilic interaction[8c] which is however not observed (*vide infra*).

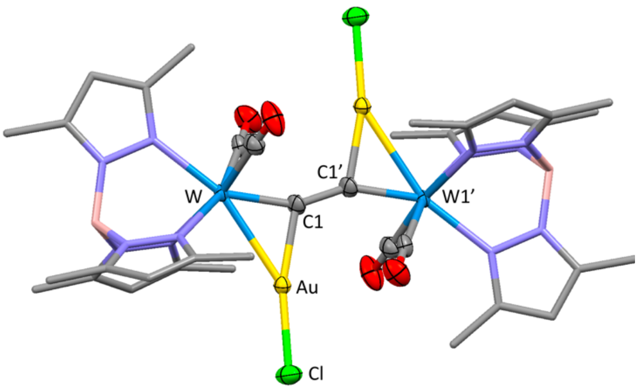

Figure 3. Molecular structure of **8** in a crystal of **8**.CH_2Cl_2 (50% displacement ellipsoids, hydrogen atoms omitted, pyrazolyl rings simplified). Selected bond lengths (Å) and angles (°): C1–C1' 1.398(16), C1–W 1.912(9), C1–Au 2.070(9), C1'–C1–W 152.7(10), C1'–C1–Au 118.9(9).

Finally, although only isolated in sufficient amounts for crystallographic characterisation, we note that a further tetrametallic dicarbido coordination mode is adopted in the decomposition product of **6**, *viz* the complex [W_2(μ-C_2Pt_2(CNMes)$_3$}(CO)$_4$(Tp*)$_2$] (**9**, Figure 4) in which two isonitrile ligated platinum atoms add to the WCCW unit is a *cisoid* manner (*cf. transoid* **8**) supported by a direct, isonitrile-bridged Pt–Pt bond (2.9250(8) Å). This is the same and demonstrably viable geometry that would be required for an aurophilic interaction in **8** discussed above.

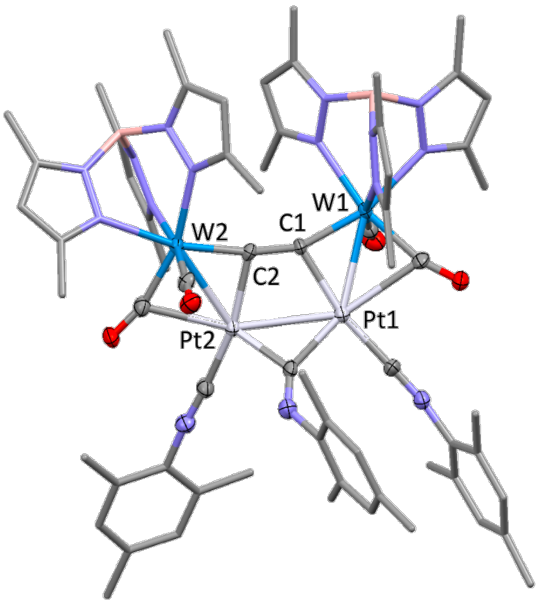

Figure 4. Molecular structure of **9** in a crystal of **9**.CH_2Cl_2 (50% displacement ellipsoids, hydrogen atoms omitted, pyrazolyl and mesityl rings simplified). Selected bond lengths (Å) and angles (deg.): Pt2–W2 2.7965(9), Pt2–Pt1 2.9250(8), Pt2–C2 2.119(5), W2–C2 1.966(5), W1–Pt1 2.8052(8), W1–C1 1.984(4), Pt1–C1 2.100(5), W2–Pt2–Pt1 112.88(2), C1–C2–W2 166.9(4), C2–C1–W1 157.1(4).

In conclusion, a study to explore the relationship between bis(carbido) complexes and their evolution into dimetallabutadiynes has uncovered seven examples of this W_2C_2 unit bound to extraneous metal centers in four unprecedented coordination modes. Factors to arrest bis(carbido) reductive coupling were not yet identified, however post-coupling elimination was sufficiently retarded to provide an intriguing glimpse of unusual coordination modes available to the dimetallabutadiyne unit.

Acknowledgements

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Keywords: Carbido • bis(carbyne) • Dicarbido • Polymetallic • Carbyne

[1] M. I. Bruce, P. J. Low, *Adv. Organomet. Chem.* **2004**, *50*, 179-444.

[2] (a) R. E. LaPointe, P. T. Wolczanski, J. F. Mitchell, *J. Am. Chem. Soc.* **1986**, *108*, 6382-6384; (b) D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne, P. T. Wolczanski, *J. Am. Chem. Soc.* **1989**, *111*, 9056-9072; (c) P. Binger, P. Müller, P. Philipps, B. Gabor, R. Mynott, A. T. Herrmann, F. Langhauser, C. Krüger, *Chem. Ber.* **1992**, *125*, 2209-2212; (d) S. Kheradmandan, K. Venkatesan, O. Blacque, H. W. Schmalle, H. Berke, *Chem., Eur. J.* **2004**, *10*, 4872-4885; (e) V. A. Williams, D. R. Manke, P. T. Wolczanski, T. R. Cundari, *Inorg. Chim. Acta* **2011**, *369*, 203-214.

[3] (a) M. L. Listemann, R. R. Schrock, *Organometallics* **1985**, *4*, 74-83; (b) R. J. Blau, M. H. Chisholm, K. Folting, R. J. Wang, *J. Am. Chem. Soc.* **1987**, *109*, 4552-4560; (c) T. M. Gilbert, R. D. Rogers, *J. Organomet. Chem.* **1991**, *421*, C1-C5; (d) K. G. Caulton, R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. B. Lobkovsky, Z. Xue, *Organometallics* **1992**, *11*, 321-326; (e) B. E. Woodworth, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1998**, *120*, 9028-9033; (f) A. L. Colebatch, R. L. Cordiner, A. F. Hill, K. T. H. D. Nguyen, R. Shang, A. C. Willis, *Organometallics* **2009**, *28*, 4394-4399; (g) J. Sun, S. E. Shaner, M. K. Jones, D. C. O'Hanlon, J. S. Mugridge, M. D. Hopkins, *Inorg. Chem.* **2010**, *49*, 1687-1698.

[4] (a) B. E. Woodworth, J. L. Templeton, *J. Am. Chem. Soc.* **1996**, *118*, 7418-7419; (b) B. E. Woodworth, P. White, J. L. Templeton, *J. Am. Chem. Soc.* **1997**, *119*, 828-829; (c) A. E. Enriquez, J. L. Templeton, *Organometallics* **2002**, *21*, 852-863.

[5] (a) A. Reinholdt, J. Bendix, A. F. Hill, R. A. Manzano, *Dalton Trans.*, **2018**, *47*, 14893-14896; (b) A. Reinholdt, J. E. Vibenholt, T. J. Morsing, M. Schau-Magnussen, N. E. A. Reeler, J. Bendix, *Chem. Sci.* **2015**, *6*, 5815-5823; (c) E. S. Borren, A. F. Hill, R. Shang, M. Sharma, A. C. Willis, *J. Am. Chem. Soc.* **2013**, *135*, 4942-4945.

[6] (a) C. Glaser, *Liebigs Ann. Chem.* **1870**, *154*, 137-171; (b) M. Heravi, M. Ghanbarian, N. Ghalavand, N. Nazari, *Curr. Org. Chem.* **2018**, *22*, 1420-1457.

[7] (a) M. I. Bruce, M. L. Cole, M. Gaudio, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2006**, *691*, 4601-4614; (b) D. J. Armitt, M. I. Bruce, M. Gaudio, N. N. Zaitseva, B. W. Skelton, A. H. White, B. Le Guennic,

J.-F. Halet, M. A. Fox, R. L. Roberts, F. Hartl, P. J. Low, *Dalton Trans.* **2008**, 6763-6775. (c) R. L. Cordiner, A. F. Hill, J. Wagler, *Organometallics* **2008**, *27*, 5177-5179; (d) R. L. Cordiner, P. A. Gugger, A. F. Hill, J. Wager, *Organometallics* **2009**, *28*, 6632-6635; (e) A. L. Colebatch, A. F. Hill, *J. Am. Chem. Soc.* **2014**, *136*, 17442-17445.

[8] (a) A. F. Hill, M. Sharma, A. C. Willis, *Organometallics* **2012**, *31*, 2538-2542; (b) W. Knauer, W. Beck, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2241-2245.

[9] (a) T. V. Ashworth, J. A. K. Howard, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.* **1979**, 42-43; (b) J. C. Jeffery, D. B. Lewis, G. E. Lewis, M. J. Parrott, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1986**, 1717-1722; (c) D. D. Devore, J. A. K. Howard, J. C. Jeffery, M. U. Pilotti, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1989**, 303-311; (d) N. Carr, M. C. Gimeno, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1990**, 2617-2624; (e) The W(μ_2-CR)Pt unit also appears in a significant number of tri- and polymetallic bridging carbyne complexes.

[10] L. M. Caldwell, *Adv. Organomet. Chem.* **2008**, *56*, 1-94.

[11] (a) P.-M. Pellny, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannerberg, U. Rosenthal, *J. Am. Chem. Soc.* **2000**, *122*, 6317-6318; (b) P.-M. Pellny, F. G. Kirchbauer, V. V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, *J. Am. Chem. Soc.* **1999**, *121*, 8313-8323; (c) M.-P. Pellny, F. G. Kirchbauer, V. V. Burlakov, W. Baumann, A. Spannenberg, U. Rosenthal, *Chem., Eur. J.* **2000**, *6*, 81-90; (d) U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V. V. Burlakov, *Angew. Chem., Int. Ed.* **1994**, *33*, 1605-1607; (e) K. Kaleta, A. Hildebrandt, F. Strehler, P. Arndt, H. Jiao, A. Spannenberg, H. Lang, U. Rosenthal, *Angew. Chem., Int. Ed.* **2011**, *50*, 11248-11252. (f) U. Rosenthal, *Angew. Chem., Int. Ed.* **2003**, *42*, 1794-1798. (g) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics*, **2005**, *24*, 456-471.

[12] R. D. Dewhurst, A. F. Hill, A. C. Willis, Organometallics, 2009, 28, 4735-4740.

[13] G. R. Clark, C. M. Cochrane, K. Marsden, W. R. Roper, L. J. Wright, *J. Organomet. Chem.***1986**, *315*, 211-230; (b) G. R. Clark, C. M. Cochrane, W. R. Roper, L. J. Wright *J. Organomet. Chem.* **1980**, *199*, C35-C38; (c) A. L. Colebatch, A. F. Hill, *Dalton Trans.,* **2017**, *46*, 4355-4365; (d) C. E. Strasser, S. Cronje, H. G. Raubenheimer, *New J. Chem.,* **2010**, *34*, 458-469.

[14] R. O. Fuller, C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *Organometallics* **2015**, *34*, 2632-2646; (b) D. Miguel, M. Moreno, J. Perez, V. Riera, D. G. Churchill, M. R. Churchill, M. R.; T. S. Janik *J. Am. Chem. Soc.* **1998**, *120*, 417-418.

[15] G. Higashihara, M. Terada, A. Inagaki, M. Akita, *Organometallics* **2007**, *26*, 439-444; (b) C. S. Griffith, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2005**, *690*, 3410-3421; (c) L. T. Byrne, J. P. Hos, G. A. Koutsantonis, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *598*, 28-35; (d) T. Yamaguchi, T. Koike, M. Akita, *Organometallics* **2010**, *29*, 6493-6502; (e) M. Akita, S. Sugimoto, M. Tanaka, Y. Moro-oka, *J. Am. Chem. Soc.* **1992**, *114*, 7581-7582; (f) M. Terada, M. Akita, *Organometallics* **2003**, *22*, 355-364.

[16] M. Terada, G. Higashihara, A. Inagaki, M. Akita, *Chem. Commun.* **2003**, 2984-2985.