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High oxidation state bromocarbyne complexes†

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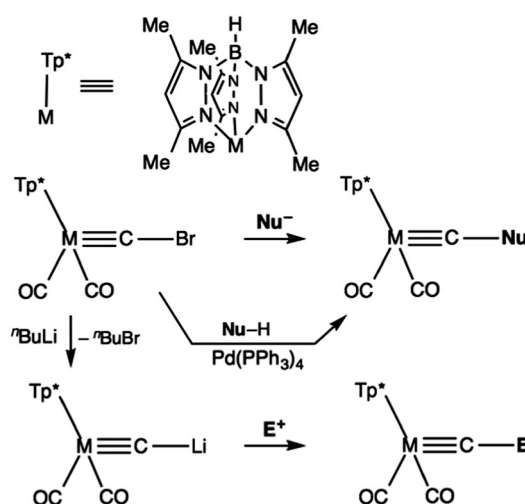
Bromination of the carbyne complexes $[W(\equiv CR)Br(CO)_2(dcpe)]$ ($R = Ph, SiPh_3$; $dcpe = 1,2$ -bis(dicyclohexylphosphino)ethane) provides high oxidation state derivatives $[W(\equiv CPh)Br_3(dcpe)]$ and $[W(\equiv CBr)Br_3(dcpe)]$, the latter *via* an unprecedented bromodesilylation process.

In 1983 Lalor reported the first halocarbyne complexes $[M(\equiv CX)(CO)_2(Tp^*)]$ ($M = Mo, W$; $X = Cl, Br$; $Tp^* =$ hydrotris(dimethylpyrazolyl)borate).¹ In the interim these have been proven to be remarkably versatile building blocks for the construction of elaborate and otherwise inaccessible carbyne derivatives *via* either nucleophilic substitution (spontaneous or Pd^0 -mediated)² or alternatively, lithium-halogen exchange to afford nucleophilic lithiocarbynes $[M(\equiv CLi)(CO)_2(Tp^*)]$ (Scheme 1).³ Such protocols are however denied wider generality in that some 33 years later Lalor's complexes still remain the only known halocarbynes with the exception of Hughes' fluorocarbynes $[M(\equiv CF)(CO)_2(L)]$ ($M = Cr, Mo, W$; $L = \eta\text{-C}_5\text{R}_5$, $R = H, Me$)⁴ for which no subsequent reactivity has been reported. Extension of Lalor's synthetic approach involving the reaction of the carbonylates $[M(CO)_3(Tp^*)]^-$ with diazonium salts in haloform solvents, to any other ligand sets or metals has not met with success despite considerable effort.^{1b} We have therefore considered alternative approaches to the synthesis of $M \equiv C_1(\pm)$ synthons so as to broaden the applicability of the methodologies outlined in Scheme 1. In this pursuit, we have recently shown that fluoride-mediated protodesilylation of the silylcarbyne complex $[W(\equiv CSiPh_3)Br(CO)_2(dcpe)]$ [$(1a, \ddagger dcpe) = 1,2$ -bis(dicyclohexylphosphino)ethane] affords a rare example of a remarkably stable 'parent' methylidyne complex $[W(\equiv CH)Br(CO)_2(dcpe)]$ (**1b**, Scheme 2).⁵

Roper first showed that it was possible to oxidise carbyne complexes without compromising the metal-carbon triple

bond⁵ and this was further developed by Mayr who demonstrated the bromination of Fischer's carbyne $[W(\equiv CPh)Br(CO)_4]$ in dimethoxyethane (dme) to afford the Schrock-type carbyne $[W(\equiv CPh)Br_3(dme)]$.⁶ We have therefore explored the possibility of preparing a high-oxidation state silylcarbyne *fac*- $[W(\equiv CSiPh_3)Br_3(dcpe)]$ (**2a**) by bromination of **1a**.

Prior to the pursuit of **2a**, we first validated the approach by brominating the new but more conventional benzylidyne complex $[W(\equiv CPh)Br(CO)_2(dcpe)]$ (**1c**, Scheme 2), obtained by a classical Fischer-Mayr oxide abstraction route.⁷ Thus treating $W(CO)_6$ sequentially with phenyl lithium, oxalyl bromide, 4-picoline and $dcpe$ provides **1c** (see Fig. 1 and ESI† for characterisation data). Treating **1c** with bromine at low temperature results in the formation of the high-valent tungsten benzylidyne complex *fac*- $[W(\equiv CPh)Br_3(dcpe)]$ (**2c**, 98%, Fig. 2). The ¹³C resonance for the benzylidyne appears at $\delta_C = 309.7$ ($^2J_{CP} = 13.4$ Hz), moved some 46 ppm to lower frequency from that for **1c** ($\delta_C = 263.7$, $^2J_{CP} = 9.3$ Hz). The ³¹P resonance at 53.1 ppm shows satellite



Scheme 1 Umpolung of bromocarbyne reactivity (Nu = nucleophile, E = electrophile, M = Mo, W).

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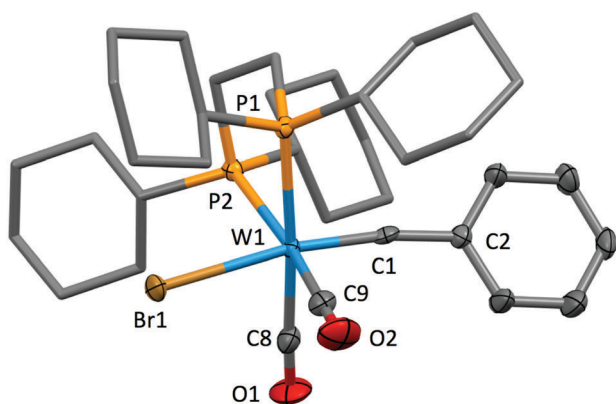
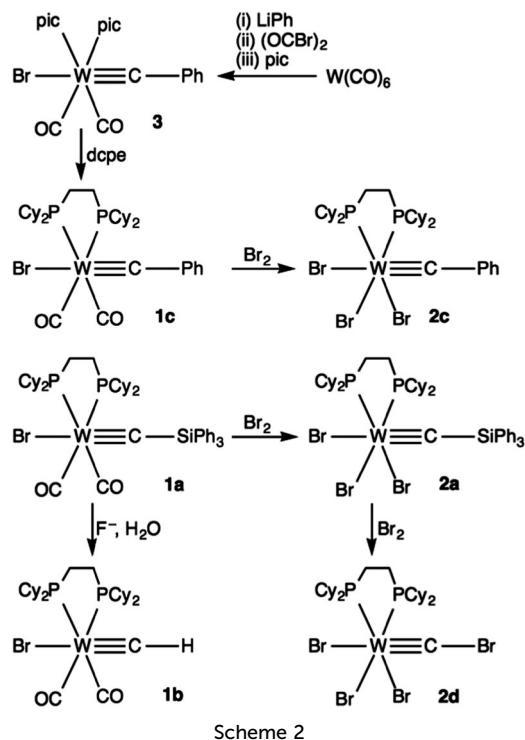


Fig. 1 Molecular structure of **1c** in a crystal (60% displacement ellipsoids, H-atoms, cyclohexyl groups simplified). Selected bond lengths (Å) and angles (°): W1–P1 2.5318(6), W1–P2 2.5407(6), W1–Br 2.6929(3), W1–C1 1.821(3), P1–W1–P2 80.38(2), C1–W1–P1 93.97(8), C1–W1–P2 97.55(8), C1–W1–Br1 171.46(8), C2–C1–W1 171.6(2).

resonances arising from coupling to ^{183}W ($^1J_{\text{WP}} = 212$ Hz) which is comparable in magnitude to that observed for **1c** (225 Hz).

With the oxidative dibromination of **1c** to provide **2c** having proceeded without issue, the corresponding reaction with **1a** was explored. Addition of bromine to a solution of **1a** at -78°C followed by slow warming to room temperature resulted in the formation of a khaki complex, the yield of which is optimised by employing two equivalents of Br_2 . The product was formulated on the basis of spectroscopic (see ESI[†]) and structural data (Fig. 3) as the bromocarbene complex $[\text{W}(\equiv\text{CBr})\text{Br}_3(\text{dcpe})]$ (**2d**) resulting from both oxidation of the metal centre and electrophilic bromodesilylation of the silylcarbene ligand (Scheme 2).

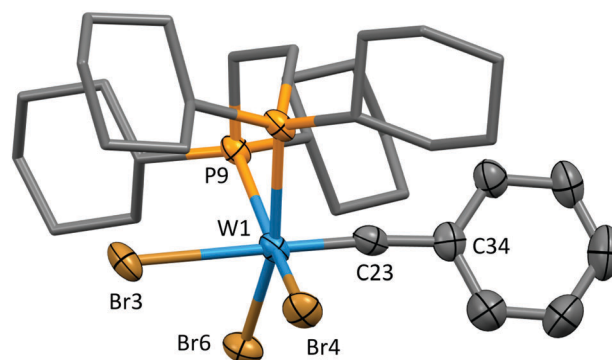


Fig. 2 Molecular structure of **2c** in a crystal (60% displacement ellipsoids, H-atoms and solvent omitted, cyclohexyl groups simplified, one of two crystallographically independent molecules shown). Selected bond lengths (Å) and angles (°): W1–Br3 2.7549(5), W1–Br4 2.4914(5), W1–Br6 2.4782(5), W1–P9 2.5786(11), W1–C23 1.789(5), C34–C23–W1 174.2(4).

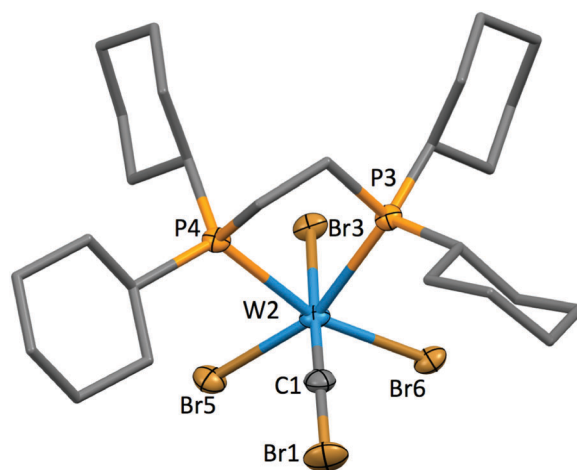


Fig. 3 Molecular structure of **2d** in a crystal of **2d**· CH_2Cl_2 (60% displacement ellipsoids, H-atoms and solvent omitted, cyclohexyl groups simplified, one of two crystallographically independent molecules shown). Selected bond lengths (Å) and angles (°): W2–Br3 2.6918(6), W2–Br5 2.5016(7), W2–Br6 2.4800(7), W2–P3 2.5862(16), W2–P4 2.5734(16), W2–C1 1.793(6), Br1–C1 1.822(6), P4–W2–P3 76.35(5), W2–C1–Br1 171.5(4).

The key spectroscopic datum of interest is the triplet ^{13}C resonance observed at $\delta_{\text{C}} = 229.0$ which shows coupling ($^2J_{\text{CP}} = 16.4$ Hz) approximately twice the magnitude of those found for lower valent dcpe tungsten carbene complexes. Within the low-valent regime, complexes of the form $[\text{M}(\equiv\text{CR})(\text{CO})_2(\text{L})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{HB}(\text{pzR}_2-3,5)_3$, $\text{R} = \text{H}, \text{Me}$)⁸ provide the most extensive range of comparative spectroscopic data. Of these, the bromocarbene complexes have characteristically high frequency resonances (e.g., $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$: $\delta_{\text{C}} = 198.0$ M = W; 202.5 M = Mo), exceeded only by the iodocarbene $[\text{W}(\equiv\text{CI})(\text{CO})_2(\text{Tp}^*)]$ ($\delta_{\text{C}} = 183.2$).⁹ Thus the ca. 81 ppm shift to high frequency of the carbene resonance for **2d** relative to **2c** is to be expected. The infrared spectrum included a comparatively strong absorption at 1260 cm^{-1} which on the basis of simulation (DFT: M06-LACVP) for the simpler model $[\text{W}(\equiv\text{CBr})\text{Br}_3(\text{dmpe})]$ ($\nu_{\text{WC}} = 1203\text{ cm}^{-1}$) we assign to the primarily ν_{WC} mode. No such



'pure' mode could be identified for the corresponding benzylidyne complex due to extensive coupling with phenyl ring modes. Infrared data for carbyne ligands are somewhat sparse in the literature and this may be traced, with good reason, to a number of factors. Firstly, they appear in the fingerprint region amongst co-ligand absorptions. The polarity of $M\equiv C$ bonds (and thus changes in dipole moments associated with IR intensities) can vary dramatically, hence the Fischer-Schrock dichotomy. Finally, and most importantly, in contrast to metal oxo and nitride ligands, for which IR data are invaluable and unambiguous, the $M\equiv C$ oscillator is invariably coupled to modes due to the substituent, a phenomenon that has been discussed in detail by Dao *et al.*¹⁰ These factors taken together mean that the value of ν_{MC} covers a wide range of both frequency and intensity such that reliable assignments are best made with recourse to simulation.

The molecular geometry of **2d** (Fig. 3) involves pseudo-octahedral tungsten with a typically short W2–C1 bond length of 1.793(6) Å that is not however significantly different (1 e.s.d.) to that found in **2c**. Carbyne ligands typically exert a significant *trans* influence and this is reflected in the W2–Br3 bond length (2.6918(6) Å) being significantly longer than those *trans* to phosphorus (2.5016(7), 2.4800(7) Å), but less elongated relative to the corresponding bromide in **2c** (126 e.s.d.), suggesting that the bromocarbyne ligand, for which no previous structural data are available, has a pronounced *trans* influence, though less than that for more conventional alkylidynes. The C1–Br1 bond length of 1.822(6) Å is somewhat longer than any previously reported C(sp)–Br bonds which span the range 1.77–1.80 Å. The acute dcpe bite angle of 76.35(5)° allows the *cis*-bromo ligands to adopt a significantly obtuse angle (109.35(2)°).

The availability of both **2c** and **2d** provides an opportunity to compare these disparate carbyne substituents. Computational interrogation of the models $[W(\equiv CR)Br_3(dmpe)]$ ($R = Ph, Br$, DFT: MO6 LACVP) indicates that replacing the phenyl substituent in **2c** with a bromide in **2d** results in an increase in the negative (natural atomic) charge on the carbyne carbon (–0.29 to –0.51). The positive charge on tungsten is essentially unchanged for the benzylidyne (+0.75) and bromocarbyne (+0.78) models.

The stepwise mechanism by which **1a** is converted to **2d** would appear to involve initial oxidative decarbonylation of the tungsten followed by slower bromo-desilylation of the silylcarbyne. We assert this sequence based on the following observations. (i) CO evolution is immediately observed at low temperature; (ii) bromination of $[W(\equiv CPh)Br(CO)_2(dcpe)]$ (**1c**) cleanly affords the benzylidyne complex $[W(\equiv CPh)Br_3(dcpe)]$ (**2c**). As to the intimate mechanism for C–Si bond cleavage, in an isolobal context Isobe provided the protocol of choice for the electrophilic bromination of alkynylsilanes by *N*-bromosuccinimide to afford alkynyl bromides,¹¹ however a silver co-catalyst ($AgNO_3$, AgF) is required, implicating silver alkynyl intermediates. In the conversion of **1a** to **2d** however direct attack by Br_2 presumably affords transient $[W(\equiv CBrSiPh_3)Br_3(dcpe)]Br$ with subsequent attack at silicon by bromide. Electrophilic *C*-halogenation of carbyne ligands has been described previously, but only in one instance (chlorination of $[Os(\equiv CR)Cl(CO)(PPh_3)_2]$ to afford $[Os(\equiv CClR)Cl_2(CO)(PPh_3)_2]$, $R = C_6H_4Me-4$)¹² and whilst

bromocarbyne complexes^{13,14} are rare and highly reactive due to the exceptional halide nucleofugacity, the complex $[Re_2(\equiv CBrSiPh_3)(CO)_9]^{15}$ provides limited precedent.

In conclusion, a considerable number of silylcarbyne complexes are available *via* classical Fischer alkoxide/oxide abstraction,^{5,15,16} Schrock α -hydrogen elimination/abstraction¹⁷ or alkynylsilane metathesis¹⁸ protocols. The demonstration that halodesilylation may be achieved without rupture of the metal-carbon multiple bond augurs well for the elaboration of further synthetically valuable halocarbyne complexes to open the 33 year hiatus in their wider exploration.

Notes and references

‡ Hereafter in compound numbers **a** = $SiPh_3$, **b** = H, **c** = Ph, **d** = Br.

§ Throughout, we employ the $[CR]^{3-}$ formalism for electron counting and the assignment of oxidation states and associated d-configurations. This is an arbitrary distinction in such highly covalent compounds and the alternative $[CR]^+$ formalism also has advocates.

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