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An anionic nucleophilic d⁴ carbyne complex†

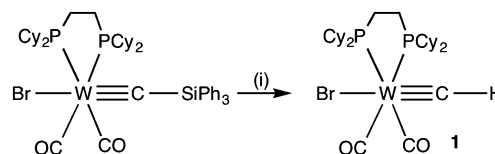
Anthony F. Hill* and Richard Y. Kong

The reaction of the methylidyne complex $[W(\equiv CH)Br(CO)_2(dcpe)]$ ($dcpe$ = 1,2-bis(dicyclohexylphosphino)ethane) with $tBuLi$ affords the intermediate anionic neopentylidyne complex $Li[W(\equiv C^tBu)(CO)_2(dcpe)]$ which acts as a metal-based nucleophile towards $tBuCl$, $tBuBr$, Ph_2E_2 (E = S, Se, Te) and $ClSnMe_3$ to afford the new carbyne complexes $[W(\equiv C^tBu)(X)(CO)_2(dcpe)]$ (X = Cl, Br, Eph, $SnMe_3$).

Anionic carbyne complexes remain rare, being limited to Schrock's archetypal $[MeN(C_2H_4)_2NMe-Li][Ta(\equiv C^tBu)(CH_2^tBu)_3]$ (**1**),¹ those of the form $[M(\equiv CR)X_4]^-$ (M = Mo, W; X = halide, siloxide, alkoxide)² in which the coordinatively unsaturated d⁰-metal³ is electrophilic and Stone's d²-carbaborane complexes $[M(\equiv CR)(CO)_2(L)]^-$ (L = $\eta^5-C_2B_9H_9R_2'$, $\eta^6-C_2B_{10}R_2'$, $R' = H, Me$)⁴ in which, whilst much of the negative charge resides in the carbaborane, the metal displays a modest degree of nucleophilicity.

A second rare class of carbyne complexes are those in which the metal has a higher d⁴ occupancy, employing the $[CR]^{3-}$ formalism,³ which are however limited to late transition metals from groups 8 and 9.⁵ We report herein the unexpected formation of an anionic d⁴-early transition metal carbyne complex that serves as a metal-based nucleophile to a wide range of electrophiles.

We have reported extensively on the synthetic utility of the lithiocarbyne complexes $[M(\equiv CLi)(CO)_2(Tp^*)]$ (M = Mo, W; Tp^* = hydrotris(dimethylpyrazolyl)borate)⁶ which are conveniently available *via* simple lithium/halogen exchange upon treating Lalor's halocarbynes $[M(\equiv CX)(CO)_2(Tp^*)]$ ⁷ with $BuLi$ and which serve as carbon-centred nucleophiles. This allows the construction of a plethora of unusual carbyne complexes that are not available *via* more conventional protocols. The tungsten derivative had however been previously reported by Templeton to arise from deprotonation of the thermally labile parent methylidyne $[W(\equiv CH)(CO)_2(Tp^*)]$ (estimated pK_a = 28.7 in THF)⁸ and



Scheme 1 (i) $[tBu_4N]F$, H_2O , $-[tBu_4N][SiF_6Ph_3]$.¹⁰

Cummins has separately reported the deprotonation of his methylidyne complex $[Mo(\equiv CH)\{N^tBuC_6H_3Me_2\}_3]$ (estimated pK_a = 30 in THF).⁹ In both cases pK_a estimates were not dissimilar to those for notionally isolobal terminal alkynes (e.g., $PhC\equiv CH$: pK_a = 28.8 in dmsO). Accordingly, with the recent report of the thermally stable methylidyne complex $[W(\equiv CH)Br(CO)_2(dcpe)]$ (**1**: $dcpe$ = 1,2-bis(dicyclohexylphosphino)ethane, Scheme 1)¹⁰ we naturally considered exploring its deprotonation as a means of generating an anionic carbido complex $[W(\equiv C)Br(CO)_2(dcpe)]^-$. Indeed the intermediacy of such a species is implicit in the formation of **1** from $[W(\equiv CSiPh_3)Br(CO)_2(dcpe)]$ *via* fluoride mediated protodesilylation with $[tBu_4N]F$ (Scheme 1).

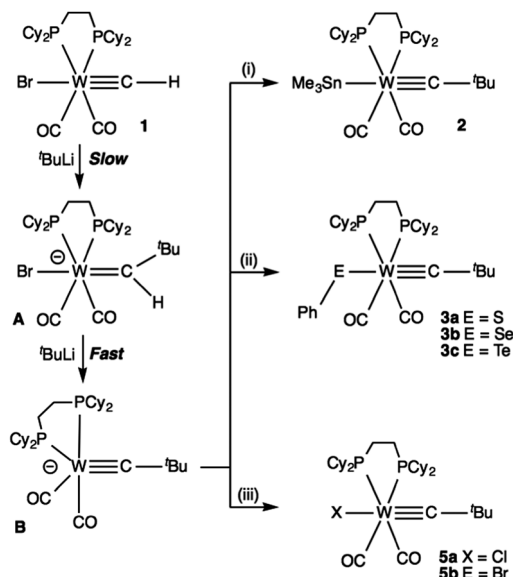
Treating **1** with a range of bases ($tBuLi$, $PhLi$, $KH/18$ -crown-6, LiN^tPr_2) and 'super-bases' (e.g., $tBuLi/HOC_2H_4NMe_2$) led to disappointing and inconclusive results. Indeed, the only base we could identify that reacted cleanly with **1** was $tBuLi$ and in excess of two equivalents were required. Electrophilic quench of the resulting species with Me_3SnCl led to clean formation of a new complex that was not the anticipated stannyl carbyne $[W(\equiv CSnMe_3)Br(CO)_2(dcpe)]$ ¹¹ but rather the neopentylidyne complex $[W(\equiv C^tBu)(SnMe_3)(CO)_2(dcpe)]$ (**2**, Scheme 2). Complex **2** was characterised on the basis of structural (see Fig. 1 and ESI†) and spectroscopic (see ESI†) data, the most informative being the triplet ($^2J_{PC}$ = 7.5 Hz) carbyne resonance observed at δ_C = 316.3 that correlates (HMBC) with the *tert*-butyl resonance observed in the 1H NMR spectrum at δ_H = 1.30. The single resonance observed at δ_P = 51.7 in the $^{31}P\{^1H\}$ NMR spectrum was straddled by satellites due to coupling to ^{183}W (220), ^{119}Sn (151) and ^{117}Sn (145 Hz) nuclei.

Research School of Chemistry, Australian National University, Canberra,

Australian Capital Territory, ACT 2601, Australia. E-mail: a.hill@anu.edu.au

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Scheme 2 (i) Me_3SnLi ; (ii) PhEPh , $\text{E} = \text{S}, \text{Se}, \text{Te}$; (iii) $t\text{BuX}$, $\text{X} = \text{Cl}, \text{Br}$. All reactions carried out in THF at -78°C with warming to room temperature after addition of electrophiles (i)–(iii).

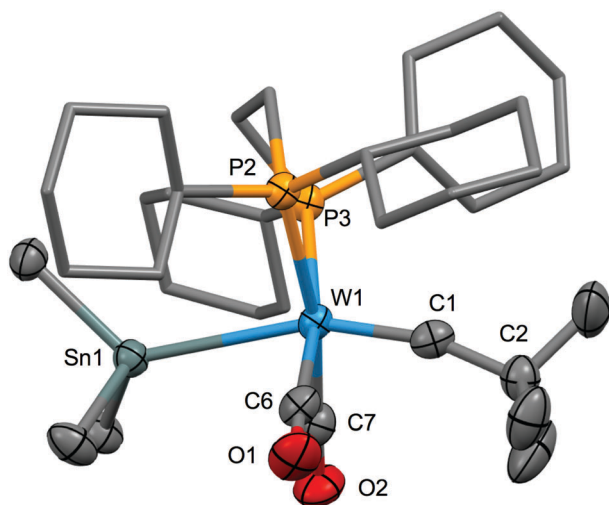


Fig. 1 Molecular structure of **2** in a crystal (60% displacement ellipsoids, H-atoms omitted, cyclohexyl groups simplified). Selected bond lengths (Å) and angles: W1-Sn1 2.9332(3), W1-P2 2.5497(9), W1-P3 2.5363(8), W1-C1 1.834(4), Sn1-W1-C1 160.73(12), W1-C1-C2 164.3(3).

The molecular structure of **2** (Fig. 1) is based on a *pseudo*-octahedral tungsten with distortion from ideal geometry being attributable to inter-ligand repulsions. The $\text{W}\equiv\text{C}$ bond-length of W1-C1 1.834(4) Å, is unremarkable, falling within the normal range for neopentylidyne complexes although all previous structural studies involved this ligand bound to high-valent tungsten. While there are copious structural data available for tungsten stannyl complexes, the only two trimethylstannyl examples $[\text{W}(\text{SnMe}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{SnMe}_3)]$ ($\text{W-Sn} = 2.8481(5)$ Å)¹² and $[\text{W}(\text{SnMe}_3)(\text{CO})_5]^-$ (2.810(8) Å)¹³ have far shorter W-Sn bonds than found in **2** (2.9332(3) Å), a manifestation of the superlative *trans* influence of carbyne ligands.

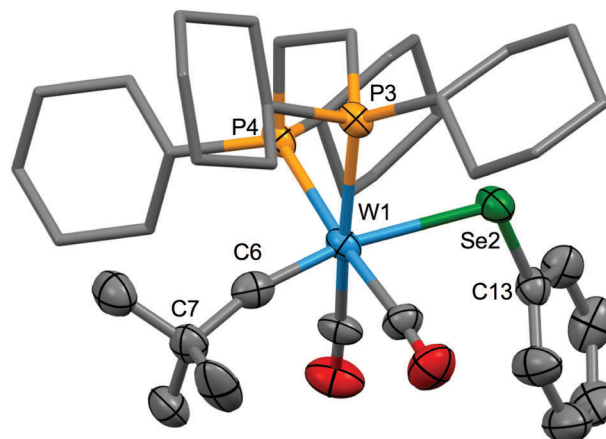


Fig. 2 Molecular structure of **3b** in a crystal (60% displacement ellipsoids, H-atoms omitted, cyclohexyl groups simplified). Selected bond lengths (Å) and angles: W1-Se2 2.7467(7), W1-P3 2.5489(14), W1-P4 2.5696(15), W1-C6 1.826(7), Se2-C13 1.927(6), C6-W1-Se2 167.9(2), C7-C6-W1 167.4(5), C13-Se2-W1 107.5(2).

The reaction proved to be comparatively general for a range of electrophiles (Scheme 2). Phenylchalcogenolato complexes $[\text{W}(\equiv\text{C}^t\text{Bu})(\text{EPh})(\text{CO})_2(\text{dcppe})]$ ($\text{E} = \text{S}$ **3a**, Se **3b**, Te **3c**; see ESI†) were obtained by employing PhEPh as the electrophilic quench and were each structurally characterised. Structural data for **3b** (Fig. 2, for depictions of **3a** and **3c** see ESI†) typify those for the series, the notable features being an insignificant impact on the $\text{W}\equiv\text{C}$ bond length, from 1.821(5) Å for **3a** to 1.823(4) Å for **3c**. In a similar manner, neither the ν_{CO} frequencies nor the chemical shift of the carbyne carbon were particularly sensitive to variations in the chalcogen (Table 1). The W-E-C angle decreases only marginally from 107.4 for **3a** to 104.8(1)° for **3c** and while this modest change might appear consistent with the usual trend for reduced s-character with heavier chalcogens, it should be pointed out that both **3b** and isomorphous **3c** participate in incipient intermolecular π -stacking of the phenyl rings (absent for **3a**, see ESI†) so as to cloud any such interpretation.

Treating the intermediate with $t\text{BuBr}$ or $t\text{BuCl}$ as mild sources of HX ($\text{X} = \text{Cl}, \text{Br}$) in E_2 reactions results not in the tertiary alkyl or hydrido $[\text{W}(\equiv\text{C}^t\text{Bu})\text{H}(\text{CO})_2(\text{dcppe})]$ (**4**) derivatives, but rather the halides $[\text{W}(\equiv\text{C}^t\text{Bu})\text{X}(\text{CO})_2(\text{dcppe})]$ ($\text{X} = \text{Cl}$ **5a**, Br **5b**), both of which were structurally characterised (see ESI†). Berke has described a range of hydrido-carbyne complexes of the form

Table 1 Selected Infrared and NMR data for new neopentylidyne complexes *trans*- $[\text{W}(\equiv\text{C}^t\text{Bu})\text{X}(\text{CO})_2(\text{dcppe})]$

| X | ν_{CO} [cm ⁻¹] | k_{CO}^a [Ncm ⁻¹] | $\delta_{\text{C}}(\text{W}\equiv\text{C})$ [ppm] | $^2J_{\text{PC}}$ [Hz] |
|--------------------------|--|---|--|---------------------------|
| SnMe_3 2 | 1961, 1899 ^b | 15.02 | 317.2 ^c | 7.5 |
| SPh 3a | 1997, 1928 ^d | 15.53 | 297.3 ^e | 9.2 |
| SePh 3b | 1984, 1915 ^b | 15.33 | 298.8 ^e | 8.7 |
| TePh 3c | 1981, 1914 ^b | 15.30 | 301.4 ^e | 8.4 |
| Cl 5a | 1991, 1915 ^d | 15.39 | 289.5 ^e | 7.6 |
| Br 5b | 1978, 1908 ^d | 15.23 | 290.4 ^e | 7.5 |

^a Cotton–Kraihanzel force constant for *cis*-dicarbonyl. ^b Measured in toluene. ^c Measured in C_6H_6 . ^d Measured in CH_2Cl_2 . ^e Measured in CDCl_3 .

$[W(\equiv C^tBu)H(L)_4]$ (L_4 = various combinations of CO, $P(OMe)_3$, PMe_3)¹⁴ and shown, *e.g.*, that phenol is a strong enough acid (pK_a 10) to cleave the hydride ligands so we may assume that **4** is viable but presumably is rapidly converted to the halide complexes by excess alkyl halide.

As noted above for **2**, the yield is maximised when two or more equivalents of tBuLi are employed and with only one equivalent we have been unable to isolate or spectroscopically identify any intermediates. We contend therefore that a two step process operates that involves slow initial nucleophilic attack at the methylidyne carbon of **1** by tBuLi to afford the anionic neopentylidene $Li[W(=CH^tBu)Br(CO)_2(dcpe)]$ (**A**, Scheme 2) which then undergoes a rapid dehydrohalogenation by a second equivalent of tBuLi to afford the anionic neopentylidyne complex $Li[W(\equiv C^tBu)(CO)_2(dcpe)]$ (**B**), precluding the accumulation of **A**. We have been unable to isolate **B** which decomposes below room temperature under the conditions of its formation. Indeed the reactions involving tBuX ($X = Cl, Br$) were specifically motivated by attempts to quench unreacted excess tBuLi .

The intermediate in the absence of an electrophilic trapping agent decomposes extremely rapidly near room temperature and it has not been possible to acquire useful infrared data, however it is unlikely that this technique would not reliably discriminate between the two alternatives. *In situ* NMR spectroscopy (d_8 -THF) proved somewhat more informative. When **1** was treated with less than 2 equivalents of tBuLi a solution of the intermediate could be maintained at $-62^\circ C$ long enough to acquire both ^{31}P , 1H and 1H - ^{13}C HMBC spectra. The $^{31}P\{^1H\}$ NMR spectrum (Fig. 3) reveals in addition to unreacted **1**, a second predominant compound at $\delta_P = 90.2$ ppm ($J_{WP} = 215$ Hz), with no evidence for any other major compounds being present.

No resonances were observed in the alkylidene region of the 1H NMR spectrum ($\delta_H = 10$ –25 ppm). The 1H - ^{13}C HMBC spectrum (see ESI†) revealed a resonance at $\delta_C = 322$ in the alkylidyne region which correlates with that observed for the tBu group (CH_3) at $\delta_H = 1.06$ but to no other (*i.e.*, alkylidene $=CH$ type, $\delta_H > 10$) resonance. These data together all support the accumulation of alkylidyne intermediate **B**, which is formed

rapidly from alkylidene **A** which does not accumulate in spectroscopically determinable amounts.

Allowing the sample to warm to room to room temperature results in rapid formation of free $dcpe$ ($\delta_P = 0.92$, no coupling to ^{183}W) which is perhaps to be expected since trialkylphosphines do not generally bind strongly to anionic metal centres. The rapid deprotonation is perhaps surprising for an anionic neopentylidene in a low oxidation state, but has precedent for high oxidation state systems, *e.g.*, $[W(=CHPh)Cl_2(CO)(PMe_3)_2]$,¹⁵ which is dehydrohalogenated by pyrrolidiny cyclopentene, though in that case an agostic C–H–W interaction contributes to the acidity.¹⁶ For the deprotonation of **B** it is therefore likely that initial halide dissociation affords the neutral α -agostic neopentylidene $[W(=CH^tBu)(CO)_2(dcpe)]$ or its carbyne tautomer $[W(\equiv C^tBu)H(CO)_2(dcpe)]$, either of which would have enhanced acidity. The sterically modest methylidyne would appear to allow nucleophilic attack (rather than deprotonation) while, *e.g.*, the more congested benzylidene $[W(\equiv CPh)Br(CO)_2(dcpe)]$ (**6**) (obtained from $[W(\equiv CPh)Br(CO)_2(picoline)_2]$ and $dcpe$), fails to undergo a similar reaction. The HOMO of the simpler model complex $[W(\equiv CMe)(CO)_2(dmpe)]^-$ (see ESI†) was found to be primarily tungsten-based, and to protrude from a trigonal bipyramidal tungsten opposite to the equatorial coordinated ethylidyne ligand, thereby accounting for the observed stereochemistry of products (**2**–**5**; electrophile *trans* to C^tBu) from electrophilic attack at **B**. While we are confident in the identity of **B**, we are unable to discount an alternative route that might also lead to it. Lithium–halogen exchange reactions between tBuLi and aryl bromides are generally considered to proceed *via* rapid single electron transfer events. Similar processes with **1** involving reduction, hydrogen abstraction and capture of the comparatively long-lived *tert*-butyl radical may well operate and account for the failure to observe **A**.

To conclude, whilst the terminal methylidyne **1** is against all expectations not susceptible to deprotonation, it appears readily converted to the first example of an early transition metal high d-occupancy carbyne complex, which displays synthetic versatility through metal-based nucleophilicity. Not all electrophiles met with success in our hands. Thus as noted, treating **B** with tBuX affords halo-neopentylidyne complexes $[W(\equiv C^tBu)X(CO)_2(dcpe)]$ rather than the desired alkyl or hydrido complexes and NH_4Cl also failed to provide an isolable hydrido derivative. The reaction of **B** with Ph_3SnCl provided primarily the chloro complex **5a**, presumably *via* single electron transfer processes that are favoured by the steric incompatibility of both reagents. We were similarly unable to isolate methyl, benzyl or trifluoromethyl complexes from reactions of **B** with CH_3I , $PhCH_2Cl$ or $(CF_3CO)_2O$ though we do not rule out their initial formation. Nevertheless, the species **B** does afford access to new carbyne complexes with bonds between tungsten and halogens, tin, sulphur, selenium and tellurium.

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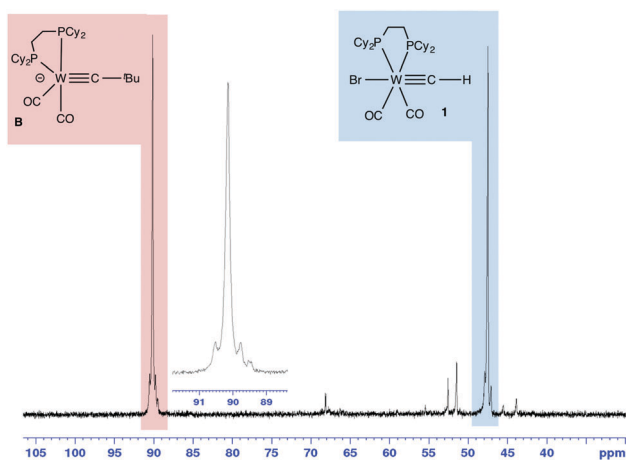


Fig. 3 $^{31}P\{^1H\}$ NMR spectrum (*in situ*, d_8 -THF) of the reaction of **1** (blue) with ca. 1.5 equivalents of tBuLi at $-30^\circ C$ to afford intermediate **B** (pink).



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