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Tetrel and Pnictogen Functionalised Propargylidyne

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The reaction of $[W(\equiv CC\equiv CSiMe_3)(CO)_2(Tp^*)]$ (Tp^* = tris(dimethylpyrazolyl)borate) with $AgNO_3$ affords $\{[W(\equiv CC\equiv CAg)(CO)_2(Tp^*)][AgNO_3]\}_n$ while $[Hg\{C\equiv CC\equiv W(CO)_2(Tp^*)\}_2]$ with nBuLi affords $[W(\equiv CC\equiv CLi)(CO)_2(Tp^*)]$. These anhydrous reagents allow the installation of main group elements (e.g., Si, Sn, Pb, P, As) as propargylidyne termini.

Propargylidyne complexes $L_nM(\equiv C-C\equiv CR)$ feature conjugated metal-carbon and carbon-carbon triple bonds, raising questions about electronic communication along the unsaturated MC_3 spine.¹ Early synthetic protocols (Scheme 1) were based on the classical Fischer carbyne synthesis *via* alkoxide or oxide abstraction from alkoxypropargylidene or propiolylate intermediates (Scheme 1).^{1b-d}

Scheme 1. Propargylidyne syntheses.¹⁻⁴

More recently, palladium-mediated cross-coupling reactions with halocarbynes and alkynyl nucleophiles have provided an alternative route² and the metathesis of diynes is also considered to implicate propargylidyne.^{3,4} These various routes are effective for the construction of hydrocarbyl-terminated propargylidyne but generally fail for the installation of main-group termini, wherein the desired terminus is intolerant of the electrophilic reagents required (Fischer route). The C–C cross-coupling route, proved successful for the formation of the tetrel-substituted propargylidyne $[W(\equiv CC\equiv CPh_3)(CO)_2(Tp^*)]$ (Tp^* = hydrotris(dimethylpyrazolyl)borate; A = C **1a**, Si **1b**, Ge **1c**) and a boryl derivative

$[W(\equiv CC\equiv CBMIDA)(CO)_2(Tp^*)]$ (**2**, MIDA = *N*-methyliminodiacetato) from $[W(\equiv CBr)(CO)_2(Tp^*)]$ (**3**)⁵ and the appropriate alkyne $HC\equiv CPh_3$ or $HC\equiv CBMIDA$ but failed in the case of $HC\equiv CSnPh_3$. The presumed stannyl derivative $[W(\equiv CC\equiv CSnPh_3)(CO)_2(Tp^*)]$ (**1d**) proved to be more reactive than the precursor alkyne towards cross-coupling, resulting in a “ $C_1+C_2+C_1$ ” construction of a C_4 chain in the dimetallahexatriyne $[(Tp^*)(CO)_2W\equiv CC\equiv CC\equiv W(CO)_2(Tp^*)]$ (**4**),^{6a} a complex that had been previously prepared by Templeton *via* a “ C_2+C_2 ” strategy.^{6b} Silylpropargylidyne, e.g., $[W(\equiv CC\equiv CSiMe_3)(CO)_2(Tp^*)]$ (**5**)^{1b} have been found to serve as tricarbido ‘ C_3 ’ synthons *via* fluoride-mediated desilylation (moist $[^nBu_4N]F$), allowing the installation of transition-metal termini to afford bi-, tri- and tetrametallic tricarbido-bridged complexes.⁷ The implicated parent propargylidyne $[W(\equiv CC\equiv CH)(CO)_2(Tp^*)]$ or its tricarbido conjugate base have, however, defied isolation and attempts to extend this protocol to main group electrophiles have been similarly unsuccessful due to incompatibility of the electrophile with fluoride or adventitious moisture.⁸ Herein, we report two new protocols that afford access to main-group element terminated propargylidyne including the first tin, lead, phosphorus and arsenic functionalised derivatives.

Prior attempts to generate a tricarbido nucleophile $[W(\equiv CC\equiv CLi)(CO)_2(Tp^*)]$ (**6**) *via* desilylation of $[W(\equiv CC\equiv C\beta\equiv C\gamma SiMe_3)(CO)_2(Tp^*)]$ (**5**) with methylolithium resulted instead in attack at C_γ to afford the anionic allenylidene complex $Li[W\{C=C=C(Me)SiMe_3\}(CO)_2(Tp^*)]$ (**7**).⁹ Accordingly, our attention turned to the mercury bis(tricarbido) complex $Hg\{C\equiv CC\equiv W(CO)_2(Tp^*)\}_2$ (**8**).¹⁰ Redox transmetalation employing mercury alkynyls has previously proven successful;¹¹ however, reaction of **8** with lithium metal, with or without 4,4'-di-*tert*-butylbiphenyl, failed to proceed. Caveats associated with extreme toxicity notwithstanding, the reaction of **8** with *n*-butyl lithium was found to cleanly proceed (THF, $-78^\circ C$) to provide a green solution of what is presumed to contain $[W(\equiv CC\equiv CLi)(CO)_2(Tp^*)]$ (**6**) and nBu_2Hg (CAUTION!); phenyl lithium failed to react with **8** under these conditions. Treating this solution with Ph_3SiCl afforded the known^{2c} silylpropargylidyne $[W(\equiv CC\equiv CSiPh_3)(CO)_2(Tp^*)]$ (**1b**) in 60% yield. Use of $ClSnPh_3$ or $ClPbPh_3$ afforded the new and first examples of stannyl and plumblyl propargylidyne $[W(\equiv CC\equiv CPh_3)(CO)_2(Tp^*)]$ (A = Sn **1d**, Pb **1e**; Scheme 2, Table 1).

Scheme 2. Generation and reactivity of tungsten tricarbido synthetic equivalents.

Table 1. Selected IR data of Heteroatom-Functionalized propargyldynes $[W(\equiv C\alpha C\beta \equiv C\gamma R)(CO)_2(Tp^*)]$.

R	ν_{CO} [cm ⁻¹] ^a	ν_{CC} [cm ⁻¹] ^a	$C\alpha[{}^1J_{WC}]$ δ_C [Hz]	$C\beta[{}^2J_{WC}]$ δ_C [Hz]	$C\gamma[{}^3J_{WC}]$ δ_C [Hz]
CPh ₃ ^{2c} 1a	1982, 1892	2132	248.8[201]	103.0[60]	56.6[7]
SiPh ₃ ^{2c} 1b	1988, 1890	2054 ^b	247.7[197]	124.0[58]	73.8[g]
GePh ₃ ^{2c} 1c	1986, 1897	2052	248.2[g]	123.6[g]	75.1[g]
SnPh ₃ 1d	1985, 1896	2033	248.5[198] ^d	127.4[57] ^e	77.7[6] ^f
PbPh ₃ 1e	1982, 1892	— ^c	249.1[199]	127.8 [g]	92.3 ^h
PPh ₂ 12a	1986, 1898	— ^c	245.8[201]	124.5[g] ⁱ	69.4[g] ^j
AsPh ₂ 12b	1985, 1897	2046	246.7[201]	123.2[58]	73.1[7]
PPh ₂ BH ₃ 9	1997, 1911	2063 ^k	242.8[g] ^l	121.8 [g] ^m	59.6[g]

^a Measured in DCM, ^b Shoulder band 2027 cm⁻¹, ^c ν_{CC} absorption not observed. ^d ${}^3J_{SnC}$ = 15 Hz. ^e ${}^2J_{SnC}$ = 94 Hz ^f ${}^1J_{SnC}$ = 519 Hz. ^g J_{SnC} based on ${}^{119}Sn$. ^h Satellite resonances not observed/resolved due to low signal/noise. ⁱ ${}^1J_{PbC}$ = 72 Hz. ^j ${}^2J_{PC}$ = 5 Hz. ^k ${}^1J_{PC}$ = 9 Hz. ^l Shoulder band 2044 cm⁻¹, ^m ${}^3J_{PC}$ = 5 Hz. ⁿ ${}^2J_{PC}$ = 16 Hz. ^o ${}^1J_{PC}$ = 106 Hz.

These derivatives join the known propargyldynes **1a–c** to afford a complete series of tetrel-functionalised propargyldynes (Table 1). The NMR data for the stannyl derivative are noteworthy in that the tricarbido bridge straddles metal centres each of which have spin active isotopes ($I = \frac{1}{2}$: ${}^{183}W$, ${}^{119}Sn$, ${}^{117}Sn$ and ${}^{115}Sn$) such that satellite isotopomer doublets are observed, the coupling of which decreases with distance from each metal.

In a similar manner, the reaction of **6** with chlorodiphenylphosphine followed by BH_3SME_2 afforded the first pnictogen-functionalised propargyldyne $[W(\equiv C\equiv C\equiv CP(BH_3)Ph_2)(CO)_2(Tp^*)]$ (**9**) in 75% yield. This result is fortunate in that attempts to prepare phosphino-functionalised propargyldynes *via* Pd⁰/Cu^I mediated cross-coupling^{2b} between $[W(\equiv CBr)(CO)_2(Tp^*)]$ and $HC\equiv CPPH_2$ or $HC\equiv CP(S)Ph_2$ failed, perhaps due to copper(I) coordination to the heteroatom(s) rather than the alkyne.

The molecular structure of **9** is depicted in Figure 1 and confirms the localisation of triple and single bonds along the near linear $W\equiv C-C\equiv C-P$ spine, with individual bond lengths

corresponding to norms for more conventional tungsten propargyldynes.^{1a}

Figure 1. Molecular structure **9** in a crystal of $9 \cdot CH_2Cl_2$ (50% displacement ellipsoids, most hydrogen atoms omitted, phenyl and pyrazolyl groups simplified). Selected bond lengths (Å) and angles (°): Selected bond lengths [Å] and angles [°]: W1–C1 1.850(3), P1–C3 1.748(3), P1–B1 1.917(4), C2–C3 1.222(4), C2–C1 1.356(4), C2–C1–W1 176.9(3), C3–C2–C1 177.4(4), C2–C3–P1 169.4(3). Inset = view along P1–W1 vector.

Whilst the synthesis of $[W(\equiv C\equiv C\equiv Cl)(CO)_2(Tp^*)]$ (**6**) from **8** provides proof of concept for the generation of a tricarbido nucleophile under strictly anhydrous aprotic and halide free conditions, the lethal dialkylmercury side product makes this approach unattractive for any but the smallest scale and careful syntheses. An alternative approach was therefore devised, based on the established utility of silver alkynyls in catalytic procedures. Treating a THF solution of **5** with ethanolic silver nitrate¹³ results in the immediate formation of a dark green poorly crystalline precipitate **10** that is only sparingly soluble in halogenated solvents (CH_2Cl_2 , $CHCl_3$). The material appears to have the gross composition $[Ag_2\{C\equiv C\equiv W(CO)_2(Tp^*)\}]NO_3$ based on elemental microanalytical data and the positive ion ESI mass spectrum that includes peaks attributable to $[HAg_n\{C\equiv C\equiv W(CO)_2(Tp^*)\}]^+$ (m/z = 681.0536, $n=1$; 1254.1947 $n=2$) with the base peak composed of $[HAgC\equiv C\equiv W(CO)_2(Tp^*)+MeCN]^+$ (m/z = 722.0789). Although the precise nature of **10** remains unknown, it is clear that it contains the components of $AgNO_3$ as indicated by comparison of the ${}^{31}P\{^1H\}$ NMR spectrum measured in the presence of PCy_3 which comprises two exchange-broadened doublet resonances ($I = \frac{1}{2}$: ${}^{107}Ag$ 51.8%, ${}^{109}Ag$ 48.2%) with that occurring to lower frequency (δ_P = 31.7, ${}^1J_{AgP}$ ~490 Hz) corresponding to $[Ag(NO_3)(PCy_3)_2]$.¹⁴ Based on the magnitude of ${}^1J_{AgP}$ for the second doublet (493 Hz), this most likely corresponds to $[Ag\{C\equiv C\equiv W(CO)_2(Tp^*)\}(PCy_3)_2]$ with three-coordinate silver (two-coordinate $[Ag(NO_3)(PCy_3)]$ has ${}^1J_{AgP}$ ~742 Hz). The structural chemistry of even simple oligomeric silver alkynyls is complex;¹⁵ however, a glimpse of the possible structural motifs present is provided by a salt obtained from addition of dppm (dppm = bis(diphenylphosphino)methane) which was crystallographically identified as the trisilver cluster $[Ag_3(\mu_3-C\equiv C\equiv W(CO)_2(Tp^*))_2(\mu-dppm)_3]NO_3$ (**[11]**NO₃, Figure 2). The “ $Ag_3(\mu_3-C)_2$ ” core of **[11]⁺** is reminiscent of the clusters $[Ag_3(\mu_3-C\equiv CR)_2(\mu-dppm)_3]^+$ (X = Ph, $C_6H_4NO_2-4$, $C\equiv CPh$,

$\text{C}\equiv\text{Cr}(\text{CO})_3(\text{bipy})$),¹⁶ and tricarbido ligands have been shown to bridge in the $\mu_4:\mu_3,\sigma$ mode on a number of occasions.^{1a,17}

Figure 2. Molecular structure $[11]^+$ in a crystal of $[11]\text{NO}_3\cdot\text{C}_6\text{H}_5\text{Me}$ (50% displacement ellipsoids, solvent, counter anion and hydrogen atoms omitted, dppm and pyrazolyl groups simplified). Poor data confirm connectivity but devalue detailed analysis of the geometric features of the structural model.

Irrespective of the intimate structure of **10**, it certainly serves the required purpose by reacting with ClPPh_2 at 0 °C in CH_2Cl_2 to afford the red air-sensitive phosphinopropargylidyne $[\text{W}(\equiv\text{CC}\equiv\text{CPPh}_2)(\text{CO})_2(\text{Tp}^*)]$ (**12a**) in 42% yield. In a similar manner treating the reagent with BrAsPh_2 affords the arsinopropargylidyne $[\text{W}(\equiv\text{CC}\equiv\text{CAsPh}_2)(\text{CO})_2(\text{Tp}^*)]$ (**12b**) in 38% yield as a somewhat more air-resistant compound.

Neither **12a** nor **12b** have so far yielded crystallographic quality crystals, however the computationally optimised geometry for the model compound $[\text{W}(\equiv\text{CC}\equiv\text{CPMe}_2)(\text{CO})_2(\text{Tp})]$ (**13a**, Tp = hydrotris(pyrazolyl)borate) displays similar bond lengths along the WCCCP spine to those observed for the borane adduct **9** (Figure 1). Based on this geometry, the derived molecular orbitals of interest are shown in Figure 3 along with those for $[\text{W}(\equiv\text{CC}\equiv\text{CAsMe}_2)(\text{CO})_2(\text{Tp})]$ (**13b**) and the simple butynylidyne $[\text{W}(\equiv\text{CC}\equiv\text{CMe})(\text{CO})_2(\text{Tp})]$ (**14**) for comparison.

Whilst ν_{CO} values calculated for **13a** (2006, 1943 cm^{-1}) are slightly higher than experimentally observed for **12a**, the value for ν_{CC} (2118 cm^{-1}) has zero infra-red intensity, consistent with the failure to experimentally observe this band for **12a**. Both the tungsten (+1.023) and phosphorus (+0.884) carry positive natural charges while C_α (−0.339) and C_γ (−0.324) are more negative than C_β (−0.116). The $\text{W}\equiv\text{C}_\alpha$ and $\text{C}_\beta\equiv\text{C}_\gamma$ bonds have Löwdin orders of 2.34 and 2.62, respectively, consistent with their multiple bond character while $\text{C}_\alpha\text{--C}_\beta$ (1.299) is closer to unity. The HOMO is of little interest in that it is associated with W-CO retrodonation and has δ -symmetry with respect to the propargylidyne axis to which it is orthogonal. The topologies of the HOMO-1 and HOMO-2, which correspond to the two $\text{W}\equiv\text{C}$ π -bonds give credence to the idea of electronic communication along the propargylidyne spine. Both involve contributions from each atom along the WCCC linkage, with the HOMO-1 also including a substantial contribution from the ‘lone’ pair on phosphorus. Accordingly, whilst the HOMO is primarily metal based, the spatial extension of the HOMO-1 along the WCCCP spine might be expected to favour electrophilic attack either at phosphorus (as demonstrated with BH_3SMe_2 to afford **9**) or the $\text{W}\equiv\text{C}$ or $\text{C}\equiv\text{C}$ multiple bonds. It is relevant that Stone has observed hydroboration of the $\text{W}\equiv\text{C}$ bond of the simple

ethynylidynes $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\text{L})]$ ($\text{M} = \text{Tp}$, $\eta\text{-C}_5\text{H}_5$, $\eta\text{-C}_5\text{Me}_5$),¹⁸ though this type of reactivity is not encountered here. For **13b** there is a modest contraction of the angle sum at arsenic (290.9°) *cf.* the phosphorus (299.4°) in **13a** suggesting reduced participation of the As(4s) orbital in bonding; however, the energies and topologies of the valence molecular orbitals are otherwise essentially unchanged by replacing phosphorus with arsenic, as inferred from the similarities in spectroscopic data for **12a** and **12b**.

Figure 3. Frontier orbitals of interest for the model propargylidynes $[\text{W}(\equiv\text{C}\text{--}\text{C}\equiv\text{CR})(\text{CO})_2(\text{Tp})]$ $\text{R} = \text{Me}$ **14**, PMe_2 **13a**, AsMe_2 **13b** (DFT: $\omega\text{B97X-D/6-31G}^*/\text{LANL2DZ}$; isovalue = 0.032).

In conclusion, two potentially generalizable protocols have been developed for the terminal functionalisation of propargylidynes under anhydrous, aprotic conditions, though each has its caveats. The transmetallation method to generate $[\text{W}(\equiv\text{CC}\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ involves generation of toxic di-*n*-butyl mercury as a side product, whilst the utility of isolable *argento* tricarbido intermediates suffers from uncertainty as to the intimate nature of the active species. Nevertheless, these routes have afforded access to the first examples of pnictogen-substituted propargylidynes (P, As) as well as those bearing the heavier tetrrels (Sn, Pb). With the isolation of $[\text{W}(\equiv\text{CC}\equiv\text{CPPh}_2)(\text{CO})_2(\text{Tp}^*)]$, the series $\text{L}_n\text{MC}_x\text{PR}_2$ ($x = 1,^{19} 2,^{20} 4^{21}$) is completed for $x = 3$. Phosphino-terminated propargylidynes present a number of potentially reactive sites along the $\text{W}\equiv\text{C}\text{--}\text{C}\equiv\text{C}\text{--}\text{P}$ spine, an intriguing situation on which we will subsequently report.

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