COMMUNICATION

A Complete Set of Pnictocarbynes: $[M(\equiv CAPH_2)(CO)_2(Tp^*)]$ ($M = Mo, W$; $A = N, P, As, Sb, Bi$; $Tp^* =$ Hydrotris(dimethylpyrazolyl)-borate)

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The first two complete series of pnictogen functionalised carbyne complexes, $[M(\equiv CAPH_2)(CO)_2(Tp^*)]$ ($M = Mo, W$; $A = N, P, As, Sb, Bi$; $Tp^* =$ hydrotris(3,5-dimethylpyrazol-1-yl)borate), have been prepared. The heavier analogues ($A \neq N$) result from successive treatment of $[M(\equiv CBr)(CO)_2(Tp^*)]$ with $nBuLi$ and $ClAPPh_2$ ($A = P, As, Sb, Bi$) and include the first examples of arsino, stibino or bismuthino carbyne complexes.

The p -block elements (groups 13-17) are diagonally divided between elements that display non-metal vs 'metalloid' character. From an organometallic perspective, this reflects the electronegativities of the elements relative to carbon (Pauling: 2.5), manifest both in polarity and the degree of covalency. Furthermore, both σ - and π -bonding to carbon, become progressively weaker on descending each group towards the metallic domain. Elements abutting this somewhat vague division (B, Si, Ge, As, Sb, Te) may show intermediate character, however the 'heavy metal' elements Ga, In, Tl, Sn, Pb, Sb and Bi (Pauling: 1.5 $\approx$ 1.8) are clearly considered metallic.

Transition metal carbyne complexes $L_nM\equiv CR$ are dominated by those bearing hydrocarbyl substituents ($R =$ alkyl, aryl *etc.*), and to a lesser extent, substituent elements above the non-metal/metalloid divide (O, N, S, Se, F, Cl, Br).¹ This is not necessarily a comment on the stability of carbynes bearing heteroatom substituents, but rather an historical consequence of the various synthetic pathways¹⁻³ not being applicable to electropositive metalloid elements as eventual carbyne substituents. Thus $[Mo(\equiv CPbPh_3)(CO)_2(Tp^*)]$ ($Tp^* =$ tris(dimethylpyrazolyl)borate)⁴ is not only the sole example of a 'heavy-metalloid' carbyne, but also completes the tetrel series $[Mo(\equiv CEPH_3)(CO)_2(Tp^*)]$ ($E = Si, Ge, Sn, Pb$). To better understand and benchmark the effect of sandwiching a carbyne carbon between d and p -block heavy metals, we have turned our attention to the isolation of the first heavy metalloid carbyne complexes of the pnictogen group. Accordingly, we report herein the first (two) complete series of carbyne complexes substituted by each and every group 15 element, *viz.* $[M(\equiv CAPH_2)(CO)_2(Tp^*)]$ ($M = Mo, W$; $A = N,$

P, As, Sb, Bi) including the heavy metals antimony and bismuth.

Aminocarbynes $L_nM\equiv CNR_2$, are available *via* a number of routes and are generally found to be especially stable, with their reduced reactivity being attributed to contributions from a 2-azavinylidene canonical description.⁵ On descending the pnictogen group however, the prevalence of carbyne complexes very rapidly declines. The first phosphinocarbynes $[Mo(\equiv CPClR)\{N^tBu(C_6H_3Me-3,5)\}_3]$ ($R = Cl, Ph$) were reported by Cummins⁶ and we have since developed routes to various phosphinocarbyne derivatives *via* the intermediacy of Lalor's halocarbynes $[M(\equiv CBr)(CO)_2(Tp^*)]$ ($M = Mo$ **1a**, W **1b**; $Tp^* =$ hydrotris(dimethylpyrazolyl)borate, Scheme 1, *vide infra*).⁷

Scheme 1. Complimentary 'umpolung' approaches for the introduction of nucleophilic (**Nu**) or electrophilic (**E**) carbyne substituents.

More prevalent are phosphonocarbynes $L_nM\equiv CPR_3$ ⁸ and amongst these, the complex $[Ti(\equiv CPMePh_2)(OTf)(L)]$ ($L = N(C_6H_3Me-4, P^iPr_2-2)_2$)^{8e} is of particular relevance in that it arises from methylation (MeOTf) of the phosphinocarbyne $[Ti(\eta^2-HCPPh_2)(Ph)(L)]$ which is in turn mooted to reversibly eliminate benzene to generate the putative phosphinocarbyne complex $[Ti(\equiv CPPh_2)(L)]$.⁹ Weber has reported extensively on the chemistry of phospho-alkenyl carbyne complexes $L_nM\equiv C-P=CR_2$, accessed *via* condensation of P -silyl phospho-alkenes with a chlorocarbyne complex.⁹ This latter approach is of particular note in that it could be extended to afford the only examples of arsenic functionalised carbyne complexes.^{9c} Whilst carbyne complexes bearing arsenic substituents are exceedingly rare, those of antimony and bismuth are at

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present unknown. Indeed, only a very limited number of isolobal *alkynylstibanes*¹⁰ and *alkynylbismuthanes*¹¹ have been described. We report herein the successful synthesis of the first (and second) complete series of carbyne complexes $[M(\equiv CPh_2)(CO)_2(Tp^*)]$ ($M = Mo, W$; $A = N, P, As, Sb, Bi$) in which the only variant is the carbyne pnictogen substituent 'A'. These series thus include the first examples of carbyne complexes bearing antimony or bismuth carbyne substituents.

The reactions of $[Mo(\equiv CBr)(CO)_2(Tp^*)]$ (**1a**) with secondary dialkylamines readily affords the corresponding aminocarbyne derivatives *via* simple nucleophilic halide substitution.¹² In contrast, no reaction took place when **1a** or **1b** were treated with $HNPPh_2$ or $LiNPh_2$ (THF, reflux, 48 hours). We therefore resorted to a conventional Fischer approach:^{5c} Sequential treatment of $[M(CO)_6]$ with $LiNPh_2$, $(CF_3CO)_2O$ and $K[TP^*]$ furnished the complexes, $[M(\equiv CNPh_2)(CO)_2(Tp^*)]$, ($M = Mo$ **2a**, Figure 1; $M = W$ **2b**) as bright orange crystalline solids in rather moderate (non-optimized) yields (Scheme 2).

Figure 1. Molecular structure of **2a** (60% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Mo–C1 1.8267(18), Mo–N1 2.3077(16), Mo–N3 2.2271(15), Mo–N5 2.2282(16), C1–N7 1.346(2), Mo–C1–N7 176.57(15). $\tau_R = 2[Mo-N1]/(Mo-N3 + Mo-N5) = 1.036$. Inset = view along Mo–C1 vector.

Although the complexes **2** provide the first structural data for diarylamino carbynes, H. Fischer has spectroscopically characterised the thermally unstable complexes *trans*- $[M(\equiv CNPh_2)Br(CO)_4]$ ($M = Cr, W$).¹³ *Dialkylaminocarbynes* are commonplace and a comparison of IR data for **2a** (CH_2Cl_2 : $\nu_{CO} = 1973, 1877\text{ cm}^{-1}$) with those for $[Mo(\equiv CNEt_2)(CO)_2(Tp^*)]$ (CH_2Cl_2 : $\nu_{CO} = 1949, 1850\text{ cm}^{-1}$)¹² suggests that the π -basicity of

Scheme 2. Synthesis and canonical descriptions of 2-azavinylidene ↔ diarylamino carbyne complexes.

the NPh_2 group is considerably reduced relative to a dialkylamino substituent. This results in an enhanced π -acidity

of the $CNPh_2$ ligand, with reduced contribution from the 2-azavinylidene description.

As noted above, this approach is *not* suitable for introducing heavier pnictogen substituents because the initial nucleophilic attack at a carbonyl ligand fails. An alternative strategy was therefore required, based on the previously reported synthesis of the diphenylphosphino carbynes, $[M(\equiv CPPH_2)(CO)_2(Tp^*)]$, ($M = Mo$ **3a**; $M = W$ **3b**) (Scheme 3).^{7a,b} Although the attempted nucleophilic substitution of **1a** with $LiPPh_2$ was found to be unsuccessful,^{7a} these products could be accessed *via* an “umpolung” approach (Scheme 1). Lithium/halogen exchange of **1a** or **1b** with nBuLi gives lithiocarbyne intermediates,¹⁴ which then act as a nucleophile towards $PClPh_2$. These lithiocarbyne intermediates and their synthetic utility were first described by Templeton,^{14f} albeit *via* a more circuitous route.

This chemistry could indeed be extended to the heavier pnictogen analogues. Thus, sequential treatment of **1a** or **1b** with nBuLi followed by $AsBrPh_2$ furnished the diphenylarsino derivatives, $[M(\equiv CAsPh_2)(CO)_2(Tp^*)]$, ($M = Mo$ **4a**; $M = W$ **4b**, Figure 2) in good yields as yellow-orange crystalline solids (Scheme 3). The only other known arsenic-substituted carbynes were reported by Weber⁸ *via* reaction of $[M(\equiv CCl)(CO)_2(Tp^*)]$ with $Me_3SiAs=C(NMe_2)_2$.

Scheme 3. Synthesis of heavier pnictogen functionalised carbyne complexes.

On treatment of the lithiocarbyne with $SbClPh_2$, the yellow diphenylstibino carbynes, $[M(\equiv CSbPh_2)(CO)_2(Tp^*)]$, ($M = Mo$ **5a**; $M = W$ **5b**) are formed. These were only isolated in very low yields (typically 10–15%), due to a combination of the difficulty in preparing a homogenous sample of $SbClPh_2$ (rapid redistribution to an equilibrium mixture of $SbCl_xPh_{3-x}$, $x = 0-3$)¹⁵ and losses during chromatography, which was required to obtain analytically pure samples of **5a** and **5b**. Neither **5a** nor **5b** have so far afforded crystallographic grade crystals. The reaction of the lithiocarbynes with $BiClPh_2$ similarly furnishes the diphenylbismuthino carbynes, $[M(\equiv CBiPh_2)(CO)_2(Tp^*)]$, ($M = Mo$ **6a**; $M = W$ **6b**) in good yields as yellow microcrystalline solids. In these cases, column chromatography was found to be unnecessary and the products were purified by successive recrystallizations.

The single crystal X-ray structures of **2a,b**, **4a,b** and **6a,b** have been determined (the structures of **3a**^{6a} and **3b**^{6b} have been previously reported). The molecular geometries of only the molybdenum complexes (**2a**, Figure 1; **4a**, Figure 2; **6a**,

Figure 3) are shown as they are visually identical to their tungsten analogues. Selected structural and spectroscopic data for the complexes are presented in Tables 1 and 2. The geometry about the nitrogen of the aminocarbyne ligands in isomorphous **2a** and **2b** is approximately trigonal planar ($\Sigma^\circ(\text{N}7) = 359.5^\circ$ for both **2a** and **2b**), consistent with reported aminocarbyne complexes and indicative of significant $\pi(\text{C})-\pi(\text{N})$ overlap (Scheme 2). In contrast, the geometry about the heavier pnictogens in complexes **3–4** and **6** is pyramidalized, angle sums decreasing monotonically down the group with increasing p^3 (i.e., no) hybridisation of the pnictogen (312.0 **3a**, 311.9 **3b**, 296.4 **4a**, 296.5 **4b**, 280.95 **6a**, 281.54° **6b**).

Table 1. Selected Structural, ^{13}C NMR and IR data for $[\text{Mo}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$

	2a	3a ^{6a}	4a	5a	6a
A =	N	P	As	Sb	Bi
$r_{\text{Mo}=\text{C}}$ (Å)	1.827(2)	1.802(2)	1.800(3)	-	1.787(9)
$r_{\text{C}-\text{A}}$ (Å)	1.346(3)	1.790(2)	1.926(3)	-	2.258(9)
$\angle_{\text{MoCA}}$ (°)	176.6(2)	166.6(1)	171.6(2)	-	175.3(5)
TR ^a	1.036	1.053	1.045	-	1.056
$\delta_{\text{C}}(\text{ppm})^b$	239.0	309.0	316.8	330.9	- ^c
$\nu_{\text{CO}}(\text{cm}^{-1})^d$	1973, 1877	1995, 1913	1998, 1914	1998, 1914	1995, 1909
$k_{\text{CO}}(\text{mdyn}/\text{\AA})^e$	14.97	15.43	15.46	15.46	15.39

^a $\text{TR} = 2r(\text{MoN}_{\text{trans}})/\Sigma r(\text{MoN}_{\text{cis}})$.^{14c} ^bMeasured in CDCl_3 . ^cNot observed due to quadrupolar ^{209}Bi ($I = 9/2$, 100%). ^dMeasured in CH_2Cl_2 . ^eCotton-Kraihanzel force constant.¹⁷

The $\text{Mo}=\text{C}$ bond distances (Table 1) are crystallographically identical (within 6 esd) in **3a**, **4a** and **6a**, but the related bond in the aminocarbyne ('2-azavinylidene') complex, **2a**, is slightly longer in comparison. These observations suggest that $\pi(\text{C})-\pi(\text{A})$ overlap is significantly reduced for $\text{A} = \text{P}$, As and Bi .

The structures of **2a** and **2b** also reveal the close proximity of the two phenyl rings (H–H distance between the closest *ortho*-protons is ca. 2.77 and 2.75 Å in the solid-state structures of **2a** and **2b**, respectively). Restricted rotation about the C–N multiple bond is manifest (on the NMR timescale) in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (25 °C), such that 8 distinct carbon resonances assigned to the phenyl rings were identified in the latter spectrum. In the solid state one phenyl ring (based on C10) conjugates with the MCN π -system, but rotates freely in solution on the NMR timescale. The phenyl rings in the analogues with heavier pnictogens, **3–6**, are equivalent on the NMR timescale (4 ^{13}C aryl resonances), further indicating unrestricted rotation of the pyramidal APh_2 unit around MC–A bonds with at best a modest π -component to the bonding.

Notably, the aminocarbynes **2a,b** exhibit a reduced *trans* influence compared to the heavier analogues despite aminocarbynes being considered to exert a comparatively strong *trans* influence relative to other carbyne ligands commensurate with 2-azavinylidene character. For complexes of the form $[\text{M}(\text{CO})_2(\text{L})(\text{Tp}^*)]$, this may be quantified by the singular parameter **TR**, defined as the ratio of the M–N bond length *trans* to L, to the average of the remaining two M–N bond lengths *trans* to CO ligands.^{14c} For the aminocarbynes **TR** is

somewhat shorter (1.036 for both **2a** and **2b**) than those observed for the carbynes substituted with the four heavier pnictogens (1.043–1.056), perhaps reflecting the impact of the increased electronegativity of nitrogen upon the σ -component to the $(\text{pz})\text{N}-\text{M}-\text{C}-\text{N}$ σ -bonding. The Cotton-Kraihanzel force constant (k_{CO}) associated with the carbonyl absorbances in the

Figure 2. Molecular structure of **4a** (60% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted for clarity, one of two crystallographically independent molecules). Selected bold lengths (Å) and angles (°): Mo1–C1 1.800(3), Mo1–N1 2.320(2), Mo1–N3 2.218(2), Mo1–N5 2.219(2), C1–As1 1.926(3), Mo1–C1–As1 171.58(17), C1–As1–C19 96.45(12), C1–As1–C25 97.24(12). $\text{TR} = 2(\text{Mo1}-\text{N1})/(\text{Mo1}-\text{N3} + \text{Mo1}-\text{N5}) = 1.045$.

Table 2. Selected Structural, ^{13}C NMR and IR data for $[\text{W}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$

	2b	3b ^{6c}	4b	5b	6b
A =	N	P	As	Sb	Bi
$R_{\text{W}=\text{C}}$ (Å)	1.837(3)	1.827(2)	1.825(5)	-	1.807(9)
$r_{\text{C}-\text{A}}$ (Å)	1.356(4)	1.783(3)	1.916(5)	-	2.258(9)
$\angle_{\text{WCA}}$ (°)	176.5(3)	166.6(2)	171.5(3)	-	174.7(5)
TR ^a	1.036	1.051	1.043	-	1.050
$\delta_{\text{C}}(\text{ppm})^b$	235.5	292.6	300.4	311.5	- ^c
$^1J_{\text{WC}}$ (Hz)	223	188	189	185	- ^c
$\nu_{\text{CO}}(\text{cm}^{-1})^d$	1960, 1859	1982, 1891	1983, 1892	1982, 1891	1979, 1889
$k_{\text{CO}}(\text{mdyn}/\text{\AA})^e$	14.73	15.15	15.17	15.15	15.11

^a $\text{TR} = 2r(\text{WN}_{\text{trans}})/\Sigma r(\text{WN}_{\text{cis}})$.^{14c} ^bMeasured in CDCl_3 . ^cNot observed due to quadrupolar ^{209}Bi ($I = 9/2$, 100%). ^dMeasured in CH_2Cl_2 . ^eCotton-Kraihanzel force constant.

Figure 3. Molecular structure of **6a** (60% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted for clarity). Selected bold lengths (Å) and

angles (°): Mo–C1 1.787(8), Mo–C2 2.001(8), Mo–C3 1.983(8), Mo–N1 2.231(6), Mo–N3 2.351(6), Mo–N5 2.221(6), C1–Bi 2.258(8), Mo–C1–Bi 175.3(5), C1–Bi–C4 88.7(3), C1–Bi–C10 91.1(3). $\tau_R = 2(\text{Mo–N3})/(\text{Mo–N1} + \text{Mo–N5}) = 1.056$. Inset = space filling representation with BiPh₂ in purple and Tp* in blue

IR spectra of the aminocarbynes **2** are appreciably smaller than their (otherwise comparable) heavier pnictogen analogues, **3a–6a** and **3b–6b** respectively. This implies that the extent of π -backbonding into the C=O π^* -orbital is comparatively greater in the less π -acidic aminocarbynes than in the four heavier pnictocarbynes.

To conclude, we have demonstrated that carbyne ligands bearing heavier pnictogens are viable and readily accessible. Though they present features in many ways analogous to aminocarbynes, demonstrable differences include (i) pyramidalisation at the pnictogen with little or no $C\pi$ - $A\pi$ overlap manifest as (ii) free rotation about the C–A bond and (iii) an increase in the trans influence of the carbyne ligand upon descending the group. This leaves unanswered, the question of these pnictogen serving as donors to extraneous metal centres, a point to which we will return in a subsequent paper. It also leaves the heavy metals of group 13 (Al–Tl) as the only p-block substituents for which carbyne complexes remain unknown

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