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Bis(alkylidynyl)arsines

Benjamin J. Frogley^a and Anthony F. Hill^{*a}

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The synthesis and characterization of the first examples of bimetallic bis(alkylidynyl)arsines, $[\text{RAs}\{\text{C}\equiv\text{M}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\text{M} = \text{Mo}$, $\text{R} = \text{Ph}$, Me ; $\text{M} = \text{W}$, $\text{R} = \text{Ph}$, Me , $n\text{Bu}$; $\text{Tp}^* = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$) are described. For the tungsten complexes, these may be prepared by a potentially generalizable route: successive treatment of $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ with $n\text{BuLi}$, AlCl_3 ($\text{A} = \text{P}$, As) and a nucleophilic source of R^- via the inferred intermediacy of $[\text{ClA}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$.

Since Fischer's seminal report,¹ the chemistry of transition metal carbyne complexes, $\text{L}_n\text{M}\equiv\text{CR}$, has been dominated by those with alkyl, aryl, thiolato or amino carbyne substituents,² with other heteroatomic substituents arising only sporadically. This should not be taken as a statement on the stability of carbynes bearing other heteroatomic substituents but rather the lack of available synthetic pathways. The classical Fischer^{1,3} and Schrock⁴ protocols are typically unsuitable for heavier main-group elements. Beyond hydrocarbyl, amino and silyl carbynes, the next largest class of p -block substituted carbynes currently known are those incorporating phosphorus. This is primarily due to the well-represented phosphoniocarbynes, $\text{LnM}\equiv\text{CPR}_3$,⁵ which are frequently observed on treatment of high-valent metal centres with phosphorus methylidene ylids.⁶ There are far fewer reports of phosphinocarbyne complexes, $\text{LnM}\equiv\text{CPR}_2$.⁷ The first of these, the molybdenum complexes $[\text{Mo}(\equiv\text{CPRCl})(\text{NR}'_2)_3]$ ($\text{R} = \text{Cl}$, Ph , $\text{NR}'_2 = \text{N}^t\text{BuC}_6\text{H}_3\text{Me-3,5}$), were reported by Cummins *via* the reaction of $[\text{Mo}(\equiv\text{CPK})(\text{NR}'_2)_3]$ with Cl_2PR .^{7a,b}

Similar chemistry can be performed with the lithiocarbynes $[\text{M}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$, W , $\text{Tp}^* = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$), which are readily accessible from their bromocarbyne precursors, $[\text{M}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$ **1a**; $\text{M} = \text{W}$ **1b**), *via* lithium/halogen exchange with $n\text{BuLi}$. These react with ClPR_2 to give phosphinocarbynes, $[\text{M}(\equiv\text{CPR}_2)(\text{CO})_2(\text{Tp}^*)]$,^{7c-g} and, in the case of the tungsten

complex **1b**, reaction with one equivalent of Cl_2PR affords the monomeric complexes $[\text{W}(\equiv\text{CPClR})(\text{CO})_2(\text{Tp}^*)]$ ($\text{R} = \text{Ph}$, Cy).^{7e} These were found to be susceptible to nucleophilic halide substitution at phosphorus and a range of derivatives could be prepared with various nucleophiles (*e.g.* MeLi , PhLi , KOPh).^{7e} The synthetic utility of chlorophosphinocarbynes has been further demonstrated by the observation that they react with a second equivalent of lithiocarbyne to yield bis(alkylidynyl)phosphine complexes, $[\text{RP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\text{R} = \text{Ph}$ **2b**; $\text{R} = \text{Cy}$ **3b**; Scheme 1).^{7g}

Scheme 1. Synthesis of bis(alkylidynyl)phosphine complexes of molybdenum and tungsten.

Despite their many similarities, the organotransition-metal chemistry of arsenic has in general been far less developed than that of phosphorus. In part this reflects well-founded concerns about its toxicity. This trend is manifest in carbyne chemistry as well – while as noted above there is an increasing number of reported phosphorus-substituted carbynes, arsenic-substituted carbynes remain exceptionally rare. In an extension of his work on phospho-alkenyl-substituted carbynes, $\text{LnM}\equiv\text{CP}=\text{CR}_2$,⁸ Weber reported the first examples of arsenic-substituted carbynes, $[\text{M}(\equiv\text{CAs}=\text{C}(\text{NMe}_2)_2)(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}, \text{W}$), *via* condensation

^a Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.

†Corresponding author: Email: a.hill@anu.edu.au

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of the chlorocarbene analogues of **1** with $\text{Me}_3\text{SiAs}=\text{C}(\text{NMe}_2)_2$.⁹ In these cases simple methylated derivatives could be prepared with $\text{MeOSO}_2\text{CF}_3$ and a remarkable trimeric arsephide derivative, $[\{(\text{Tp}^*)(\text{CO})_2\text{M}=\text{CAS}\}_3]$ formed on treatment with $\text{Au}(\text{CO})\text{Cl}$.^{8d} The only other examples of arsenic-substituted carbynes, $[\text{M}(\equiv\text{CASPh}_2)(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}, \text{W}$), were very recently prepared *via* the reaction of lithiocarbynes and BrAsPh_2 .¹⁰

Synthetic hurdles notwithstanding, we reasoned that the intermediacy of chlorobis(alkylidynyl)phosphines generated *in situ* might allow for a range of derivatives to be accessed by treatment with appropriate nucleophiles. Furthermore, the similarities and differences in phosphine and arsine reactivity led us to consider whether this strategy could be extended to give unprecedented bis(alkylidynyl)arsines. The inclusion of heteroatom junctions between two metal carbyne units is of interest with respect to the degree of intermetallic electronic communication and whether this might be ‘switched’ by chemical modification of the central heteroatom (Lewis basic/nucleophilic in the case of As^{III}). Herein we report the successful synthesis of several bis(alkylidynyl)phosphines and the first examples of bis(alkylidynyl)arsines.

The tungsten lithiocarbene **1b** reacts with half an equivalent of Cl_2PR to give bis(alkylidynyl)phosphines, $[\text{RP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\text{R} = \text{Ph}$ **2b**; $\text{R} = \text{Cy}$ **3b**; Scheme 1).^{7b} The molybdenum analogues, $[\text{RP}\{\text{C}\equiv\text{Mo}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\text{R} = \text{Ph}$ **2a**, $\text{R} = \text{Cy}$ **3a**), are now also accessible by the same procedure from **1a** and were prepared during the course of this work. If **1b** is instead treated with PCl_3 the chloro derivative, $[\text{ClP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$, is generated *in situ* although a pure sample could not be isolated due to its hydrolytic instability and tendency to convert into phospho-acyl (and other decomposition) products.^{7b} Nonetheless, treatment of a freshly generated solution of this species with phenyllithium was found to generate **2b** *via* nucleophilic substitution at phosphorus. Utilizing this strategy, a low-temperature solution of the tungsten bromocarbene **1b** was treated with *n*-butyllithium followed by 0.5 equiv. PCl_3 to give a dark red solution consistent with the predominant formation of the spectroscopically observable chlorobis(alkylidynyl)phosphine intermediate $[\text{ClP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\delta_{\text{P}} = 124.9$ ppm). Treatment of this solution with methylithium caused an immediate colour change to dark orange, and the methylbis(alkylidynyl)phosphine $[\text{CH}_3\text{P}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ (**4**, Scheme 1) was isolated following chromatographic purification of the reaction mixture. Treating the chloro-intermediate instead with *n*-BuLi gives the *n*-butyl analogue, $[\text{nBuP}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ (**5**, Figure 1). Both complexes were obtained in moderate yields as bright orange solids. The slightly superior yield of **5** may also benefit from being a product of a presumed side reaction where the initially formed monomeric $[(\text{Tp}^*)(\text{CO})_2\text{W}=\text{CPCl}_2]$ reacts with residual *n*-BuLi to give $[(\text{Tp}^*)(\text{CO})_2\text{W}=\text{CPCl}^{\text{nBu}}]$, which then proceeds to form **5** on reaction with a second equivalent of lithiocarbene. Some

Figure 1. Molecular structure of **5** in a crystal of **5**· CH_2Cl_2 showing 50% displacement ellipsoids. Hydrogen atoms and a minor disorder component are omitted and the phenyl and pyrazolyl rings are simplified for clarity. Selected bond distances (Å) and angles (°): $\text{W1}-\text{C1}$ 1.833(6), $\text{C1}-\text{P}$ 1.857(6), $\text{P}-\text{C2}$ 1.825(6), $\text{C2}-\text{W2}$ 1.822(6), $\text{P}-\text{C7}$ 1.858(17), $\text{W1}-\text{N1}$ 2.207(5), $\text{W1}-\text{N3}$ 2.311(5), $\text{W1}-\text{N5}$ 2.234(5), $\text{W2}-\text{N7}$ 2.197(5), $\text{W2}-\text{N9}$ 2.295(6), $\text{W2}-\text{N11}$ 2.223(6), $\text{W1}-\text{C1}-\text{P}$ 170.0(4), $\text{W2}-\text{C2}-\text{P}$ 151.6(5), $\text{C1}-\text{P}-\text{C2}$ 95.6(3), $\text{C1}-\text{P}-\text{C7}$ 99.1(7), $\text{C2}-\text{P}-\text{C7}$ 94.2(6). $\text{TR} = 2(\text{W1}-\text{N3})/(\text{W1}-\text{N1} + \text{W1}-\text{N5}) = 1.041$. $\text{TR} = 2(\text{W2}-\text{N9})/(\text{W2}-\text{N7} + \text{W2}-\text{N11}) = 1.038$.^{2e} Inset: View along the $\text{W1}\cdots\text{C1}$ vector and space-filling representation.

evidence for this pathway is afforded in the isolation of small amounts (*ca* 5–10%) of **5** during the syntheses of **2b** and **4** *via* this route.

To our surprise, the procedure employing an intermediary chlorobis(alkylidynyl)phosphine could *not* be extended to give the molybdenum analogues. Treatment of **1a** with *n*-BuLi followed by PCl_3 gave dark brown solutions with complex **1H** and $^{31}\text{P}\{\text{1H}\}$ NMR spectra, indicating formation of numerous undesired and unidentified products, none of which predominated. Subsequent treatment with organolithium reagents was nonetheless attempted but, while their formation cannot be ruled out, we were unable to isolate any bis(alkylidynyl)phosphine product. The distinction in reactivity between the Mo and W complexes is unclear, although anecdotally we have observed Mo carbynes to have a greater penchant towards side reactions such as dimerization¹² and, *e.g.*, formation of Templeton’s non-classical vinylidene.^{5f}

Selected spectral and structural data for the complexes described in this paper are presented in Table S1 (See ESI). Spectral data associated with the ‘ $\text{M}(\text{CO})_2(\text{Tp}^*)$ ’ fragments are reassuringly similar to those already available for carbynes with this ligand set^{2d} and hence call for little comment. In the $^{13}\text{C}\{\text{1H}\}$ spectra, the chemical shifts of carbyne carbon nuclei in **2–5** resonate at low-field positions between 290–303 ppm, comparable to the monomeric $[\text{M}(\equiv\text{CPh}_2)(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$: 309.0 ppm, $^1J_{\text{CP}} = 84$ Hz;^{7c} $\text{M} = \text{W}$: 292.6 ppm, $^1J_{\text{CP}} = 75$ Hz, $^1J_{\text{CW}} = 188$),^{7f} although in the $^{31}\text{P}\{\text{1H}\}$ spectra, the phosphorus nuclei in **2–5** resonate far further downfield (56–92 ppm) than the monomeric phosphinocarbynes ($\text{M} = \text{Mo}$: 35.5 ppm;^{8c} $\text{M} = \text{W}$: 32.0 ppm, $^2J_{\text{PW}} = 69$ Hz).^{7f}

Treatment of the lithiocarbynes **1** with half an equivalent of Cl_2AsPh furnishes the desired bis(alkylidynyl)arsines, $[\text{PhAs}\{\text{C}\equiv\text{M}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\text{M} = \text{Mo}$ **6a**; $\text{M} = \text{W}$ **6b**; Scheme 2) in good yields as orange solids following chromatographic purification. Similarly, with Cl_2AsMe the related species $[\text{CH}_3\text{As}\{\text{C}\equiv\text{M}(\text{CO})_2(\text{Tp}^*)\}_2]$ ($\text{M} = \text{Mo}$ **7a**; $\text{M} = \text{W}$ **7b**) are obtained as dark yellow solids. While these routes predetermine the third arsenic substituent, treatment of **1b** with $n\text{BuLi}$ followed by AsCl_3 gives an intensely dark red solution which is presumed to be the chlorobis(alkylidynyl)arsine intermediate, $[\text{ClAs}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ (tentatively $\delta_{\text{C}} = 296.0$ in d^8 -toluene), although we have not been successful in isolating this compound (See ESI). Subsequent treatment *in situ* with PhLi gives **6b** (25%), with MeLi gives **7b** (22%), and with $n\text{BuLi}$ gives $[n\text{BuAs}\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]$ (**8**, 27%). Employing this chloroarsino intermediate in this case results in rather poor yields, but does

in principle proffer a route that allows late installation of the final arsenic substituent that obviates dichloroarsine intermediates. We suspect, albeit without evidence, that this is due to the sensitivity of the presumed chloro-intermediate and kinetically facile access to other decomposition products. As with the phosphorus analogues, no products were isolated at all when the molybdenum lithiocarbyne was treated sequentially with AsCl_3 and an organolithium reagent.

With the exception of a minor (*ca* 10 ppm) down-field shift for the carbyne carbon resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, spectroscopic data for complexes **6–8** do not differ significantly from those of the related phosphorus species. The structures of **6a**, **6b** and **8** have been determined by X-ray crystallography, although the extensive disorder in **8** compromises the precision and comparative utility of its structural model. The molecular geometry of **6b** is shown in Figure 2, and those of **6a** and **8** are shown in Figures S3 and S5 in the ESI, respectively.

Figure 2. Molecular structure of **6b** showing 50% displacement ellipsoids. Hydrogen atoms are omitted and the phenyl and pyrazolyl rings are simplified for clarity. Selected bond distances (Å) and angles (°): W1–C1 1.808(5), C1–As 1.921(5), As–C2 1.927(5), C2–W2 1.819(5), As–C7 1.954(7), W1–N1 2.222(4), W1–N3 2.325(4), W1–N5 2.214(4), W2–N7 2.316(4), W2–N9 2.208(4), W2–N11 2.211(5), W1–C1–As 171.3(3), C1–As–C2 96.4(2), As–C2–W2 168.0(4), $\text{TR} = 2(\text{W1–N3})/(\text{W1–N1} + \text{W1–N5}) = 1.048$ $\text{TR} = 2(\text{W2–N7})/(\text{W2–N9} + \text{W2–N11}) = 1.048$.^{2e} Insets: view along the W1···C1 vector and space-filling representation.

The geometry about arsenenic is approximately trigonal pyramidal ($\Sigma^\circ(\text{As}) = 298\text{--}299^\circ$) and the C–As–C angles subtended by the two carbyne carbons are $95.7(2)^\circ$ and $96.4(2)^\circ$, respectively. The $\text{M}\equiv\text{C}$ distances (**6a**: 1.790(4), 1.809(5) Å; **6b**: 1.808(5), 1.819(5) Å; **8**: 1.835(11), 1.784(13) Å) are comparable to those of the diphenylarsinocarbynes $[\text{M}(\equiv\text{CAsPh}_2)(\text{CO})_2(\text{Tp}^*)]$ ($\text{M} = \text{Mo}$ 1.800(3); $\text{M} = \text{W}$ 1.825(5) Å)¹¹ and other reported carbynes with the $\text{Tp}^*(\text{CO})_2$ ligand set.^{2d} Minor differences in bond distances and angles in the two tungsten moieties are most likely a result of solid-state packing effects, as NMR spectroscopy indicates that the complexes are on average C_s -symmetric in solution. The carbyne carbon–arsenic bond distances (*ca* 1.92–1.95 Å) are in good agreement with the limited structural precedent available for organic ethynylarsines¹³ (e.g., tris(phenylethynyl)arsine, As–C 1.907(6) Å, $\Sigma^\circ(\text{As}) = 289^\circ$),^{13c} and those calculated (B3YLP-LANL2DZ) for $\text{MeAs}(\text{C}\equiv\text{CH})_2$ (As–C $\equiv$ 1.918, As–C(Ph) 1.998 Å; $\equiv\text{C}\text{--As}\text{--C}\equiv$ 98.3°).

In conclusion, we report two synthetic routes which now allow a range of bis(alkylidynyl)phosphines and arsines to be prepared. Treatment of the lithiocarbynes $[(Tp^*)(CO)_2M\equiv Cl]^-$ ($M = Mo, W$) with one half equivalent of dichlorophosphines, Cl_2PR , or arsines, Cl_2AsR , furnishes the respective bis(alkylidynyl)phosphine or arsine, with the third phosphorus or arsenic substituent determined by the group "R" ($R = Ph, Cy, Me$). Alternatively, treatment of the tungsten lithiocarbyne with PCl_3 or $AsCl_3$ furnishes chlorobis(alkylidynyl)phosphine or arsine intermediates, respectively. While these halo derivatives were too sensitive to isolate, they serve as intermediates to stable alkyl and aryl derivatives. This promising result implies that other, more complex, derivatives might also be prepared with useful functionalities installed on a phosphorus or arsenic bridging two transition-metal carbynes – a matter we are presently exploring

Conflict of interest

The authors declare no conflicts of interest.

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