The significance of phosphonocarbynes in halocarbyne cross-coupling reactions

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Competent intermediates in palladium(0)-copper(I) mediated catalytic cross coupling reactions of the bromocarbyne complex $[W(\equiv CBr)(CO)_2(Tp^*)]$ (Tp^* = hydrotris(dimethylpyrazolyl)borate) have been isolated however heterobimetallic phosphonocarbyne complexes $[WPd(\mu-CPPH_3)Br(CO)_2(PPh_3)_x(Tp^*)]$ are identified as productive ($x = 1$) or non-productive ($x = 0$) tangents to the catalytic cycle.

Lalor's halocarbynes $[M(\equiv CX)(CO)_2(Tp^*)]$ ($M = Mo, X = Cl, Br$ **1a**; $M = W, X = Cl, Br$ **1b**; Tp^* = hydrotris(dimethylpyrazolyl)borato)¹ are highly versatile precursors to a range of novel carbyne complexes not otherwise accessible via conventional strategies. Functionalisation may involve one of three possible approaches, (a) Spontaneous nucleophilic halide substitution;^{1,2} (b) palladium(0) mediated nucleophilic halide substitution (Scheme 1);³ or (c) lithium-halogen exchange (ⁿBuLi) to afford $[M(\equiv CLi)(CO)_2(Tp^*)]$ ($M = Mo, W$) for subsequent reaction with electrophiles.⁴

Scheme 1. Selected palladium(0)-mediated cross coupling reactions of $[M(\equiv CBr)(CO)_2(Tp^*)]$ ($M = Mo$ **1a**, W **1b**);³ (i) $[Pd(PPh_3)_4]$, HPO_3Et_2 , Et_3N ; (ii) $[Pd(PPh_3)_4]$, H_2PR , Et_3N , $R = Ph, Cy$; (iii) $[Pd(PPh_3)_4]$, $[RuAu(\mu-C_4)(PPh_3)(dppe)(Cp^*)]$, CuI , Et_3N . (iv) $Me_3SiC\equiv C\equiv C\equiv C-SiMe_3$, $[Pd(PPh_3)_4]$, CuI , Et_3N .

The Pd^0 -mediated protocols most likely proceed *via* C–Br oxidative addition, nucleophilic bromide metathesis and reductive elimination sequences and support for the first such step is provided by Beck's spectroscopic characterisation of the μ -carbido complex $[MoPt(\mu-C)Br(CO)_2(PPh_3)_2(Tp^*)]$ (**2a**)⁵ *cf.* the structurally characterised complex $[WNi(\mu-C)Cl(CO)_2(PEt_3)_2(Tp^*)]$ (**3**), obtained from $[W(\equiv CLi)(CO)_2(Tp^*)]$ and $[NiCl_2(PEt_3)_2]$.⁶ This latter complex is thermally unstable and evolves under ambient conditions to $[WNi(\mu-CPEt_3)Cl(CO)_2(PEt_3)(Tp^*)]$ (**4**), the only known example of a heterobimetallic phosphonocarbyne complex. A small number of homometallic μ -phosphonocarbynes have, however, arisen from the reactions of phosphorus ylides with high-valent metal centres.⁷ The formation of **4** is relevant to Pd^0 -mediated P–C cross coupling reactions for the formation of *phosphonito* and *phosphino*-carbynes,^{3c-e} some of which, *e.g.*, secondary phosphino derivatives $[W(CPHR)(CO)_2(Tp^*)]$ ($R = Cy, Ph$) are not accessible via the alternative reactions of $[W(\equiv CLi)(CO)_2(Tp^*)]$ with halophosphines.⁴

Recently, we have demonstrated that Pd^0/Cu^I -mediated cross coupling protocols are effective for the formation of novel propargylidyne complexes⁸ and the first pentadiynylidyne complex⁹ via reactions of **1b** with 1-alkynes and 1,3-diynes. To better understand the catalytic manifold, we have now explored the stoichiometric reactions of **1a** and **1b** with zerovalent group 10 metal complexes. In so doing, we have now isolated μ -carbido complexes that are also competent entry points to the catalytic cycle, in addition to characterising catalytically *inactive* phosphonocarbyne complexes that represent irreversible termination points.

Heating **1b** with $[Pt(PPh_3)_4]$ results in the high yield formation of the heterobimetallic μ -carbido complex $[WPt(\mu-C)Br(CO)_2(PPh_3)_2(Tp^*)]$ (**2b**, 77%, Scheme 2, Figure 1). Complex **2b** adheres to the Class B,^{2m,4b,c,5,6,10,11} 'metallacarbyne' valence bond description rather than the more commonly encountered symmetrical Class A dimetallacumulene scenario. The $W\equiv C$ and $Pt-C$ separations fall within norms for triple¹² and single¹³ bonds, respectively, and the geometry at platinum may be described as d^8 -square planar. Comparison of the $Pt-Br$ bond length (2.5274(7) Å) with that observed for $[Pt(C\equiv CMe_2O_2H)Br(PPh_3)_2]$ (2.478(1) Å)¹³ might suggest that the μ -carbido exerts a more pronounced *trans* influence than a conventional alkynyl. The juxtaposition of the bulky phosphine and Tp^* ligands results in rotamers being observed in the NMR spectra (see Table 1 and ESI) at room temperature.

Table 1. Selected spectroscopic and structural data for μ -carbido and μ -phosphoniocarbonyl complexes (M = Mo, W; M' = Pd, Pt).

	δ_{C} ppm	$^1J_{\text{PC}}$ Hz	δ_{Pt} ppm	δ_{P} ppm	$^1J_{\text{PTP}}$ Hz	$^2J_{\text{PP}}$ Hz	r_{MeC} Å	$r_{\text{C-M'}}$ Å	$\angle_{\text{MCM'}}$ °
2a^d	339.0	6	-3810 ^e	23.8 ^c	3197	438	1.828(3) ^d	1.951(3)	174.0(2)
		9		19.4	3206				
2b^e	318.6	<i>g</i>	-3718	27.0	3202	443	1.856(6)	1.934(6)	169.2(3)
	317.1	<i>g</i>	-3821	23.3	3187	444	-	-	-
				23.9					
2c	353.8	<i>g</i>	-	25.9	-	423	-	-	-
				20.7					
2d	333.3	<i>g</i>	-	23.6	-	428	-	-	-
				28.5					
5a	330.8	<i>g</i>	-	26.2	-	-	1.808(6)	1.922(6)	166.1(3)
							1.805(6)	1.923(6)	166.5(3)
6^b	375.9	70	-	46.0		31	1.79(1) ⁱ	2.01(1)	167.9(8)
		8		35.5					
7ⁱ	<i>b</i>	<i>g</i>	-	13.4 ⁱ		<i>g</i>	1.962(6)	2.016(6)	86.5(3)
				10.7	-	<i>g</i>			
8	232.1	<i>g</i>	-	7.18	-	-	1.913(5)	2.014(5)	88.0(2)
[9]⁺	241.6	<i>g</i>	-	10.2	-	-	-	-	-

^a NMR Measured in C₆D₆. ^b Not observed. ^c $^2J_{\text{PP}}$ not reported. ^d Data from this work, see also ref. 5. ^e Measured in CDCl₃. ^f $^2J_{\text{PP}}$ = 443 Hz. ^g Not resolved. ^h Measured in CD₂Cl₂. ⁱ Imprecise structure determination. ^j Excess PPh₃ present.

Scheme 2. Synthesis of Class B μ -Carbido and phosphoniocarbonyl complexes. (i) [Pd₂(dba)₃]; (ii) [M(PPh₃)₄]. *Crystallographically characterised

Beck's complex [MoPt(μ -C)Br(CO)₂(PPh₃)₂(Tp*)] (**2a**) could also be prepared directly from [Pt(PPh₃)₄] (rather than *via* [Pt(η -C₂H₄)(PPh₃)₂]) and was also structurally characterised (see ESI) and although the geometry is superficially similar to **2b**, the Pt1–Br1 bond length is considerably elongated (2.5448(3) Å). In a similar manner, the reaction of [Mo($\equiv$ CBr)(CO)₂(Tp*)] (**1b**) with [Pd(PPh₃)₄] results in a spectroscopically observable complex [MoPd(μ -C)Br(CO)₂(PPh₃)₂(Tp*)] (**2c**), which also exists as a pair of two rotamers (*ca* 10:1) and although full spectroscopic characterisation was possible, attempts to slowly obtain crystallographic grade crystals resulted in phosphine loss

and formation of the tetrametallic halide-bridged dimer [Mo₂Pd₂(μ -C)₂(μ -Br)₂(PPh₃)₂(Tp*)₂] (**5a**). The characterisation of **5a** included crystallographic analyses (Figure 2) which confirmed the tetrametallic nature and that the Pd–Br bonds *trans* to the carbido were significantly lengthened *cf.* those *trans* to phosphine. These halide bridges could be readily cleaved, e.g., by 1,2-bis(diphenylphosphino)ethane (dppe) to afford the complex [MoPd(μ -C)Br(CO)₂(dppe)(Tp*)] (**6**), the connectivity of which was confirmed by an imprecise crystallographic determination (*R*₁ = 0.096, see ESI).

Figure 1. Molecular structure of **2b** in a crystal (50% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Pt1–Br1 2.5274(7), Pt1–P1 2.3265(12), Pt1–P2 2.3256(12), Pt1–C1 1.934(6), W1–C1 1.856(6), W1–C1–Pt1 169.2(3), C1–Pt1–Br1 169.19(15), P2–Pt1–P1 160.28(5). Insets = view along Br1–Pt1 vector and space filling representation indicating steric clash between Tp* (green) and phosphine (orange) ligands.

Attempts to isolate the corresponding tungsten-palladium analogue **2d** (or **5b**), implicated in Pd⁰/Cu^I-mediated cross couplings led to a surprising result. In non-polar solvents such as benzene or toluene, the analogous tetrametallic complex [W₂Pd₂(μ -C)₂(μ -Br)₂(PPh₃)₂(Tp*)₂] (**5b**) most likely forms but did not accumulate in spectroscopically observable quantities. When, however, crude **2d** was dissolved in chloroform, a subsequent slow rearrangement occurred leading to two different new heterobimetallic phosphoniocarbonyl complexes, [WPd(μ -C)Br(CO)₂(PPh₃)_n(Tp*)] (*n* = 1 **7** Figure 3, *n* = 0 **8** Figure 4) which exist in an equilibrium that initially confounded interpretation of the ³¹P{¹H} NMR data for the mixture. Remarkably, **7** and **8** differ only in the presence or absence of a

Figure 2. Molecular structure of **5a** in a crystal (50% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Pd1–Br1 2.5653(8), Pd1–Br2 2.5046(8), Pd1–P1 2.2675(15), Pd1–C1 1.922(6), Pd2–Br1 2.5100(8), Pd2–Br2 2.5668(8), Pd2–P2 2.2676(15), Pd2–C2 1.923(6), Mo1–C1 1.808(6), Mo2–C2 1.805(6), Mo1–C1–Pd1 166.1(3), Mo2–C2–Pd2 166.5(3). A dichloromethane solvate was also structurally characterised (see ESI).

phosphine ligand coordinated to palladium and the resonance due to the free phosphine is broad indicating participation in the dynamic process. Accordingly, the phosphoniocarbene salt $[W(\equiv CPh_3)(CO)_2(Tp^*)]Br$ **[9]**Br was prepared *via* the reaction of **1b** with PPh_3 in refluxing acetonitrile¹⁴ and treated with $[Pd_2(dba)_3]$ to provide a sample of **8** devoid of adventitious phosphine. Consequently, the $^{31}P\{^1H\}$ NMR spectrum of pure **8** comprised a sharp resonance ($\delta_P = 7.18$, $^2J_{WP} = 128$ Hz), but on addition of an equivalent (or more) of PPh_3 , the equilibrium with **7** was re-established. The phosphoniocarbene resonance for (**8**) appears at $\delta_C = 232.1$ in the $^{13}C\{^1H\}$ NMR spectrum but was not located for **7** due to dynamic processes.

Figure 3. Molecular structures of **7** in a crystal (50% displacement ellipsoids, hydrogen atoms omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°): W1–Pd1 2.7271(5), W1–C1 1.962(6), W1–C2 1.998(6), W1–C3 2.018(7), Pd1–C1 2.016(6), Pd1–C2 2.598(6), Pd1–C3 2.571(6), Pd1–Br1 2.5461(7), Pd1–P2 2.3670(16), P1–C1 1.724(6), W1–C1–Pd1 86.5(3), P1–C1–W1 143.0(3), P1–C1–Pd1 130.4(3), O1–C2–W1 171.9(5), O2–C3–W1 169.4(5). Inset shows view along the Pd1–W1 vector.

The molecular structure of complex **7** (Figure 3) is related to the previously described tungsten-nickel complex **4**,⁶ however complex **8** is noteworthy for the low-coordination number adopted by palladium. Zwitterionic canonical descriptions of both **7** and **8** (Scheme 2) place a negative charge on zerovalent palladium, consistent with the presence of charge-compensating semi-bridging carbonyl ligands.

The coordination of a metal-carbon triple bond to a second metal invokes a dimetallacyclopropene description which for electron counting purposes provides two valence electrons to the appended metal, *cf.* isolobally related alkyne coordination. In the event that the metal remains coordinatively unsaturated (as in **8**), the metal-carbon triple bond provides a further pair of electrons from the π -bond orthogonal to the dimetallacyclopropene ring, *cf.* isolobally related 4-electron alkyne coordination.¹⁵ Structural data for the two complexes **7** and **8** therefore provide a useful dichotomy through which to explore this question. Removal of the phosphine from **7** to afford **8** results in a pronounced lengthening (*ca* 0.05 Å) of the

W–C multiple bond as bonding electron density is delocalised towards palladium, while the Pd–C and Pd–W bonds remain unchanged. This lengthening of the W–C bond is accompanied by a modest straightening of the W–C–P angle from 143.0(3) to 152.8(3)°, which is most likely a simple corollary of the reduced coordination number at palladium but also consistent with semi-bridging character.¹⁶

Figure 4. Molecular structures of **8** in a crystal of **8**·(CHCl₃)₃ (50% displacement ellipsoids, hydrogen atoms omitted, phenyl groups simplified). Selected bond lengths (Å) and angles (°): W1–Pd1 2.7290(4), W1–C2 2.022(5), W1–C1 1.913(5), W1–C3 2.009(6), Pd1–Br1 2.4765(6), Pd1–C2 2.164(5), Pd1–C1 2.014(5), P1–C1 1.748(5), C1–Pd1–Br1 133.16(13), W1–C1–Pd1 88.00(19), P1–C1–W1 152.8(3).

Returning to the role these various species play in Pd⁰-mediated reactions, it could be demonstrated that **2d** could replace $[Pd(PPh_3)_4]$ as a pro-catalyst resulting in similar activities to those observed for $[Pd(PPh_3)_4]$ mediating the formation of $[W(\equiv C-C\equiv CR)(CO)_2(Tp^*)]$ ($R = SiMe_3$, Ph) from **1a** and $HC\equiv CR$ (Table S1, ESI). In contrast, while the complex **7** displayed modest but inferior activity most likely resulting from degradation to liberate phosphine-ligated Pd⁰ species, the complex **8** was not active. Furthermore, the phosphonium salts **[9]X** ($X = Br, PF_6$) as substrates *do not* provide propargylidynes under these standard conditions. Thus formation of **8** and **[9]**⁺ represent detrimental tangents to the catalytic cycle (Scheme 3), which however do not compete appreciably under the standard mild conditions and a phosphine ligand is required for palladium(0) to participate in the catalytic cycle.

In conclusion, a significant number of new Class B μ -carbido complexes has been isolated and these have been confirmed as key competent species in the Pd⁰-mediated cross-coupling reactions of bromocarbynes. The catalytic cycle (Scheme 3) is however somewhat more complicated due to tangential exits arising from carbido-phosphine coupling to afford catalytically inactive phosphoniocarbene complexes that display varying degrees of coordinative unsaturation. Together these results demonstrate not only the fundamental interest of μ -carbido complexes but also their practical significance.

Scheme 3. Catalytic cycle for propargylidyne synthesis. Productive catalysis in green, termination in red. [W] = W(CO)₂(Tp*)

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