COMMUNICATION

Synthesis of pyridyl carbyne complexes and their conversion to *N*-heterocyclic vinylidenes

R/

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

A new synthetic approach to hetero-aryl substituted carbyne complexes has allowed the synthesis of pyridyl functionalised carbynes and bis(carbynes), alkylation of which affords the first *N*-heterocyclic vinylidene complexes.

The vast majority of simple aryl-substituted carbyne complexes are available *via* either Fischer's seminal oxide/alkoxide-abstraction routes¹ or Schrock's α -metal-hydride elimination² or alkyne scission/metathesis³ protocols. Given the centrality of carbynes to alkyne metathesis processes, it is not surprising that the major focus has been on carbynes with hydrocarbon substituents.⁴ Our own interest in carbyne complexes has been concerned with employing the metal-carbon multiple bond as a 'solder' for connecting metal centres *via* electronically conductive bridging ligands,⁵ within the broader context of so-called molecular wires.⁶ One such approach, explored by Hopkins, has involved incorporating 4-pyridyl groups.⁷ An oligomeric 4-lutidinylcarbyne complex was obtained *via* scission of 4-butynyl lutidine (Chart 1a) while coupling of a 4-ethynyl benzylidene with 4-bromopyridine allowed late introduction of a pyridyl group (Chart 1b). Finally, a phenanthroline substituted carbyne complex (Chart 1c) was recently isolated from the direct attack of a lithiocarbyne on a platinum coordinated phenanthroline ligand.⁸ The formation of this last example is specific to the platinum precursor and accordingly, we have entertained the possibility of preparing uncoordinated pyridyl-functionalised carbynes *via* a synthetic approach that might offer more generality. The Fischer route is inappropriate because it involves treating an acylate or alkoxycarbene with strong Lewis acids (*e.g.*, BBr₃, [Me₃O]BF₄, (CF₃CO)₂O, O₂C₂Cl₂, OSOCl₂ etc.) that are incompatible with a pyridyl group. Similarly,

Chart 1. Pyridyl or phenanthroline functionalised carbynes.

α -elimination strategies call for coordinatively unsaturated metal centres that are typically deactivated by pyridine coordination. We report herein a new method for the preparation of (hetero)aryl carbynes, illustrating the protocol with the synthesis of mono- and bis(carbyne)functionalised pyridines, which themselves provide access to the first examples of *N*-heterocyclic vinylidene complexes.

Heating the stannylcarbyne complex $[\text{W}(\equiv\text{CSn}^t\text{Bu}_3)(\text{CO})_2(\text{Tp}^*)]$ (**1**)^{9,10} with 2-bromopyridine in the presence of $[\text{Pd}(\text{PPh}_3)_4]$ and $[\text{AuCl}(\text{SMe}_2)]$ in toluene provides the 2-pyridylcarbyne $[\text{NC}_5\text{H}_4\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}-2]$ (**2**, Scheme 1, Figure 1) in good yield (71%, Scheme 1). Notably, no reaction occurs at all in the absence of the gold(I) additive from which it may be inferred that transmetalation from tin to gold must occur *en route* to Pd(II). Indeed, reaction of **1** with $[\text{AuCl}(\text{SMe}_2)]$ alone gives the octametallic carbido ring $[\text{W}(\equiv\text{CAu})(\text{CO})_2(\text{Tp}^*)]_4$.^{9a} The role of the gold(I) additive is reminiscent of the "copper effect," whereby a copper(I) additive significantly increases the rate of traditional Stille coupling reactions.¹¹ A comparable effect with gold(I) co-catalysts has also been noted recently and has been found especially useful for the coupling of bulky groups which are otherwise unreactive under conventional Stille coupling conditions.¹² This protocol is not limited to monosubstitution such that the reaction of **1** with half an equivalent of 2,6-dibromopyridine with the same catalyst loadings furnishes the 2,6-bis(carbyne)pyridine complex $[\text{NC}_5\text{H}_3\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2-2,6]$

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

* Corresponding author. E-mail: a.hill@anu.edu.au

CCDC 1955818–1955824 contain the supplementary crystallographic data for this paper and are available free of charge from The Cambridge Crystallographic Data Centre.

Scheme 1. Synthesis of pyridyl-substituted carbynes via Pd(0)/Au(I)-catalysed cross-coupling reactions.

(**3**, Scheme 1). Longer reaction times (14 hours, toluene reflux) and reduced 45% yield presumably reflect the unfavorable steric congestion attending close proximity of the bulky Tp^* ligands. Selected spectroscopic and structural data for **2**, **3** and all other new compounds reported herein are presented in Table 1.

Table 1. Selected spectroscopic and structural data for **2–10**.

	δ_{C} ^a	$^1J_{\text{CW}}$ ^b	r_{WC} ^c	$\angle_{\text{WC-C}}$ ^d	ν_{CO} ^e
2	275.9	190	1.810(7)	167.8(7)	1981, 1889
3	276.7	191			1980, 1890
[4]⁺	260.3	— ^f			2010, 1924
[5]⁺	251.5	— ^f	1.843(7)	168.9(6)	2010, 1925
[6]⁺	251.5	190	1.820(3)	173.9(3)	2009, 1922
[7]⁺	251.9	199	1.810(11) 1.820(11)	175.3(9) 169.1(9)	2006, 1923
8	262.1	— ^f	1.929(15)	151.9(12)	2016, 1933
9	260.8	95	1.894(13) 1.922(11)	149.0(10) 149.2(8)	2015, 1942
10	265.8	205	1.799(7)	170.1(6)	2005, 1988, 1916, 1897

^a Measured in CDCl_3 (ppm). ^b Measured in CDCl_3 (Hz). ^c (Å). ^d (°). ^e Measured in CH_2Cl_2 (cm^{-1}). ^f Too broad or poor signal-to-noise to determine coupling constants.

Figure 1. Molecular structure of **2** in a crystal of **2**· CH_3CN (50% displacement ellipsoids, pyrazolyl groups simplified and solvent omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.810(7), C1–C4 1.463(10), C4–C5 1.397(11), C5–C6 1.408(11), C6–C7 1.378(14), C7–C8 1.387(13), C8–N7 1.345(10), N7–C4 1.363(11), W1–C1–C4 167.8(7).

The NMR data for **2** and **3** are consistent with the wealth of those reported for carbynes ligated by poly(pyrazolyl)borates,^{4c} featuring typical Tp^* and pyridyl signatures. The carbyne carbon nuclei resonate at $\delta_{\text{C}} = 275.9$ ($^1J_{\text{CW}} = 190$) and 276.7 ($^1J_{\text{CW}} = 191$

Hz), respectively, close to that of the simple benzyldiyne analogue $[\text{W}(\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]$ (277.9 ppm, $^1J_{\text{CW}} = 187$ Hz).¹³ The molecular structure of **2** (Figure 1) reveals that the $\text{W}\equiv\text{C}$ (1.810(7) Å) and $\text{C}-\text{C}$ (1.463(10) Å) distances associated with the carbyne unit are indicative of localised triple and single bonding, respectively.

The pyridyl nitrogens of both **2** and **3** are protonated by strong acids and on addition of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ the simple derivatives $[\text{HNC}_5\text{H}_4\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]\text{BF}_4$ [**4**] BF_4 and $[\text{HNC}_5\text{H}_3\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2\text{-2,6}]\text{BF}_4$ [**5**] BF_4 , respectively, are prepared in good yields (Scheme 2). Protonation is readily reversed by treatment with bases such as NEt_3 to return the precursors essentially quantitatively. Complex [**4**]⁺ appears empirically to be far more susceptible towards deprotonation and even washing a solid sample with diethyl ether or *n*-pentane begins to effect deprotonation. Accordingly, NMR spectroscopy was conducted in the presence of a slight excess of $\text{HBF}_4\cdot\text{Et}_2\text{O}$. Both complexes **2** and **3** are irreversibly methylated by methyl trifluoromethanesulfonate to afford $[\text{MeNC}_5\text{H}_4\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2]\text{O}_3\text{SCF}_3$ [**6**] O_3SCF_3 and $[\text{MeNC}_5\text{H}_3\{\text{C}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)\}_2\text{-2,6}]\text{O}_3\text{SCF}_3$ [**7**] O_3SCF_3 , respectively, in equally good yields.

Scheme 2. Protonation and methylation reactions of pyridyl-substituted carbynes.

Protonation and methylation is accompanied by an increase of *ca* 30 cm^{-1} in the carbonyl stretching frequencies in the infrared spectra of **4–7**, consistent with a reduction in electron density at the tungsten metal centre compared to their precursors. The carbyne carbon resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are shifted marginally (15–25 ppm) up-field. Together these data might suggest a contribution from canonical forms which locate the positive charge at tungsten (e.g., the vinylidene representation for [**6**]⁺ Chart 2b). Vinylidene complexes bearing nitrogen substituents are rare, being limited to the salts $[\text{Ru}\{\text{C}=\text{CPh}(\text{N}=\text{NC}_6\text{H}_3\text{Me}_2)(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)\}]\text{BF}_4$ ¹⁴ and $[\text{W}\{\text{C}=\text{C}(\text{NHCH}_2\text{Ph})_2\}(\text{CO})_2(\text{Tp}^*)]\text{PF}_6$ ($\delta_{\text{C}} = 248.1$; $\nu_{\text{CO}} = 2020$, 1936 cm^{-1}) for which descriptions as an amidinium carbyne or

N-acyclic carbene-stabilised carbonium complex have been suggested.¹⁵ The latter draws analogy with phosphoniocarbynes¹⁶ and the pyridinium carbyne [Mo(CNC₅H₄NMe₂-4)(CO)₂(Tp*)]⁺ ($\delta_{\text{C}} = 214.1$; $\nu_{\text{CO}} = 2012, 1929$ cm⁻¹, Mo≡C = 1.807(4) Å).¹⁷ Whilst technically [4]⁺–[7]⁺ provide the first examples of *N*-heterocyclic vinylidene complexes, the structural data collected for 5–7 (Figures S1–S2 in the ESI and Figure 2, respectively) do not, however, provide compelling support for this notion. The tungsten–carbon distances are not significantly elongated compared to 2, nor are the C_{carbyne}–C_{pyridyl} distances markedly shortened. Thus canonical forms (a) and (c) would each appear to provide useful contributions to the bonding description.

Figure 2. Molecular structure of the cation of [7]⁺ in a crystal of [7]O₃SCF₃·(CHCl₃)_{2.5} (50% displacement ellipsoids, one of two crystallographically independent molecules shown, pyrazolyl groups simplified and solvent and anion omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.810(11), C1–C4 1.445(14), C8–C10 1.436(15), C10–W2 1.820(11), W1–C1–C4 175.3(9), W2–C10–C8 169.1(9). Inset: space-filling diagram with the (Tp*)(CO)₂W' units coloured green and blue.

Chart 2. Canonical forms for a pyridinium carbyne complex [6]⁺ and related 'carbonium' species. (a) Carbyne; (b) *N*-heterocyclic vinylidene; (c) NHC-stabilised carbonium.

Alternative sites of the (alkylidynyl)pyridines 2 and 3 are potentially available for metal coordination. Selected metal centres readily coordinate to the tungsten–carbon triple bond and treatment with [AuCl(SMe₂)] (a reagent with demonstrated proclivity for M≡C bonds^{5b,18}) results in coordination of 'AuCl' across the multiple bond. This occurs once for 2 to give the heterobimetallic derivative [NC₅H₃{CWAuCl(CO)₂(Tp*)}-2] (8) and twice for 3 to give the trimetallic complex [NC₅H₃{CWAuCl(CO)₂(Tp*)}-2,6] (9) (Scheme 3). Coordination of the gold(I) fragments results in a minor (*ca* 10 ppm) up-field shift in the carbyne carbon resonance in the ¹³C{¹H} NMR spectra and a halving of the ¹J_{CW} coupling constants, consistent with a reduction in the *s*-character of the tungsten–carbon bonds. The geometries of both complexes have been structurally authenticated (Figures S3 and S4 in the

Scheme 3. Addition of gold(I) and platinum(II) reagents to complexes 2 and 3.

ESI). The two gold units in 9 orient away from each other and do not support an *aurophilic* Au⋯Au interaction¹⁹ such as those observed previously in carbynes bridged by single phosphorus^{16b} or tellurium²⁰ atoms; presumably they are held too remotely for this to occur.

The pyridyl nitrogen is also capable of coordinating to metal centres and on treatment of 2 with K[PtCl₃(C₂H₄)]·H₂O (Zeise's salt), a chloride ligand on platinum is displaced and the heterobimetallic complex [Cl₂(η-C₂H₄)PtNC₅H₄{C≡W(CO)₂(Tp*)}-2] (10) is formed. In this complex the otherwise typically labile ethene ligand is retained and is located *trans* to the pyridyl nitrogen. The ¹H and ¹³C{¹H} NMR spectra are not profoundly influenced by Pt(II) coordination beyond the appearance new resonances at $\delta_{\text{H}} = 4.63$ and $\delta_{\text{C}} = 75.9$ in their respective spectra due to the platinum-bound ethene H₂C=CH₂ ligand. Their observation as singlets devoid of observable ¹⁹⁵Pt satellites is most likely a product of a rapid fluxional process; the dynamics of Pt(II) olefin complexes is well-documented.²¹ The carbyne carbon nuclei in 10 resonate *ca* 10 ppm further up-field upon Pt(II) coordination compared to 2 and the platinum centre gives rise to a broad resonance at $\delta_{\text{Pt}} = -2864$ ppm in the ¹⁹⁵Pt NMR spectrum.

The molecular structure of 10 (Figure 3) provides further confirmation of pyridyl *N*-coordination to Pt(II) and retention of the ethene ligand. The W≡C and C1–C4 distances are crystallographically identical to those of the precursor 2, indicating that metal coordination in this site has at best a very minor influence on the structure of the alkylidyne motif. The ethylene ligand aligns approximately with the W≡C axis, between the two carbonyl ligands on W such that the two ends of the olefin are inequivalent in the solid state. NMR spectroscopy confirms that this conformation is not rigidly maintained in solution. Structural parameters associated with the platinum fragment are in good agreement with the small number of other reported [Pt^{II}(C₂H₄)L₃] complexes.²² The pyridyl–platinum interaction is rather labile and addition of one equivalent triphenylphosphine rapidly results in displacement and quantitative recovery of 2. Attempts to prepare derivatives with two equivalents of 2 coordinated to

Figure 3. Molecular structure of **10** (50% displacement ellipsoids, pyrazolyl groups simplified for clarity). Selected distances [Å] and angles [°]: W1–C1 1.799(7), C1–C4 1.452(10), N7–Pt1 2.067(6), Pt1–C9 2.144(9), Pt1–C10 2.142(9), Pt1–Cl1 2.294(2), Pt1–Cl2 2.294(2), W1–C1–C4 170.1(6), N7–Pt1–C9 160.5(4), N7–Pt1–C10 162.1(4), N7–Pt1–Cl1 89.07(17), N7–Pt1–Cl2 90.05(17).

platinum by treatment of **2** with half an equivalent of $K[PtCl_3(C_2H_4)] \cdot H_2O$ (40 °C, 1:1 CH_2Cl_2 :ethanol), provided an orange-brown solid, however the 1H NMR spectroscopic data was exceptionally broadened, even down to –50 °C, and single crystals proved elusive. A yellow-brown product was also obtained when **3** was treated with one equivalent of Zeise's salt (RT, 1:1 CH_2Cl_2 :ethanol) but this compound also manifested 1H NMR broadening and aversion to crystallisation. Thus, while initially promising, unequivocal characterisation of these two products remains an ongoing challenge. In both cases, rapid fluxional processes are likely to be occurring. In the latter case, the steric bulk about the pyridyl nitrogen (see inset, Figure 2) might contribute to the increase in lability compared to **10**.

In conclusion, the synthesis of 2-pyridylcarbynes has been achieved *via* the Pd^0/Au^I -mediated coupling of stannyl carbynes with 2-bromopyridine or 2,6-dibromopyridine. This strategy promises considerable generality for installing a wide range of previously inaccessible, functional substituents on metal carbynes. These may, in turn, ultimately find use in a range of applications by virtue of their potentially 'switchable' influence on electronic, optical or physical properties as exemplified here by reversible protonation or metal coordination, including the synthesis of the first examples of *N*-heterocyclic vinylidenes. The scope and properties of new complexes prepared by this strategy are the subject of ongoing research on which we will report subsequently.

Acknowledgements

We gratefully acknowledge the Australian Research Council (DP170102695 and DP190100723) for funding. The authors declare no conflicts of interest.

Notes and references

- (a) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 564-565.

- (a) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 2935-2935. (b) R. R. Schrock, *Chem. Rev.*, 2002, **102**, 145-180. (c) R. R. Schrock, *Chem. Commun.*, 2005, 2773-2777.
- M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74-83.
- (a) C. Shi and G. Jia, *Coord. Chem. Rev.*, 2013, **257**, 666-701. (b) L. M. Caldwell, *Adv. Organomet. Chem.*, 2008, **56**, 1-94.
- (a) A. F. Hill and R. A. Manzano, *Angew. Chem., Int. Ed.*, 2019, **58**, 15354-15357. (b) A. R. Delaney, B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2019, **48**, 13674-13684. (c) R. D. Dewhurst, A. F. Hill and A. C. Willis, *Organometallics*, 2005, **24**, 13, 3043-3046. (d) R. D. Dewhurst, A. F. Hill and M. K. Smith, *Angew. Chem., Int. Ed.*, 2004, **43**, 476-478. (e) A. F. Hill and R. A. Manzano, *Angew. Chem., Int. Ed.*, 2019, **58**, 7357-7360.
- (a) D. C. Milan, A. Vezzoli, I. J. Planje and P. J. Low, *Dalton Trans.*, 2018, **47**, 14125-14138. (b) Y. Tanaka, M. Kiguchi and M. Akita, *Chem. Eur. J.*, 2017, **23**, 4741-4749.
- (a) T. P. Pollagi, S. J. Geib and M. D. Hopkins, *J. Am. Chem. Soc.*, 1994, **116**, 6051-6052. (b) D. B. Moravec and M. D. Hopkins, *J. Phys. Chem., A*, 2013, **117**, 1744-1755.
- B. J. Frogley and A. F. Hill, *Chem. Commun.*, 2019, **55**, 12400-12403.
- (a) E. S. Borren, A. F. Hill, R. Shang, M. Sharma and A. C. Willis, *J. Am. Chem. Soc.*, 2013, **135**, 4942-4945. (b) A. Reinholdt, J. Bendix, A. F. Hill and R. A. Manzano, *Dalton Trans.*, 2018, **47**, 14893-14896.
- R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 5177-5179.
- (a) L. S. Liebeskind and R. W. Fengl, *J. Org. Chem.*, 1990, **55**, 5359-5364; (b) S. P. H. Mee, V. Lee and J. E. Baldwin, *Angew. Chem. Int. Ed.*, 2004, **43**, 1132-1136.
- J. del Pozo, D. Carrasco, M. H. Pérez-Temprano, M. García-Melchor, R. Álvarez, J. A. Casares and P. Espinet, *Angew. Chem. Int. Ed.*, 2013, **52**, 2189-2193.
- K. C. Stone, G. M. Jamison, P. S. White and J. L. Templeton, *Inorg. Chim. Acta*, 2002, **330**, 161-172.
- I. R. Whittall, M. P. Cifuentes, M. J. Costigan, M. G. Humphrey, S. C. Goh, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1994, **471**, 193-199.
- K. Helmdach, J. Ruger, A. Villinger and W. W. Seidel, *Chem. Commun.*, 2016, **52**, 2616-2619.
- (a) G. M. Jamison, P. S. White and J. L. Templeton, *Organometallics*, 1991, **10**, 1954-1959. (b) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, 2017, **46**, 4355-4365. (c) A. L. Colebatch, A. F. Hill and M. Sharma, *Organometallics*, 2015, **34**, 2165-2182.
- R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 4532-4540.
- (a) G. A. Carriedo, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597-1603. (b) G. A. Carriedo, V. Riera, G. Sánchez and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1988, 1957-1962. (c) C. E. Strasser, S. Cronje and H. G. Raubenheimer, *New J. Chem.*, 2010, **34**, 458-469; (d) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, 2017, **46**, 4355-4365; (e) B. J. Frogley, A. F. Hill and C. S. Onn, *Dalton Trans.*, 2019, **48**, 11715-11723; (f) B. J. Frogley and A. F. Hill, *Angew. Chem. Int. Ed. Engl.*, 2019, **58**, 8044-8048.
- H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370-412.
- B. J. Frogley, A. F. Hill, R. A. Manzano and M. Sharma, *Chem. Commun.*, 2018, **54**, 1702-1705.
- T. A. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801-3812.
- (a) W. C. Deese, D. A. Johnson and A. W. Cordes, *Inorg. Chem.*, 1981, **20**, 1519-1522. (b) N. Carr, L. Mole, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Dalton Trans.*, 1992, 2653-2662. (c) V. G. Albano, C. Castellari, V. De Felice, A. Panunzi and F. Ruffo, *J. Organomet. Chem.*, 1992, **425**, 177-188.