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Bimetallic ethynylanthracenyl functionalised carbynes

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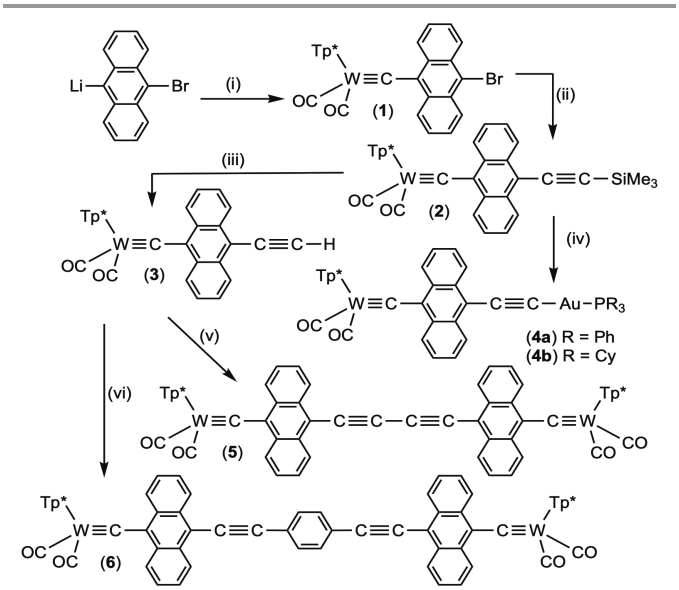
Mono- and Bimetallic Anthracenes functionalised by alkynyl and alkylidynyl substituents are obtained via sequential cross-coupling reactions of the 9-bromoanthracenyl carbyne [W{≡CC(C$_6$H$_4$)$_2$CBr}(CO)$_2$(Tp*)].

Carbon-rich, highly unsaturated ligands that bridge two or more metal centres often exhibit electronic, photochemical, photophysical or redox properties which make them attractive targets for use in molecular devices.[1] Bis(alkynyl) connectivities, L$_n$M–C≡C–R–C≡C–ML$_n$ are amongst the most commonly employed due to typically reliable and generalisable alkynyl installation protocols which allow wide variability in the identity of the metal, ancillary ligands, and the spacer group 'R,' which can itself introduce its own electronic or optical features. Complexes of more strongly π-accepting bis(carbyne) ligands L$_n$M≡C–R–C≡ML$_n$, by contrast, are far rarer due to the more circuitous synthetic routes which deter more adventurous exploration and which are generally less tolerant of functionality. Among the host of conceivable spacer groups is the 9,10-anthracen-diyl core which in addition to providing an electronically conjugating pathway between metals, imbues spectacular electro-optical properties on its derivatives including electro-, photo- and chemiluminescence.[2] Of particular intrigue is the possibility of constructing assemblies with two or more interactive anthracenyl units.[2c] The first demonstration of 9,10-di(alkynyl)anthracene bridging two metals was provided by Sonogashira[3a] and many further examples have appeared in the interim.[3] A recurrent feature has been not only the intriguing photochemistry but the possibility of bridging ligand redox non-innocence.[3h]

The first anthracene substituted carbyne complexes were only very recently reported[4] including the complex [W{≡CC(C$_6$H$_4$)$_2$CBr}(CO)$_2$(Tp*)] (**1**: Tp* = hydrotris(dimethylpyrazolyl)borate, Scheme 1).[4b] Complex **1** appeared to present an ideal starting point for the elaboration of novel architectures by virtue of the 9-Br functionality being amenable to palladium-mediated cross-coupling protocols. Herein we report that **1** can indeed serve as a precursor to access a variety of elaborate and novel ditungsten carbon-wire type compounds that include either one or two anthryl chromophores.

The complex **1** was found to undergo Sonogashira coupling with ethynyltrimethylsilane to afford [W{≡CC(C$_6$H$_4$)$_2$C-C≡CSiMe$_3$}(CO)$_2$(Tp*)] (**2**, Scheme 1, ESI†).



Scheme 1. Synthesis of anthracenyl carbynes. (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate*). Reagents and conditions:* (*i*) [W(CO)$_6$], (CF$_3$CO)$_2$O, K[Tp*];[4b] (*ii*) [Pd(PPh$_3$)$_4$], CuI, HC≡CSiMe$_3$, Et$_3$N; (*iii*) K$_2$CO$_3$, MeOH/CH$_2$Cl$_2$/H$_2$O; (*iv*) NaOH, [AuCl(PR$_3$)] (R = Ph, Cy), MeOH; (*v*) CuI, air, THF/Et$_3$N; (*vi*) 1,2-C$_6$H$_4$I$_2$, [Pd(PPh$_3$)$_4$], CuI, THF/Et$_3$N.

Mayr previously demonstrated a post-installation carbyne modification approach with the 4-iodobenzylidyne complexes [W(≡CC$_6$H$_4$I-4)Cl(CO)$_2$(L$_2$)] (L$_2$ = *N,N,N′,N″*-tetramethyl-ethylenediamine or bis(diphenylphosphino)ethane, dppe) which underwent Sonogashira cross-coupling reactions with several alkynes.[5] Hopkins has also described Sonogashira coupling processes involving the terminal ethynyl group of [W(≡CC$_6$H$_4$C≡CH)Cl(dppe)$_2$][6] and accordingly **2** was desilylated (K$_2$CO$_3$) in the presence of either aqueous methanol to afford the terminal alkyne [W{≡CC(C$_6$H$_4$)$_2$CC≡CH}(CO)$_2$(Tp*)] (**3**) or alternatively halogold complexes [AuCl(PR$_3$)] to afford [W{≡CC(C$_6$H$_4$)$_2$CC≡CAuPR$_3$}(CO)$_2$(Tp*)] (R = Ph **4a**, Cy **4b**, Figure 1). A small number of phosphine-gold derivatives of alkynyl anthracenes have been reported previously[7] and gold alkynyls have been shown by Cross[8] and Bruce[9] to serve as effective stoichiometric 'bench-ready' alkynyl transmetallating agents. The formulations of **2**, **3** and **4** follow from spectroscopic data (Table 1) and for **2**, **3** and **4b** their identities were crystallographically confirmed (see Figure 1 and ESI†).

Table 1. Selected spectroscopic and structural data for **1**–**6**.

	$\delta_{\equiv C}$ [a]	r_{WC} (Å)	$\angle_{WCC}$ (°)	ν_{CO} [b]	λ_{max} [c]

1[4b]	278.5	1.833(3)	179.0(2)	1977, 1888	428, 453, 486
2	279.5	1.831(4)	177.5(3)	1975, 1887	442, 470, 504
3	279.1	1.825(4)	178.2(3)	1976, 1888	435, 463, 496
4a	281.2	–	–	1972, 1883	454, 482, 517
4b	281.6	1.832(8)	178.0(6)	1971, 1883	454sh, 484, 516
5	279.0	1.844(7)	171.4(6)	1976, 1889	539br, 600br
6	279.4	1.819(5)	177.7(5)	1975, 1888	526sh, 554

[a] Measured in $CDCl_3$ at RT (L ≠ Tp*) or –40 °C (L = Tp*). [b] Measured in CH_2Cl_2 (cm^{-1}). [c] Visible region listed, measured in CH_2Cl_2 (nm).

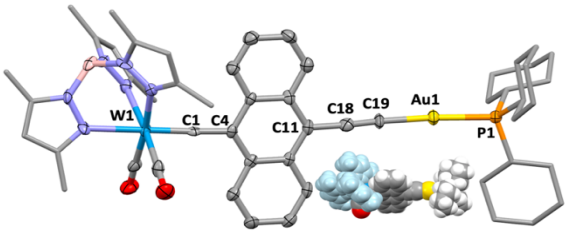


Figure 1. Molecular structure of **4b** in a crystal of **4b**.C_6H_{12}.$(CHCl_3)_{1.5}$ (50% displacement ellipsoids, pyrazolyl and cyclohexyl groups simplified and hydrogen atoms and solvent omitted). Selected bond lengths (Å) and angles (°): W1–C1 1.832(8), C1–C4 1.433(10), C19–C18 1.196(10), Au1–C19 2.010(7), C4-C1-W1 178.0(6), C18-C19-Au1 176.5(7), C19-Au1-P1 176.2(2). Inset = space filling representation to illustrate steric clash between the anthryl groups and the bulky Tp* ligand (light blue).

The representative molecular geometry of **4b** is depicted in Figure 1 and demonstrates features common to all three. Specifically, in all cases (*i*) the anthryl plane resides between two sterically obstructive pyrazolyl groups; (*ii*) the alkylidyne exerts a substantial *trans* influence upon the unique pyrazolyl donor;[10] (*iii*) No noteworthy intermolecular associations occur (*e.g.*, anthracene C–H···π or π-stacking interactions[4b]) and (*iv*) variations in the remote 10-anthryl substituents (H,[4a] Br, $C{\equiv}W(CO)_2(Tp^*)$,[4b] $C{\equiv}CSiMe_3$, C≡CH, $C{\equiv}CAuPR_3$) have minimal impact on the geometrical features of the tungsten coordination sphere.

In each case and for compounds to follow, the NMR resonances for the anthryl bridge were broad at room temperature but resolved into eight unique 1-proton resonances at low temperature (typically –40°) due rotation about the anthryl-$C_{carbyne}$ bond being arrested by steric inhibition from the two pyrazolyl groups (Inset, Figure 1). The $^{13}C\{^1H\}$ carbyne resonances and ν_{CO}-associated infrared data are unremarkable, falling within the ranges found for simpler benzylidyne derivatives.[10]

The ethynyl group in **3** can be subsequently deployed in further coupling reactions, two examples of which serve to illustrate the utility, affording carbyne derivatives of di(9-anthryl)butadiyne[11] and 1,4-di(9-anthrylethynyl)benzene.[12] Both of these electronically conductive cores have attracted interest in the photophysical context of, *e.g.*, organic light-emitting transistors and organic field-effect optical waveguides. An aerobic solution of **3** and copper(I) iodide in the presence of NEt_3 undergoes classical Glaser coupling to furnish $[(Tp^*)(CO)_2W(\equiv CC(C_6H_4)_2CC{\equiv}CC{\equiv}CC(C_6H_4)_2CC{\equiv}W(CO)_2(Tp^*)]$ (**5,** Figure 2) as a deep imperial purple solution and black solid (Scheme 1), wherein two anthracenyl carbyne units are bridged by a 1,3-diyne moiety. If **3** is instead treated anaerobically with *p*-diiodobenzene and NEt_3 in the presence of catalytic $[Pd(PPh_3)_4]$ and CuI, a very bright 'hot pink' solution of $[(Tp^*)(CO)_2W(\equiv CC(C_6H_4)_2CC{\equiv}CC_6H_4C{\equiv}CC(C_6H_4)_2CC{\equiv}W(CO)_2(Tp^*)]$ (**6**, Figure 3), is formed, wherein the same anthracenyl carbyne groups are bridged by a *p*-diethynylbenzene moiety. Notably, slow crystallisation of this compound affords bright pink crystals, although rapid removal of solvent provides a green-brown amorphous solid.

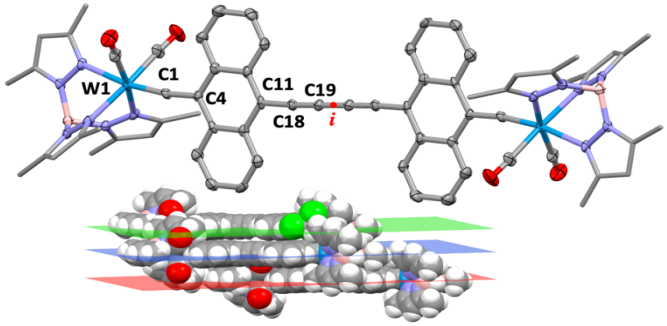


Figure 2. Molecular structure of **5** in a crystal of **5**.$(CHCl_3)_2$ (50% displacement ellipsoids, only one-half of the molecule is crystallographically unique ($P2_1/n$, inversion at ***i***), pyrazolyl rings simplified, solvent and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.844(7), C1–C4 1.433(9), C11-C18 1.428(9), C19–C19 1.369(14), C18-C19- C19' 179.6(12). Inset = 3 adjacent molecules the bridge mean planes of which are separated by 3.666 Å ($2xr_{vdW}(C)$ = 3.4 Å).

The structural changes are again remote from the tungsten centre and so the definitive NMR spectroscopic characterisation rests primarily on the disappearance of the acetylenic proton resonance and, in the case of **6**, a large singlet at 7.84 ppm integrating for four protons corresponding to the central phenylene ring. In the solid-state structures of **5** (Figure 2) and **6** (Figure 3), both of which are crystallographically centrosymmetric (Point group C_{2h}; Space group No. 14: $P2_1/n$ or $P2_1/c$), the two anthracene (and phenyl for **6**) ring systems are essentially co-planar and whilst parallel in adjacent molecules, π-stacking is neither cause nor effect of the packing. In the case of **5** there is a modest degree of sigmoidal bowing along the path from N1 (the *trans* pyrazolyl donor) to its symmetry-generated mirror, however such deformations along carbon wires have long been attributed to low-energy lattice forces.[13] We note that, unsurprisingly, geometry optimisation of the model complex $[(Tp)(CO)_2W(\equiv CC(C_6H_4)_2CC{\equiv}C\text{-}C{\equiv}CC(C_6H_4)_2C\text{-}C{\equiv}W(CO)_2(Tp)]$ (**5'**: Tp = tris(pyrazolyl)borate) results in linearisation of the bridge (see ESI†). In the case of **6**, the anthryl and phenylene planes are essentially co-planar in the solid state, however for 1,4-di(9-anthrylethynyl)benzene it was suggested that rotation of the central phenylene unit is essentially frictionless such that both co-planar and orthogonal rapidly interconverting conformers coexist in solution.[12b]

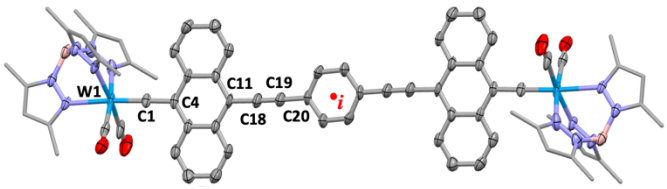


Figure 3. Molecular structure of **6** in a crystal showing 50% displacement ellipsoids. Only one-half of the molecule is crystallographically unique ($P2_1/c$, inversion at *i*). Pyrazolyl rings are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.819(5), C1–C4 1.444(7), C11–C18 1.429(7), C18–C19 1.197(8), C19–C20 1.429(8), W1–C1–C4 177.7(5), C11–C18–C19 178.0(7), C18–C19–C20 177.7(8).

Conventional arylcarbynes generally contain weak visible-region absorptions ($d_{xy}\rightarrow\pi^*_{M\equiv C}$, $\pi_{M\equiv C}\rightarrow\pi^*_{M\equiv C}$) in their electronic spectra.[14] The electronic spectra of **1**-**6** are, however overwhelmingly dominated by intense absorbances at wavelengths below 600 nm corresponding to the anthracene ring system(s) (Table 1, Figure 4).

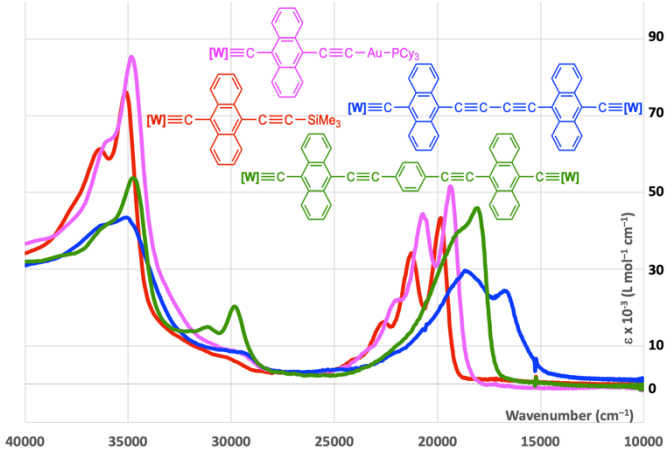


Figure 4. Electronic spectra of **2** (red), **4b** (pink), **5** (blue) and **6** (green) displaying red-shift and loss of vibronic fine-structure upon extension of conjugation (ε per tungsten).

The complexes **2**, **3** and the aurated examples **4** clearly display the expected vibronic progression for the $S_0 \rightarrow S_1$ (HOMO-b_{2g} → LUMO-b_{3u}) excitation, albeit substantially red-shifted from that for anthracene itself (378 nm). In contrast, the ditungsten derivatives each display intense featureless absorptions (**5**: 536, 601; **6**: 529, 551 nm, Figure 4), the broadness of which precluded resolution of vibronic fine structure. These absorptions are also noticeably red-shifted relative to absorptions for **1**–**4**, di(9-anthryl)butadiyne (λ_{max} = 430 nm),[11a] and 1,4-di(9-anthrylethynyl)benzene (λ_{max} = 429 nm),[12b] however none of the new complexes were found to be observably emissive upon excitation at 330 nm or their λ_{max} values. This lends some credence to the notion of electronic interaction between the metal and carbyne ligand such that the large spin-orbit coupling (ξ = 3100-2600 cm^{-1} for W^{III-V}) of the metal electrons shortens the lifetime of the excited singlet state (S_1) which progresses (inter-system crossing) to a long-lived triplet (T_1) state which is prone to non-radiative decay processes.[4b,14,15] These may perhaps be obviated by judicious tuning of the ancillary ligands on tungsten so as to preserve or (perhaps even enhance) their optical properties.

Replacement of the Tp* ligands in **5** and **6** by the computationally more frugal Tp ligand provides the hypothetical complexes **5'** and **6'**. The frontier orbitals of interest that arise from optimised geometries (DFT:ωBP97X-D/6-31G*/LANL2Dζ(W); Figures 5 and 6) are superficially similar, despite the difference in butadiynyl C≡C-C≡C or diethynyl-*p*-phenylene C≡CC_6H_4C≡C spacers.

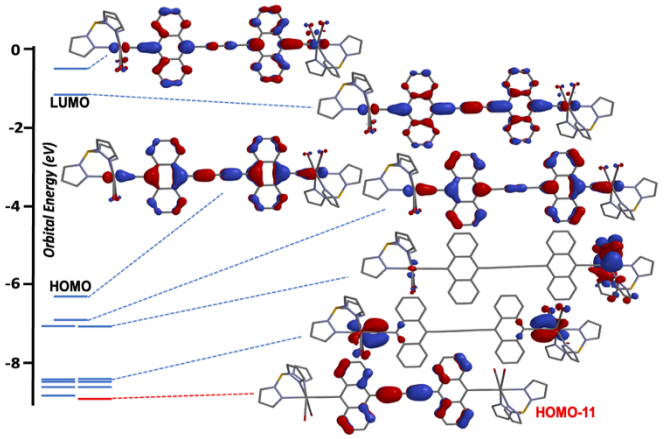


Figure 5. Frontier orbitals of interest for **5'**.

For **5'** and **6'** (and experimentally determined for **5** and **6**) the two anthracene spacers are coplanar with WTp cages that are anti-disposed along the W···W (z) vector. The HOMO-1, HOMO, LUMO and LUMO+1 orbitals are primarily anthracene based and underpin the notable features in the electronic spectrum and in each case only a rather modest contribution is observed from tungsten *d*π orbitals. For both **5'** and **6'** two d_{xy} orbitals comprise a pair of degenerate orbitals (HOMO-2,3) involved in carbonyl retrodonation above a quartet of orbitals that primarily that comprise the WC carbyne multiple bonds. The HOMO-8 and 9 are exclusively anthracene-based such that the most notable difference between **5'** and **6'** is that inclusion of a phenylene spacer into the butadiynyl linkage results in the insertion of an orbital (HOMO-4, red Figure 6) between the MCO retrodative and WC carbyne π-orbitals, which might be viewed as the phenylene-extended version of the butadiynyl orbital HOMO-11 in **5'** (red, Figure 5). The localisation of frontier orbitals on the anthryl cores of **5** and **6** is further supported by the observation of a single oxidation event in each of the cyclic voltammograms (ESI), consistent with bridging ligand redox non-innocence. Charge transfer transitions from d_{xy} orbitals to the $\pi^*_{W\equiv C}$ orbitals that conjugate out to the anthracene bridge, whilst allowed, are likely to be comparatively weak relative to the dominant anthracene-localised processes. For **6'**, TD-DFT analysis (ωBP97X-D/6-31G*/LANL2Dζ(W)) suggests that the lowest energy intense absorption (482 nm, 20,750 cm^{-1}) is comprised primarily of HOMO→LUMO (68%) and HOMO-1→LUMO+1 (28%) transitions involving only modest contributions from the WC π-bonding orbitals. The absorption at *ca* 460 nm arises from multiple excitations. These appear to be from HOMO-2/3 ($W(CO)_2$) to the LUMO and LUMO+1/5/6, of the dianthryl spine.

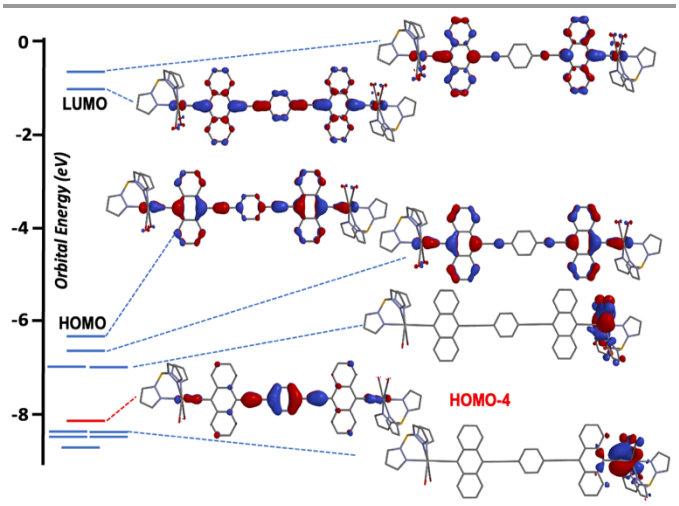


Figure 6. Frontier orbitals of interest for **6'**.

In conclusion, we have demonstrated that metal-carbon multiply bonded termini may be readily installed into carbon-wire type architectures by employing Sonogashira cross-coupling reactions of the C_{aryl}–Br bond of a 9-bromo-10-(alkylidynyl)anthracene, affording mono and bimetallic examples, the electrooptical properties of which are substantially associated with the dianthryl bridge.

Acknowledgements

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