Pentadiynylidyne and Pentacarbido Complexes

Anthony F. Hill[a] and Richard A. Manzano[a]

Abstract: The reaction of the halocarbonyne \([\text{W}(\equiv\text{CBr})\{\text{CO}\}_2\{\text{Tp}^*\}]\) \((\text{Tp}^* = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate})\) with trimethylsilyl- butadiyne, mediated by \([\text{Pd}(\text{PPh}_3)_2]\) and \(\text{CuI}\), affords the first pentadiynylidyne complex \([\text{W}(\equiv\text{CC}C\equiv\text{CC}C\equiv\text{SiMe}_3)\{\text{CO}\}_2\{\text{Tp}^*\}]\), desilylation of which provides a generalisable route to heterobimetallic pentacarbido complexes including \([\text{W}(\equiv\text{CBr})(\text{CO})\{\mu-\text{C}(\pi-\mu-\text{C}(\pi-\text{C}(\pi-\mu-\text{C}(\pi-\text{C}))))\}]\) and \([\text{Pd}(\text{P}(\text{CO})\text{H})(\mu-\text{C}(\pi-\mu-\text{C}(\pi-\text{C}(\pi-\mu-\text{C}(\pi-\text{C}))))\{\text{CO}\}_2\{\text{Tp}^*\}]\).

Propargyldyne complexes, \([\text{W}(\equiv\text{CC}C\equiv\text{C}X)(\text{CO})_3]\) \((X = \text{Cl}, \text{Br}, \text{I}; \text{Chart 1})\), were first reported by E. O. Fischer,[1] Their instability, however, somewhat impeded further study until thermally stable derivatives were developed by ourselves and H. Fischer.[2] Amongst these, ‘half-sandwich’ examples \([\text{W}(\equiv\text{CC}C\equiv\text{C}X)(\text{CO})_2\{\text{L}\}]\) \((R = \text{Ph}, \text{Bu}; \text{L} = \text{Tp}, \text{Tp}^*, \text{Cp}, \text{C}_2\text{B}	ext{H}_3\text{Me}_2; \text{X} = \text{H}, \text{halogen})\) proved to be versatile building blocks for bridge-assisted metal-metal bond forming processes.[3,4] Our own studies demonstrated that the silyl derivatives \([\text{W}(\equiv\text{CC}C\equiv\text{C}X)(\text{CO})_2\{\text{L}\}]\) \((L = \text{Tp} = \text{hydrotris(5pyrazolyl)}\text{borate}); \text{Tp}^* = \text{hydrotris(3,5dimethylpyrazolyl)}\text{borate})\) could be desilylated to afford tricarbido synths for the construction of heterometallic tricarbido and hexacarbido complexes.[5] Very recently, propargyldyne complexes have emerged from being simply fundamental laboratory curiosities to new serve as competent mediators for the diyne/alkyne cross metathesis.[6] The development of propargyldyne/tricarbido chemistry along these various avenues led us to consider the viability of pentadiynylidylenes and whether similarly rich chemistry might follow based on 5-carbon chain ligands. We report herein the synthesis of the first such pentadiynylidyne complex and demonstrate that it may indeed serve as an entry point into the uncharted chemistry of bi- and polymetallic pentacarbido complexes.

---

(a) \(L_\text{MM}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{R}\)  (b) \(L_\text{MM}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{M}_\text{Mn}^\text{II}\)
(c) \(L_\text{MM}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{R}\)  (d) \(L_\text{MM}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{C}C\equiv\text{M}_\text{Mn}^\text{II}\)

Chart 1. (a) Propargyldyne, (b) tricarbido, (c) pentadiynylidyne and (d) pentacarbido complexes and their cumulenic valence isomers.

The syntheses of propargyldyne complexes have previously employed variations in the conventional E. O. Fischer synthesis which relies on an alkynyl lithium reagent attacking a CO ligand of \([\text{W}(\text{CO})_3]_2\).[1,2] Simple extension of this approach to employing \(\text{LiC}C\equiv\text{CC}C\equiv\text{SiMe}_3\)[6] has so far failed in our hands, most likely due to the reduced nucleophilicity of the extended diynyl lithium reagent. It should however be noted that the more exotically lithium species \([\text{Re}(\text{C}1\text{L})\{\text{NO}\}(\text{PPh}_3)\{\text{η}-\text{C}_5\text{Me}_3\}]\) does react with \([\text{Mn}(\text{CO})_3\{\text{η}-\text{C}_5\text{Me}_3\}]\) to provide the corresponding acylate. Subsequent modification affords the pentacarbido salt \([\{\text{η}-\text{C}_5\text{Me}_3\}\text{Mn}(\mu-\text{C}(\pi-\mu-\text{C}(\pi-\text{C}(\pi-\mu-\text{C}(\pi-\text{C}))))\text{Re}\}\text{BF}_4\) with spectroscopic data for which are more consistent with a cumulenic \(\text{Mn} = C = C = C = C = \text{Re} = \text{spine}.\)[7] We have therefore considered an alternative approach involving a Sonogashira type \(\text{C}C\equiv\text{C}\text{C}C\equiv\text{C}\) cross-coupling process, recently optimized[8] for reactions between the halocarbonyne \([\text{W}(\equiv\text{CBr})(\text{CO})_2\{\text{Tp}^*\}]\) \((1)[9]\) and simple 1-alkynes. Treating 1 with \(\text{HC} = \text{C}C\equiv\text{CC}C\equiv\text{SiMe}_3\) in the presence of \([\text{Pd}(\text{PPh}_3)_2]\) \((5 \text{ mol%})\) and \(\text{CuI} (10 \text{ mol%})\) in triethylamine results in the high yielding (90%) formation of the first pentadiynylidyne complex \([\text{W}(\equiv\text{CC}C\equiv\text{CC}C\equiv\text{SiMe}_3)\{\text{CO}\}_2\{\text{Tp}^*\}]\) \((2, \text{Scheme 1}).\)

Scheme 1. Synthesis of a pentadiynylidyne complex.

The progressive diminution of the magnitudes of \(J_{\text{WC}}\) and \(J_{\text{WC}}\) couplings along the \(\text{WC}C\equiv\text{Si}\text{Me}^\text{III}\) chain (see ESI) allows confident \(^{13}\text{C}\) NMR identification of the resonances for each of the five carbon nuclei of interest \((\Delta C = 244.9 \text{ C}_2, 93.3 \text{ C}_3, 56.6 \text{ C}_4, 89.5 \text{ C}_5, 90.3 \text{ C}_6, \text{Table 1})\) whilst the localization of \(\text{WC}C\equiv\text{Si}\text{Me}^\text{III}\) triple and \(\text{C} = \text{C}\) single bonds follows from a crystallographic analysis (Figure 1, Table 2) that confirms the pentadiynylidyne valence bond description.

Figure 1. Molecular structure of 2 in a crystal (50% displacement ellipsoids, hydrogen atoms omitted, pyrazolyl rings simplified, one of two crystallographically independent molecules shown). Selected averaged bond lengths (Å) and angles (deg.) for the two molecules: \(W1-C1 1.855(5), S1-C5 1.846(5), C1-C2 1.353(7), C2-C3 1.215(7), C3-C4 1.373(7), C4-C5 1.208(7), W1-C1-C2 170.5(4), C1-C2-C3 176.6(6), C3-C4-C5 174.5(6), C4-C5-S1 174.8(5).

[a] Prof. Dr. A. F. Hill and Mr R. A. Manzano
Research School of Chemistry
The Australian National University
Canberra, ACT 2601, Australia
E-mail: a.hill@anu.edu.au
Although the WC₂Si spine is slightly bowed, this distortion is not reproduced in the optimized geometry (DFT:B3LYP-LANL2DZ, gas phase, SPARTAN-18®), indicating that it is a soft response to crystal packing forces. The frontier molecular orbitals derived from this geometry (Figure 2) suggest considerable electronic delocalization along the WC₅ spine. Based on these orbitals, the color of complex 2 (Figure 3) would appear to arise from two absorptions of interest. The first weak absorption (λ_max = 562 nm) corresponds to a dₓᵧ→π⁺W₅C transition[10] whilst the second considerably more intense absorption (λ_max = 403 nm) is attributed primarily to π₋W₅C, i.e., from the W≡C π-bonding orbital to the W≡C π-antibonding orbital, both of which are extensively delocalized along the Cs spine. These are both to higher wavelength of the corresponding absorptions for [W=C(SiMe₃)(CO)₂(Tp⁺)] and [W=C=C(SiMe₃)(CO)₂(Tp⁺)].[4a]

Table 1. Selected NMR Data (δ (ppm)) for Cs and Cs Bridged species [M] = M(CO)₂(Tp), M = Mo, W

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cα</th>
<th>Cβ</th>
<th>Cy</th>
<th>Cδ</th>
<th>Cε</th>
</tr>
</thead>
<tbody>
<tr>
<td>[W]C≡C(SiMe₃)²⁺</td>
<td>247.3</td>
<td>120.4</td>
<td>79.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[W]C≡C(SiMe₃)²⁻</td>
<td>244.9</td>
<td>93.3</td>
<td>56.6</td>
<td>89.5</td>
<td>90.3</td>
</tr>
<tr>
<td>[W]C≡Ru(PPh₃)(Cp)⁺</td>
<td>273.8</td>
<td>142.1</td>
<td>131.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[W]C≡Ru(PPh₃)(Cp)⁻</td>
<td>251.9</td>
<td>85.3</td>
<td>65.7</td>
<td>140.4</td>
<td></td>
</tr>
<tr>
<td>[Mo]C≡Ru(dppe)(Cp)⁺</td>
<td>200.0</td>
<td>92.65</td>
<td>n.r.</td>
<td>53.66</td>
<td>n.r.</td>
</tr>
<tr>
<td>[W]C≡H(CO)(PPh₃)⁺</td>
<td>245.1</td>
<td>91.0</td>
<td>56.6</td>
<td>91.4</td>
<td>117.0</td>
</tr>
</tbody>
</table>

* [W] = W(CO)₂(Tp), n.r. = not reported

Figure 2. Optimised molecular geometry and associated frontier orbitals for the complexes [W≡C≡C≡C≡SiMe₃(δ,δ')] (n = 0, 1, 2; [W] = W(CO)₂(Tp), DFT:B3LYP-LANL2DZ, isovalue = 0.032 au).

The energies, calculated at the same level of theory, of the corresponding orbitals for the known ‘C₁’ [W≡C≡C≡SiMe₃(CO)₂(Tp⁺)] and ‘C₂’ [W≡C≡C≡SiMe₃(CO)₂(Tp⁺)] congener are also presented in Figure 2, from which it is clear that (i) the dₓᵧ orbital, which is primarily associated with W(CO)₂ retrodonation, is essentially invariant across the series such that increases in the λ_max for the dₓᵧ→π⁺W₅C transition are due to progressive conjunctive stabilisation of the π₋W₅C orbitals (LUMO, LUMO+1). (ii) The pair of π₋W₅C orbitals (HOMO-1, HOMO-2) increase in energy with chain extension resulting in an increase in both the intensity (ε) and wavelength of the π₋W₅C→π⁺W₅C absorption(s).

Figure 3. UV-Vis Spectra of the complexes [W≡C≡C≡SiMe₃(CO)₂(Tp⁺)] (n = 0, 1, 2).

For the related propargylidyne complex [W≡C≡C≡SiMe₃(CO)₂(Tp⁺)] desilylation with [BroNF] (1.0 M in moist THF) does not afford an isolable parent propargylidyne but does provide in situ a reagent that may be used for constructing tricarbido-bridged bimetallic complexes via halide substitution or C–H activation. In a similar manner, from the reaction of 2 with [BroNF] we failed to isolate either [W≡C≡C≡C≡C≡CH(CO)₂(Tp⁺)] (3) or its conjugate base [BroNF][W≡C≡C≡C≡C≡CH(CO)₂(Tp⁺)] [BroNF][4]. We, however, present evidence for the generation of both these species via trapping reactions with suitable metal reagents (Scheme 2).

Treating 2 with [RuCl(PPh₃)₂(t-Bu₂C₆H₅)] in the presence of KF in methanol/THF (1:1) allowed the isolation of the bimetallic pentacarbido complex [(Tp⁺)(CO)₂W≡C≡CC≡C≡CRu(PPh₃)₂(Cp)] (6) known[40] and because the only previously reported bimetallic pentacarbido complex other than the cumulenic Re₂C₆H₁₂ complex discussed above[9] is [(Tp⁺)(CO)₂Mo≡C≡C≡C≡CRu(dppe)(Cp)⁺] (7, Cᵖ⁺ = C₂Me₃), which arose from the Pd²⁺Cu¹ mediated reaction of [Mo≡C≡C≡CH(CO)₂(Tp⁺)] with [Ru(C≡C≡CC≡CAuPPh₃)(dppe)(Cp)][11].

Scheme 2. Trapping of a pentacarbido nucleophile.
Figure 4. Molecular structure of 5 in a crystal of 5.CHCl₃ (50% displacement ellipsoids, hydrogen atoms and solvent omitted, phenyl and pyrazolyl groups simplified). Selected bond lengths (Å) and angles (°): W1-C1 1.870(5), Ru1-C5 1.965(5), C1-C2 1.338(5), C2-C3 1.234(7), C3-C4 1.345(5), C4-C5 1.232(7), W1-C1-C2 175.8(5), C1-C2-C3 175.5(5), C2-C3-C4 179.0(5), C4-C5-Ru1 174.6(4), P1-Ru-P2 101.29(4)°.

Table 2. Selected Geometric Data (Å) for C₃ and C₅ Bridged species [W] = W(CO)₅(Tp⁺)

The isolation of 5 lends support to the in situ generation of [W≡CC≡CSiMe₃][CO]₅(Tp⁺)] using a source of activated terminal alkynes such as benzene. We therefore suggest that the first step in the formation of 7 involves halide metathesis by the anion [4] to afford [unobserved] [(Ph₃P)₂(CO)[μ-C₃]W(CO)₅(Tp⁺)] (8) which then reacts with one equivalent of the parent complex 3 to provide 7. Similar behavior was observed when [W≡CC≡CSiMe₃][CO]₅(Tp⁺)] was treated with Vaska’s complex and [BuN]F to provide complex [(Ph₃P)₂(CO)HIr(μ-C₃)]W(CO)₅(Tp⁺)]₃ (9) [40].

Scheme 3. Synthesis of a bis(pentacarbido) complex.

The molecular structure of 7 was confirmed by a crystallographic analysis, the results of which are summarised in Figure 5. The molecule adopts a crystallographically imposed centrosymmetric geometry which is accommodated by positional disorder of the trans hydride and carbonyl ligands bound to octahedral iridium. It is immediately obvious that the pentacarbido ‘wires’ are somewhat flexible, culminating in a sigmoidal distortion of the NWC₆Ir₆W backbone which would otherwise be expected to be linear. Distortions of long polycarbaryl chains in the solid state are often observed, [a] as is the bending of carbyne ligands [b] and in both cases these deformations are generally attributed to crystal packing forces.

Figure 5. Molecular structure of 7 in a crystal of 7.CHCl₃ (50% displacement ellipsoids, hydrogens and solvent molecules omitted, phenyl and Tp⁺ ligands simplified). Selected bond lengths (Å) and angles (°): W1-C1 1.838(11), C1-C2 1.338(15), C2-C3 1.234(15), C3-C4 1.345(7), C4-C5 1.232(7), C5-W1 1.369(14), C3-W1 1.210(14), 1.383(13); 1.168(14).
In conclusion, we have shown that not only (i) pentadiynylidyne ligands viable and accessible; (ii) The photophysical properties arise from transitions between frontier orbitals that intimately combine both metal and carbon-chain character; (iii) They may serve as building blocks for assembling bi- and tri-metallic pentacarbido complexes, the carbon wires of which by necessity involve metal-carbon multiple bonding in contrast to even-numbered dimetallated carbon chains. This synthetic approach offers some generality, adding to the two previously known examples of pentacarbido bridged bimetallics, [(η⁵-C₅Cl₅)(CO)₂Mn(μ-C₅)Re(NO)(PPh₃)(η⁵-C₅Me₅)]BF₄[7] and [(Tp*)(CO)₂Mo(μ-C₅)Ru(dppe)(η⁵-C₅Me₅)].[11] We therefore suggest that carbyne-based carbon-wire ligands offer exactly the same features, albeit enhanced, that have made conventional poly-yne based carbon-wire materials such a fertile area for study.

Acknowledgements

We are grateful to the Australian Research Council (DP170102695 and DP190100723) for funding.

Keywords: Pentadiynylidyne • Carbon Wires • Tungsten • Polymetallic • Carbyne

The first pentadiynylidyne complex \([\text{W}(\equiv\text{CC}≡\text{CCH})(\text{CO})_2(\text{Tp}^*)]\) may be desilylated in the presence of metal halo complexes to construct hetero bi- and trimetallic pentacarbido complexes.

Anthony F. Hill* and Richard A. Manzano

Page No. – Page No.

Pentadiynylidyne and Pentacarbido Complexes