Confluence of Disparate Carbido Chemistries: [WRuAu₂(μ-C)₂Cl₂(CO)₂(PCy₃)₂(Tp*)]

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linkages within the same polymetallic assembly, we now report

Chart 1. Trichotomous μ -Carbido Bonding Scenarios and their Archetypes.^{1a,3b,5}

the first such complex which features both (unconventional) Class **B** and Class **C** carbido bridges

$$\begin{array}{c}
 \text{PCy}_3 \\
 | \\
 \text{Cl} - \text{Ru} \equiv \text{C} : \\
 | \\
 \text{PCy}_3
 \end{array}
 \xrightarrow{\text{ClAu(THT)}}
 \begin{array}{c}
 \text{PCy}_3 \\
 | \\
 \text{Cl} - \text{Ru} \equiv \text{C} : \rightarrow \text{Au} - \text{Cl} \\
 | \\
 \text{PCy}_3
 \end{array}
 \quad \text{3}$$

$$\begin{array}{c}
 \text{PCy}_3 \\
 | \\
 \text{Cl} - \text{Ru} \equiv \text{C} : \\
 | \\
 \text{PCy}_3
 \end{array}
 \xrightarrow{\text{ClAu(THT), AgOTf}}
 \begin{array}{c}
 \text{PCy}_3 \\
 | \\
 \text{Cl} - \text{Ru} \equiv \text{C} : \rightarrow \text{Au}^+ \leftarrow \text{C} \equiv \text{Ru} - \text{PCy}_3 \\
 | \qquad \qquad \qquad | \\
 \text{PCy}_3 \qquad \qquad \text{C}_6\text{H}_5\text{P} \qquad \text{Cl}
 \end{array}
 \quad \text{4}$$

$$\begin{array}{c}
 \text{Tp}^* \\
 | \\
 \text{W} \equiv \text{C} - \text{SnMe}_3 \\
 | \quad | \\
 \text{OC} \quad \text{OC}
 \end{array}
 \quad \text{2a}
 \xrightarrow{\text{ClAuAsPh}_3}
 \begin{array}{c}
 \text{Tp}^* \\
 | \\
 \text{W} \equiv \text{C} - \text{Au} - \text{AsPh}_3 \\
 | \quad | \\
 \text{OC} \quad \text{OC}
 \end{array}$$

$$\begin{array}{c}
 \text{ClAuSMe}_2 \\
 \hline
 \text{AsPh}_3
 \end{array}
 \xrightarrow{\quad}
 \begin{array}{c}
 (\text{Tp}^*)(\text{OC})_2\text{W} \\
 \diagup \quad \diagdown \\
 \text{C} \quad \text{C} \\
 \diagdown \quad \diagup \\
 \text{Au} \cdots \text{Au} \\
 \diagup \quad \diagdown \\
 \text{C} \quad \text{C} \\
 \diagdown \quad \diagup \\
 (\text{Tp}^*)(\text{OC})_2\text{W}
 \end{array}
 \quad \text{7}$$

$$\begin{array}{c}
 \text{Tp}^* \\
 | \\
 \text{W} \equiv \text{C} - \text{Au} - \text{PPh}_3 \\
 | \quad | \\
 \text{OC} \quad \text{OC}
 \end{array}
 \xrightarrow{\text{PPh}_3}
 \begin{array}{c}
 \text{Tp}^* \\
 | \\
 \text{W} \equiv \text{C} - \text{Au} - \text{PPh}_3 \\
 | \quad | \\
 \text{OC} \quad \text{OC}
 \end{array}$$

$$\begin{array}{c}
 \text{Tp}^* \\
 | \\
 \text{W} \equiv \text{C} - \text{Au} - \text{PET}_3 \\
 | \quad | \\
 \text{OC} \quad \text{OC}
 \end{array}$$

Scheme 1. Prior synthesis of gold μ -carbido complexes.

We have previously shown that the stannylcarbyne complex $[W(\equiv CSnMe_3)(CO)_2(Tp^*))]$ (**2a**) undergoes transmetalation with $[AuCl(THT)]$ (THT = tetrahydrothiophene) to afford the spectacular octametallic gold carbido complex

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[W₄Au₄(μ-C)₄(CO)₈(Tp*)₄]. A similar reaction with [AuCl(PEt₃)] however provides the monomeric μ-carbido [WAu(μ-C)(CO)₂(PEt₃)(Tp*)] (Scheme 1).⁶ We therefore reasoned that a similar reaction might proceed between [W(=CSnⁿBu₃)(CO)₂(Tp*)] (**2b**)⁷ and the gold carbido complex [RuAu(μ-¹³C)Cl₃(PCy₃)₂] (**3**). A reaction does indeed ensue between equimolar amounts of **3** and **2b** however the product obtained in *ca* 42% yield by fractional crystallisation from the reaction mixture corresponds to a *digold* species [WRuAu₂(μ-C)₂Cl₃(CO)₂(PCy₃)₂(Tp*)] (**5**, Scheme 2, see ESI). The complex **5** was indeed found to be a bis(μ-carbido) complex but not entirely of the form anticipated.

Scheme 2. Synthesis of an unsymmetrical bis(μ-carbido) complex **5**, including proposed mechanism by which the two distinct phosphines (red and blue) undergo site exchange on the ³¹P{¹H} NMR timescale (100% ¹³C labelled carbido indicated in bold (C)).

The identity and molecular structure of **5** were confirmed through a crystallographic study, the results of which are summarized in Figure 1 and confirm that **5** is a 'AuCl' adduct of the desired target complex **6**. Although solution spectroscopic data are consistent with a time-averaged local C_s symmetry with a mirror plane that includes the unique pyrazolyl bridge and ruthenium bound chlorides (one ³¹P, one CO and two pyrazolyl environments), the space-filling representation (Figure 1 inset) which has chemically inequivalent phosphines reveals why this is not likely to be a ground state conformation. The unusually broad nature of the ruthenium bound μ-carbido ¹³C resonance (δ_C = 420.1, h.h.w = 113 Hz) relative to that of the precursor **3**

Figure 1. Molecular structure of **5** in a crystal (60% displacement ellipsoids, hydrogen atoms omitted, phosphine and pyrazolyl substituents simplified). Selected bond lengths (Å) and angles (°): W1–Au1 2.8748(3), W1–C1 1.887(5), Au1–Au2 3.1596(3), Au1–C1 2.092(5), Au1–C2 1.967(6), Au2–Cl3 2.3027(15), Au2–C1 1.945(5), Ru1–C2 1.664(6), W1–Au1–Au2 77.819(8), C1–Au1–W1 40.97(15), C1–Au1–Au2 36.87(15), C2–Au1–W1 155.75(16), C2–Au1–Au2 126.27(16), C2–Au1–C1 162.8(2), Cl3–Au2–Au1 137.30(5), C1–Au2–Au1 40.18(15), C1–Au2–Cl3 177.43(16), W1–C1–Au1 92.4(2), W1–C1–Au2 164.5(3), Au2–C1–Au1 103.0(2). Inset = Space filling representation of steric bulk associated with Tp* (blue) and PCy₃ (cyan) ligands.

(δ_C = 395.3, h.h.w. = 13 Hz) indicates that free rotation of the RuCl₂P₂ unit about the RuC–Au axis is somewhat constrained on the ¹³C (126 MHz) NMR timescale, but not that of ³¹P (202 MHz, –23 to +25 °C). For the two chemically inequivalent phosphines to exchange sites, loss of direct Au–W bonding seems plausible, perhaps supplemented by development of bonding between tungsten and the second gold centre (**5'**), such that the CRuCl₂P₂ unit moves far enough from the bulky W(CO)₂(Tp*) moiety so as to allow freed rotation about the Au–CRu axis, thereby exchanging the phosphine sites. Given the steric bulk of the PCy₃ and Tp* ligands (Figure 1, inset), this latter interpretation seems viable and is related to a similar fluxional process that has been computationally interrogated for the octametallic tetracarbido complex [W₄Au₄(μ-C)₄(CO)₈(Tp*)₄] (**7**).⁶

The geometries at the two μ-carbido centres are quite distinct. That at C2 is comparatively conventional amongst the variety of bi- and tri-metallic μ-carbido complexes arising from coordination of **1** to late transition metals, e.g., the Ru1=C2 separation (1.664(6) Å) is identical to that observed for the precursor [RuAu(μ-C)Cl₃(PCy₃)₂] (**3**: 1.664(3) Å), whilst the slight elongation of the C2–Au1 bond (1.967(6) Å) relative to that in **3** (1.921(3) Å) may be accounted for by the increased coordination number at Au1. Less conventional coordination is observed for the carbido ligand (C1) which bridges one tungsten and two gold centres by adopting an unusual T-shaped geometry. Thus angles along the W1–C1–Au2–Cl3 spine are all close to linear (164.5(3), 177.43(16)°) whilst Au1 is near orthogonal to this (W1–C1–Au1 92.4(2), Au2–C1–Au1 103.0(2)°). The appending of both 'AuCl' and 'Au1' units to C1 results in a statistically insignificant elongation of the W1–C1 bond (1.887(5) Å) relative to simple class **B** metallacarbynes, e.g., [W₂Ni(μ-C)Cl(CO)₂(PEt₃)₂(Tp*)] (1.867(4) Å, 5 e.s.d.).^{2c} In this respect, the coordination mode of C1 could also be

described as have semi-bridging carbyne character. The Au1–Au2 ‘bond’ (3.1596(3) Å) is best viewed as *auophilic*⁸ in nature. With the structural features of both the ‘CRuCl₂(PCy₃)₂’ and ‘CW(CO)₂(Tp*)’ moieties not greatly perturbed by association with the Au and AuCl units, one might expect that the assembly is labile, as is certainly implicit from the fluxionality evident from the NMR spectra. This is indeed the case in that such data must be acquired over a short time frame following dissolution of **5** (¹³C enriched at Ru) as the complex slowly evolves with liberation of **3** (¹³C enriched) to afford the previously reported cyclic tetracarbido complex [W₄Au₄(μ-C)₄(CO)₈(Tp*)₄] (**7**).⁶

To understand the bonding in **5**, it is first useful to note that gold (I) is unusual in displaying a proclivity for having ligands in heterobimetallic complexes adopting semi-bridging character. In the case of carbyne ligands such a possibility was first mooted by Stone⁹ who observed the unsymmetrical disposition of carbyne substituents in a range of tungsten-gold μ-carbyne complexes. In the interim, such behaviour has also been observed for bridging carbene,¹⁰ thiocarbonyl,¹¹ and alkynyl¹² ligands spanning W–Au bonds in addition to further carbyne examples.¹³ As the chemistry of μ-boryl,¹⁴ μ-borylene and μ-borido¹⁵ ligands develops, similar patterns are beginning to emerge also. In each case, the bonding is best viewed as comprising a formal, albeit polar, metal-gold bond, supplemented by σ-retrodonation to the semi-bridging carbyne from the filled d¹⁰-gold(I) centre (Figure 2), as also observed for this metal coordinated by Z-type ligands.¹⁶ Thus for carbyne ligands (CR) bridging two mid-transition metals, the C–R vector is close to perpendicular to the M–M’ bond (Figure 2d), as exemplified by [WCr(μ-CC₆H₄Me-4)(CO)₄(η-C₅H₅)(η-C₆Me₆)] for which the angles between the carbyne substituent and either metal are crystallographically identical (131.7(4), 131.5(4)°).¹⁷ When a carbyne bridges two disparate metal centres such as d⁶-W and d¹⁰-Au, the Au–C–W angle is close to 90° with the carbyne substituent only slightly bent back from 180° (Figure 2b and c). A complete listing of geometric features for all *triangulo*-WC³Au based connectivities from the CCDC is provided in the ESI. In addition, those for the (at present) hypothetical [WAu(μ-CH)Cl(CO)₂(η-C₅H₅)] (**8**; DFT-B3LYP-LANL2DZ) are included for which any inter- or intramolecular non-bonding interactions are obviated. The experimental features closely resemble those calculated for **8**. Gold(I) would appear to represent the extreme of the symmetrical to semi-bridging continuum and similar arguments underpin Cotton’s description of semi-bridging carbonyl ligation.¹⁸

Figure 2. Semi-bridging Character of Carbynes.

In conclusion, the first heterotypal bis(carbido) complex has been isolated and fully characterised to reveal both polar-covalent (Class C) and metallacarbyne (Class B) carbido ligands. The appending of a AuCl unit to this later carbido bridge is akin to that occasionally observed for more conventional semi-bridging μ-carbyne ligands.

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Notes and references

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