COMMUNICATION

Simple Generation of a Dirhodium μ -Carbido Complex *via* Thiocarbonyl ReductionHarrison J. Barnett,^a Liam K. Burt^a and Anthony F. Hill^{*a}

The reaction of $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ with excess catecholborane affords the cumulenic carbido complex $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$ which undergoes phosphine and halide substitution to afford a range of complexes in which the $\text{Rh}=\text{C}=\text{Rh}$ spine remains intact. Amongst these, the reactions with $\text{K}[\text{L}]$ ($\text{L} = \text{H}_2\text{B}(\text{pz})_2$, $\text{H}_2\text{B}(\text{pzMe}_2)_2$, $\text{HB}(\text{pz})_3$; $\text{pz} = \text{pyrazol-1-yl}$) afford $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2(\text{L})_2]$ whilst with $\text{K}[\text{HB}(\text{pzMe}_2)_3]$ the unsymmetrical complex $[\text{Rh}_2\text{H}(\mu\text{-C})(\mu\text{-C}_6\text{H}_4\text{PPh}_2\text{-2})\{\text{HB}(\text{pzMe}_2)_3\}_2]$ is obtained in which the carbido ligand spans $\text{d}^6\text{-Rh(III)}$ and $\text{d}^8\text{-Rh(I)}$ centres.

Bimetallic complexes bridged by a μ -carbido ligand L_nMCML_n fall into three distinct classes in which the linear MCM spine (Chart 1) may be described as cumulenic (A), metallacarbyne (B) or polar-covalent (dative) (C).

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

Class A,^{1,2} are typified by Mansuy's archetypal complex $[\text{Fe}_2(\mu\text{-C})(\text{TPP})_2]$ (TPP = tetraphenylporphyrinato)^{1a} and feature two formal $\text{M}=\text{C}$ double bonds with, in all but a couple of cases,^{1b,2} identical ML_n termini. Class B 'metallacarbynes',³ involve disparate metal termini which form metal-carbon single and triple bonds to satisfy the different electronic needs of the metals. The first of these, $[(\text{tBuO})_3\text{W}=\text{C}-\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$,^{3a} arose from an alkyne metathesis type reaction of $[\text{Ru}(\text{C}\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{W}(\equiv\text{CEt})(\text{O}^t\text{Bu})_3]$. In the interim, Class B have become the most prevalent,³ due in part to the development of halo- or lithiocarbyne chemistry. Class B μ -carbido intermediates are also implicated in palladium(0) mediated cross coupling reactions of bromocarbynes.⁴ A third class of μ -carbido complex emerged more recently for which neither class A nor B descriptions appear adequate. The terminal carbido complex $[\text{Ru}(\text{C})\text{Cl}_2(\text{PCy}_3)_2]$ reacts with coordinatively unsaturated metal centres to afford a range of heterobimetallic μ -carbido complexes⁵ in which the bonding to the extraneous metal is akin to that of CO ,⁶ *i.e.*, comprises

synergic σ -donor and π -acceptor components resulting in a polar-covalent (dative) association.

We have previously described the synthesis of a remarkably simple class A μ -carbido complex $[\text{Re}_2(\mu\text{-C})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ *via* desulfurisation of a thiocarbonyl ligand^{1d} and a Class B tetrametallic bis(μ -carbido) complex $[\text{Mo}_2\text{Ir}_2(\mu\text{-C})_2(\text{CO})_6(\text{PPh}_3)_2(\text{Tp}^*)_2]$ ($\text{Tp}^* = \text{hydrotris(dimethylpyrazolyl)borato}$) *via* insertion of iridium(I) into the CSe bond of a selenocarbonyl ligand.^{3e} Recently, Braun has shown that the thiocarbonyl complexes $[\text{Rh}(\text{SR})(\text{CS})(\text{PET}_3)_2]$ ($\text{R} = \text{BPin}, \text{GePh}_3$) react with $[\text{Rh}(\text{BPin})(\text{PET}_3)_3]$ to afford $[\text{Rh}_2(\mu\text{-C})(\text{SR})(\text{SBPin})(\text{PET}_3)_4]$.⁷ Thus chalcocarbonyl C-chalcogen bond cleavage provides a route to carbido complexes that perhaps promises some generality, given that thiocarbonyl complexes are known for many transition metals.⁸ Herein we report the remarkably facile desulfurisation of Wilkinson's prototypical thiocarbonyl complex $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ (**1**)⁹ to afford a μ -carbido complex, the synthetic versatility of which we demonstrate through ligand substitution and oxidative addition processes.

Whilst Vaska's complex reacts with catecholborane (HBCat) to afford $[\text{IrH}(\text{BCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$,^{10a} the isoelectronic but less easily oxidised complex **1** fails to react with HBCat, B_2Cat_2 , HBCat or B_2Pin_2 under ambient conditions (Cat = catecholato, Pin = pinacolato). However, slow progressive addition of HBCat to a solution of **1** in benzene at 50°C over 15 hours results in deposition of an orange complex formulated as $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{PPh}_3)_4]$ (**2**, Scheme 1) on the basis of spectroscopic ($\delta_{\text{C}}(\mu\text{-C}) = 424.4$, $^1J_{\text{RhC}} = 47$ Hz, $^2J_{\text{PC}}$ not resolved), ESI-MS, elemental microanalytical and crystallographic data (Figure 1).

Scheme 1. Synthesis and Reactions of a μ -Carbido Complex **2**.

The molecular structure has approximate (non-crystallographic) D_{2d} symmetry with equal Rh=C bond lengths (1.773(3), 1.780(3) Å; Class A). Previously, we have computationally interrogated the remarkably low rotation barrier for the metal termini of $[\text{Re}_2(\mu\text{-C})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (cf. allenes)^{1d} and suggest a similar situation presents itself here such that the disposition of the phosphine ligands is primarily steric in origin, as depicted in Figure 1. The mechanism whereby **1** is converted to **2** with net loss of the elements of CS_2 remains obscure. We can, however, discount the participation of some otherwise plausible mechanistic candidates. Specifically, the reactions of **1** with either $[\text{RhH}(\text{BCat})\text{Cl}(\text{PPh}_3)_2]$ (**3**)^{10b} or $[\text{RhCl}(\text{BCat})_2(\text{PPh}_3)_2]$ (**4**)^{10c} though complex, fail to result in spectroscopically detectable amounts of **2** under these conditions (C_6D_6 , 50 °C). Furthermore the yields of **2** are not improved by inclusion of a further equivalent of $[\text{RhCl}(\text{PPh}_3)_3]$. Although $\text{S}=\text{PPh}_3$ is observed (^{31}P NMR) in the supernatant from the formation of **2**, triphenylphosphine does not react *directly* with **1**, being present in excess under the conditions of its formation.

Figure 1. Molecular structure of **2** in a crystal of $2\text{CH}_2\text{Cl}_2$ (60% displacement ellipsoids, phosphine substituents simplified). Insets $^{13}\text{C}\{^1\text{H}\}$ resonance for $\mu\text{-C1}$ (50% ^{13}C -enriched) and space filling representation depicting inter-digitation of adjacent phosphines based on P1, P2 (green) and P3, P4 (pink).

The halide of **2** is labile, as evidenced *inter alia* by reactions with poly(pyrazolyl)borates $\text{K}[\text{H}_n\text{B}(\text{pz})_{4-n}]$ and $\text{K}[\text{H}_n\text{B}(\text{pzMe}_2)_{4-n}]$ ($n = 1, 2$; $\text{pz} = \text{pyrazol-1-yl}$; $\text{pzMe}_2 = 3,5\text{-dimethylpyrazol-yl}$; Scheme 2). These led to the isolation of the complexes $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}_2]$ (**5a**), $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pzMe}_2)_2\}_2]$ (**5b**) and $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2\{\text{HB}(\text{pz})_3\}_2]$ (**6a**), each of which retains an intact $\text{Rh}=\text{C}=\text{Rh}$ spine (Figure 2).

Scheme 2. Poly(pyrazolyl)borate Ligated μ -Carbido Complexes.

Figure 2. Molecular structures of (a) $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pz})_2\}_2]$ (**5a**) in a crystal of **5a**· CH_2Cl_2 , (b) $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{pzMe}_2)_2\}_2]$ (**5b**) in a crystal of **5b**· C_6H_{14} and (c) $[\text{Rh}_2(\mu\text{-C})(\text{PPh}_3)_2\{\text{HB}(\text{pz})_3\}_2]$ (**6a**) in a crystal (60% displacement ellipsoids, phosphine and pyrazolyl substituents simplified).

No structural data were previously available for 5-coordinate rhodium complexes of the $\text{H}_n\text{B}(\text{pz})_{4-n}$ or $\text{H}_2\text{B}(\text{pzMe}_2)_2$ chelates, suggesting that the preference for the d^8 -square planar geometry characteristic of rhodium(I) outweighs any advantage from even *H-anagostic* B–H–Rh coordination,¹¹ though this is more favoured for the $\text{H}_2\text{B}(\text{mt})_2$ chelate (methimazolyl).¹² Even the $\text{HB}(\text{pz})_3$ ligand usually fails to coordinate all three pyrazolyl groups to rhodium(I) in the solid state (polyhapto ligands notwithstanding), e.g., in the 4-coordinate complex $[\text{Rh}(\text{PPh}_3)_2\{\kappa^2\text{-N,N'}\text{-HB}(\text{pz})_3\}]$,¹³ although

oxidation to Rh(III) is usually accompanied by cage closure and adoption of the $\kappa^3\text{-N,N',N''}$ ('octahedral enforcer') mode. Thus adoption of the κ^3 -mode in **6a** is somewhat unusual, though NMR data indicate that the ligand undergoes site exchange in solution, most likely via $\kappa^2\text{-N,N'}$ coordination.

For each of **5a**, **5b** and **6a**, the carbido atom lies on a 2 or 2_1 axis, such that only half of each molecule is crystallographically unique and the two Rh=C bonds are identical. For **5a** (1.7644(11), 1.7680(11) Å, two independent molecules) and **5b** (1.7794(9) Å) these are similar to those found for **2**. Surprisingly, however, the Rh1=C1 bond length in **6a** (1.7761(7) Å) also falls within this range, despite the increased coordination number (5 vs 4) and generally cluttered environment around rhodium. In each case, the Rh1=C1=Rh1 angle is somewhat less than 180° (**5a**: 169.1(7); **5b**: 168.8(6) - 170.4(6); **6a**: 163.7(4)°) suggesting the energy required for deformation of the cumulenyl spine can be comparable to crystal packing and intramolecular non-bonding effects, as is also encountered for non-linear carbyne and alkynyl ligands. It should be noted that the new thiocarbonyl complex [Rh(CS)(PPh₃){HB(pz)₃}] (**8**)¹⁴ does *not* appear to react with HBCat to afford **6a** under conditions so far explored, including those optimised for the synthesis of **2**.

The bulky HB(pzMe₃)₃ ligand has played a crucial enabling role in the development of group 6 carbido chemistry^{4c-f,15} and so the reaction of **2** with K[HB(pzMe₃)₃] was also explored. Whilst the early stages of the reaction may well proceed in a manner akin to the formation of **6a**, if the complex [Rh₂(μ-C)(PPh₃)₂{HB(pzMe₂)₃}₂] (**6b**) actually forms then it does not endure but rather converts *via* phosphine expulsion to a new unsymmetrical μ-carbido complex [Rh₂H(μ-C)(μ-C₆H₄PPh₂-2){HB(pz)₃}₂] (**7**) in which the *single* remaining PPh₃ ligand has undergone a bimetallic *ortho*-metallation (Scheme 2, Figure 3). The diamagnetism of the complex indicates that a Class A description is still appropriate.

The C₆H₄PPh₂-2 ligand is commonly encountered bridging two metal centres,¹⁶ however, when the metals are bridged by a further atom (typically hydride or halide), these atoms exclusively lie off the metal-metal vector. In the case of **7** a slightly bent Rh=C=Rh unit (165.9(3)°) results in an intermetallic separation of 3.531 Å which is still comfortably bridged by the 2-phosphinophenyl group. This group twists such that the Rh1–Rh2 vector is at 34.1° to the P1–C11–C12 plane, suggesting unforeseen coordinative flexibility for this bridging group. Despite the two rhodium centres being in different oxidation states (I vs III) and adopting different coordination numbers (5 vs 6), the Rh^I=C1 (1.740(6) Å) and Rh^{III}=C1 (1.818(6) Å) bond lengths are only marginally different (8 pm, 13 e.s.d.). The presumed effects of the increased oxidation state (contraction) thus appear to be counterbalanced by the increased coordination number and reduced retrodonation (elongation). The octahedral geometry around Rh2 provides an opportunity to explore the *trans* influence of the carbido linkage relative to hydrido and σ-aryl ligands. Thus the Rh–N distances for pyrazolyl groups coordinated *trans* to the carbido (2.182(5) Å) and hydrido ligands (2.203(5) Å) are very similar (4 e.s.d.) and somewhat longer than that *trans* to the cyclometallated σ-aryl (2.158(5) Å, Δ = 8 e.s.d.). Putting aside the caveats associated with comparing *trans* influences in 4 and 6 coordinate

complexes, the molecular structure of **5b** also suggests identical *trans* influences for the carbido and phosphine ligands.

Figure 3. Molecular structure of [Rh₂(μ-C)(μ-C₆H₄PPh₂-2){HB(pzMe₂)₃}₂] (**7**) in a crystal (60% displacement ellipsoids, phosphine and pyrazolyl substituents simplified). Inset = ¹³C{¹H} resonance for ¹³C-enriched μ-C1.

Complexes bearing both hydrido and cyclometallated 2-phosphinoaryl ligands can often represent ground-state tautomers of the corresponding coordinatively unsaturated arylphosphine complex *via* reversible C–H bond activation/reformation.^{16,17} In the case of **7** we see no evidence for this. NOE experiments fail to reveal any correlation between the hydride resonance and those for the remaining *ortho*-hydrogen atoms of the C₆H₄PPh₂ ligand, whilst exposure of **7** to CO fails to trap a coordinatively unsaturated tautomer as “[Rh₂(μ-C)(CO)(PPh₃){HB(pzMe₂)₃}₂]” akin to **5a**, **5b** or **6a**. Although **7** would therefore appear to form irreversibly, it is nevertheless of interest that **6a** appears indefinitely stable, at least under mild conditions, *i.e.*, the small change from HB(pz)₃ to HB(pzMe₂)₃ has a dramatic impact on the reactivity of the rhodium centre. The activation of C–H bonds by ‘M{HB(pzMe₂)₃}’ (M = Rh, Ir) platforms has been studied in considerable detail.¹⁸ It is also worth noting that whilst **7** presents both hydrido and σ-aryl groups *cis* to the carbido ligand, we see no evidence for the operation of migratory insertion processes that are ubiquitous in rhodium mediated catalysis.

In conclusion, the facile synthesis and synthetic utility of a remarkably simple dirhodium μ-carbido complex has been demonstrated. This has allowed the isolation of a range of dinuclear μ-carbido complexes in which the rhodium centres are either d⁸-Rh(I) or d⁶-Rh(III) and adopt coordination numbers of 4, 5 or 6. These include both symmetrical and unsymmetrical examples, with all adhering to the Class **A** (dimetallacumulenic) bonding scenario. The reluctance of complex **7** to enter into classical organometallic ligand coupling processes (C–H reductive elimination, migratory insertion involving hydride or aryl ligands with the carbide ligand or extraneous CO) attest to the chemically robust nature of the Rh=C=Rh linkage.

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