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A Dirhoda-Heterocyclic Carbene

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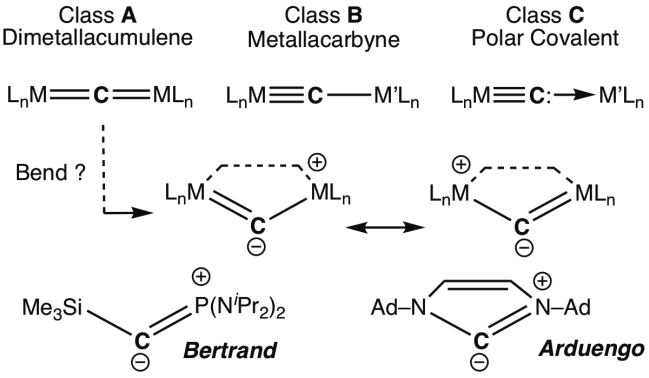
Abstract: The linear μ-carbido complex [Rh_2(μ-C)Cl_2(dppm)$_2$] (dppm = bis(diphenylphosphino)methane) reacts with dimethylacetylene dicarboxylate (DMAD) to afford [Rh_2(μ-C)(μ-DMAD)Cl_2(dppm)$_2$], which features a bent RhCRh linkage (124.7°) that might be described as a dirhoda-heterocyclic carbene, as demonstrated by coordination to further metal centres.

The demonstrations by Bertrand[1] and Arduengo[2] that two-coordinate divalent carbon derivatives (carbenes, Scheme 1) could be isolated were followed with remarkable rapidity by applications in all manner of fields of chemical research, most notably in catalysis,[3] and as supporting groups for the stabilisation of unusual coordination numbers and geometries.[4] Amongst these many curious species, 'bent allenes' or 'carbodicarbenes' in which a central carbon is ligated by two *N*-heterocyclic carbenes (NHC) provide further examples wherein non-linear geometry at two-coordinate carbon results in the development of nucleophilic character.[5,6]



Scheme 1. Nucleophilic non-linear two coordinated carbon species,[1,2,5] and linear μ-carbido coordination modes.[8-11]

Two-coordinate carbon is also found in bimetallic μ-carbido complexes[8-11] and in all cases the established geometry at carbon is linear, notwithstanding minor deformations from crystal packing effects. The single exception is the unstable μ-carbido complex [Ru_2(μ-C)(μ-N^{t}Bu)(η-C_5Me_5)$_2$], which although not isolable, could be spectroscopically observed (δ_C = 675) at low temperature. Computational modelling and reactivity studies pointed towards a bent nucleophilic carbido ligand with singlet carbene character.[12]

The intimate bonding within linear metal-carbon-metal spines falls into one of three classes (Scheme 1), depending on the effective atomic number requirements of the metal termini. Whilst metallacarbynes (Class **B**) and polar covalent (Class **C**) examples represent the fastest growing cohorts, the symmetrical dimetallacumulenic form (Class **A**)[10] is the oldest, dating back to Mansuy's archetypal [Fe_2(μ-C)(TPP)$_2$] (TPP = tetraphenylporphyrinato).[11] The dimetallacumulene description calls to mind isolobal analogies with allene itself, which we have, however, had reason to question. Allene has a high barrier (*ca* 200 kJmol^{-1}) to rotation of the termini about the central carbon due to the 2σ,2π 3-centre, 8-electron bonding manifold being compromised on approach to a requisite D_{2h} transition state. In contrast, the simple μ-carbido complex [Re_2(μ-C)(CO)$_4$(η-C_5H_5)$_2$] has a negligible rotation barrier (*ca* <16 kJmol^{-1}), which is attributed to the bonding being better described as a 2σ,4π 3-centre, 12-electron system which is not significantly disrupted at any rotational angle.[10c] To further test the allene analogy, one might ask how the nature of the μ-carbido centre might respond to departure from linearity: Is there a μ-carbido version of a bent allene? Does this impart nucleophilic character on the μ-carbido centre? We report herein, the isolation and characterisation of the first stable example of a bent μ-carbido complex which allows these questions to be addressed.

The A-frame μ-carbido complexes [Rh_2(μ-C)X_2(μ-dppm)$_2$] (X = Cl **1a**, Br **1b**; dppm = bis(diphenylphosphino)methane)[13] comprise two formally d^8-square planar Rh(I) centres[14] that one might anticipate would be prone to oxidative addition or ligand addition processes. In the case of halogenation, such a process may well operate, however the final products of the reactions of **1a** with $PhICl_2$ or of **1b** with [pyH][Br_3] were the novel μ-halocarbyne complexes [Rh_2(μ-CX)(μ-X)X_4(μ-dppm)$_2$] (X = Cl **2a,** X = Br **2b**). While investigating the possibility of ligand addition to the coordinatively unsaturated rhodium centres, the reaction of **1a** with dimethyl acetylenedicarboxylate (DMAD) was explored, given that this alkyne readily forms adducts with other Rh(I) and Ir(I) centres, when less activated alkynes fail.[15] A rapid reaction ensued to provide a single major red product following chromatographic purification (silica gel) in 93% yield, which was identified as [Rh_2(μ-C)(μ-DMAD)Cl_2(μ-dppm)$_2$] (**3**, Scheme 2). The formulation of **3** followed from spectroscopic and mass spectrometric data and was confirmed by a crystallographic analysis, the results of which are summarized in Figure 1.

The most notable features of the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra relate to the molecular symmetry that they imply. Thus a single doublet resonance is observed in the ^{31}P{^{1}H} NMR spectrum ($CDCl_3$: δ_P = 12.5) with only one observable Rh-P coupling constant ($^1J_{RhP}$ = 137 Hz) being indicative of an increase in coordination at rhodium and negligible inter-rhodium interaction (absence of $^3J_{RhP}$) relative to those for the precursor **1a** ($^{1,3}J_{RhP}$ = 150, 40 Hz). Two distinct multiplet resonances due to the diastereotopic phosphino methylene protons (δ_H = 2.29, 3.60) indicate that the complex has two, but not three mirror planes,

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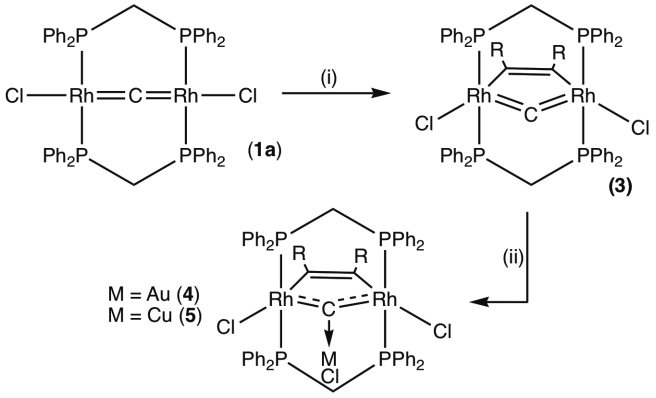
i.e., that the opposite faces of the P_4Rh_2 A-frame are distinct (*cf.* a single resonance for *ca* D_{2h}-symmetric **1a**).



Scheme 2. Synthesis of a bent μ-carbido complex **3** and *Rh*HC complexes **4** and **5** (R = CO_2Me**).** (i) RC≡CR, CH_2Cl_2, 30 min. (ii) [AuCl(SMe_2)] or [CuCl(SMe_2)], CH_2Cl_2, 30 min.

The signals in the $^{13}C\{^1H\}$ NMR spectrum of most interest derive from the original μ-carbido and the added alkyne, however in the absence of ^{13}C-isotopic enrichment,[10g] their identification was problematic due to their association with the six 100% abundant I = ½ nuclei of the $^{31}P_4{}^{103}Rh_2$ core. This was eventually resolved through recourse to HMBC-^{1}H,^{13}C measurements which revealed correlations between the methyl ester proton (δ_H = 2.39) and μ-alkyne carbon (δ_C = 74.8) resonances. The μ-carbido resonance was unable to be located through 1D $^{13}C\{^1H\}$ or 2D ^{31}P-$^{13}C\{^1H\}$ NMR studies due to the low solubility of the complex in organic solvents, though it is expected to be increasingly downfield relative to that found for [Rh_2(μ-^{13}C)Cl_2(PPh_3)$_4$] (δ_C = 424.4, $^1J_{RhC}$ = 47 Hz).[10g]

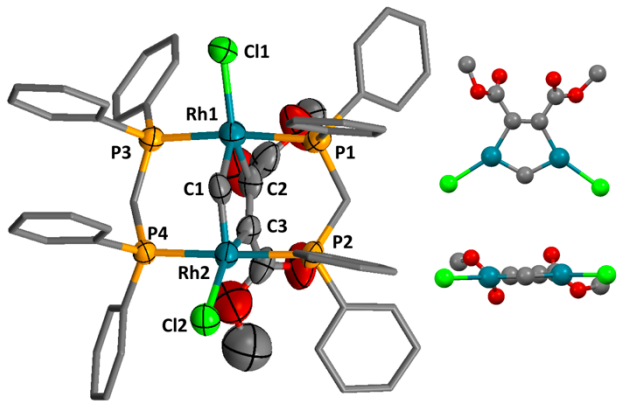
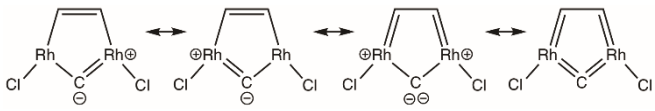


Figure 1. Molecular structure of **3** (50% displacement ellipsoids, hydrogen atoms omitted and phosphine substituents simplified, one of two positionally disordered CO_2Me orientations shown). Selected distances [Å] and angles [°]: Rh1–Cl1 2.451(4), Rh1–C2 2.008(14), Rh1–C1 1.851(19), Rh2–Cl2 2.447(4), Rh2–C1 1.860(16), Rh2–C3 2.006(17), C2-Rh1-Cl1 154.3(5), C1-Rh1-Cl1 117.3(5), C1-Rh1-C2 88.4(7), C1-Rh2-Cl2 118.3(6), C1-Rh2-C3 88.6(8), C3-Rh2-Cl2 153.0(5).

The molecular geometry of **3** is depicted in Figure 1 and confirms the symmetrical μ:σ,σ' binding of the DMAD ligand. The rhodium-carbon (2.008(14), 2.006(17) Å) and alkyne C–C (1.30(2) Å) bond lengths are comparable to those found in [Rh_2(μ-CO)(μ-DMAD)(μ-dppm)$_2$] (2.004(6) and 1.32(1) Å, respectively)[16] and are consistent with a degree of multiple bonding in each. Interest however focus on the μ-carbido ligand for which the rhodium carbon bonds (1.851(19), 1.860(16) Å) most definitely reflect multiple bonding although they are significantly elongated relative to the precursor **1a** (1.732(11), 1.757(11) Å). Most significant, however, is the bent nature of the Rh–C–Rh linkage (124.7(10)°) that separates the two rhodium atoms (3.279(2) Å) beyond accepted bonding norms ($2r_{cov}$(Rh) = 2.84 Å).[17] These geometrical data are therefore consistent with a combination of the diamagnetic canonical forms depicted in Scheme 3. This in turn calls for **3** to be considered within the burgeoning field of metalla-aromatics,[18] adopting what is clearly a delocalised π-system for the planar CRh_2C_2 ring (max. dev. = 0.011 Å by C2).



Scheme 3. Canonical descriptions of the delocalised bonding in the core of **3.**

Electronic delocalization is also substantiated by computational interrogation[19] of the simpler model complex [Rh_2(μ-C)(μ-HCCH)Cl_2(μ-dmpm)$_2$]. Optimization resulted in an essentially identical geometry for the CRh_2C_2 core, despite variation in the alkyne and phosphine substituents. Figure 2 depicts molecular orbitals of interest, which present remarkably similar topologies to those of a conventional *N*-heterocyclic carbene, *e.g.*, *N,N'*-dimethylimidazolylidene.

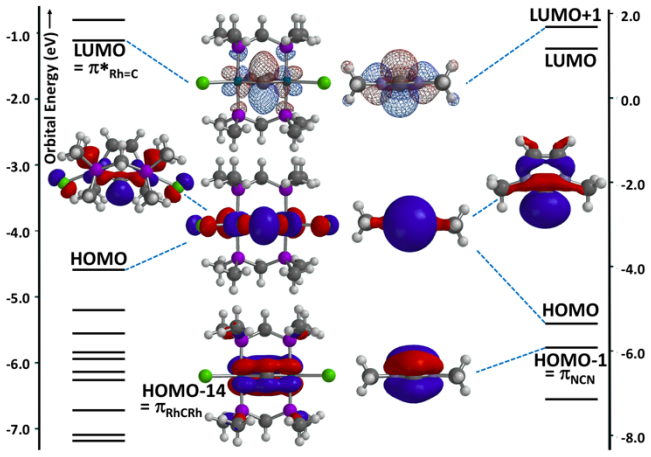


Figure 2. Molecular orbitals of interest to an incoming electrophile for [Rh_2(μ-C)(μ-C_2H_2)Cl_2(dmpm)$_2$] (left) and *N,N'*-dimethylimidazolylidene (right).

The radially directed in-plane HOMO is of σ-symmetry and includes contribution from the d_z2 orbital on each metal if the Rh=C vector is taken as the z-axis for each square-pyramidal

(Rh-τ_5 = 0.31) metal. Similarly, the LUMO, of π-symmetry with respect to the ring plane, is primarily localised on the carbido atom but with notable contribution, in a Rh-C π^* antibonding manner, of the d_{yz} orbital on each rhodium, denoting the trans P···P vector as the y axis.. The HOMO-LUMO gap of 4.4 eV is intermediate between those found for *N*-heterocyclic carbenes and cyclic alkyl aminocarbenes[20] and the μ-carbido is found to carry a substantial negative charge (Natural = -0.41, Mulliken = -0.24, Electrostatic = -0.87). The rhodium-carbon interactions have considerable multiple bond character (Löwdin B.O. 1.71) relative to those of alkyne carbons (0.98). Typically, the ν_{MCM} infrared absorption for μ-carbido linkages is rarely identified or reported, reflecting the weak vibrational change in dipole for the non-polar linear arrangement. In the case of **3** with a bent Rh=C=Rh linkage, an absorption is observed at 798 cm^{-1} which is absent from the infrared spectrum of the precursor and most likely corresponds to the calculated value (765 cm^{-1}) for the asymmetric Rh=C=Rh stretching mode, which also includes a small amount of dmpe alkyl libration. The symmetric stretch is not infrared active and neither was it evident in the Raman spectrum though it is calculated to appear at 566 cm^{-1}.

The most immediate test of the *N*HC *cf. Rh*HC analogy would be to demonstrate coordination of the 'carbene' to a metal centre. This was easily achieved by treating **3** with one equivalent of [AuCl(SMe$_2$)] to afford the complex [Rh$_2$Au(μ_3-C)(μ-DMAD)Cl$_3$(dppm)$_2$] (**4**), the $^{31}P\{^1H\}$ and ^1H NMR data (δ_P = 7.8, $^1J_{RhP}$ = 130 Hz; δ_H = 2.39 OCH_3, 3.60, 2.29 PCH_2) for which confirm the retention of molecular C_{2v} symmetry. The infrared data for **4** are remarkably similar to those for **3** with the notable exception of the conspicuous absence of an absorption around 798 cm^{-1}, adding support to the assignment of this band for the precursor to the ν_{as}(Rh=C=Rh) mode. The formulation as a trigonal μ_3-carbido complex was confirmed by a crystallographic analysis (Figure 3) which revealed rather modest variations in the geometrical parameters of the CRh_2C_2 ring *cf.* those for **3**, in addition to a C1–Au bond length (1.982(8)Å) that is comparable to those for conventional gold(I)-NHC complexes. The rhodium-carbido bond lengths are marginally extended relative to the precursor **3** (1.851(7) and 1.867(7) Å for Rh1 and Rh2 respectively). A ligated water molecule was also identified coordinated to one rhodium although the Rh-O1 separation (2.417(8) Å) is particularly long and as indicated by the spectroscopic data this does not remain coordinated in solution.

In a similar manner the reaction of **3** with cuprous chloride results in the formation of the copper chloride adduct [Rh$_2$Cu(μ_3-C)(μ-DMAD)Cl$_3$(dppm)$_2$] (**5**). In the solid state, as with **4**, one water molecule coordinates to one rhodium however this does not remain coordinated in solution. The molecular structure is essentially identical with that of **4** (see ESI, Figure S1).

The dirhodium heterocyclic carbene **3** is by any standards sterically encumbered, taking up 63.8% buried volume[21] in the complex **4** (Figure 4), which far exceeds that of most conventional *N*HC ligands.[22] This presumably contributes to the remarkable thermal and aerobic stability of the shielded carbene donor.

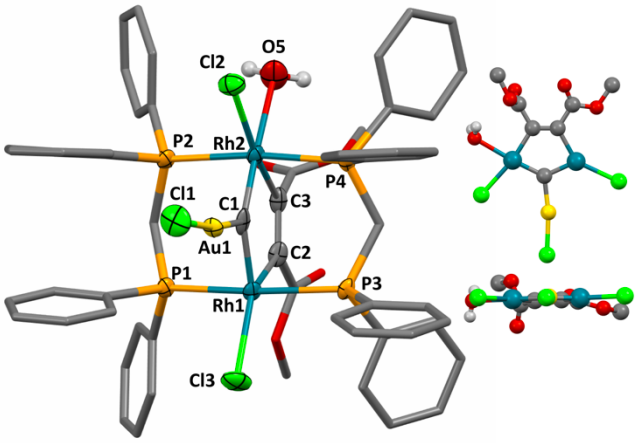


Figure 3. Molecular structure of **4** in a crystal of **4**.H_2O.CH_2Cl_2 (50% displacement ellipsoids, hydrogen atoms and solvent omitted and phosphine substituents simplified). Selected distances [Å] and angles [°]: Rh1-C1 1.852(8), Rh1-C2 2.033(7), Rh1-Cl2 2.490(2), Rh2-C1 1.869(7), Rh2-C3 2.019(7), Rh2-Cl3 2.486(2), Au1-C1 1.979(7), Au1-Cl1 2.308(2), C2-C3 1.33(1), Rh1-C1-Rh2 128.8(4), Rh2-C3-C2 121.7(5), C1-Au1-Cl1 171.5(2).

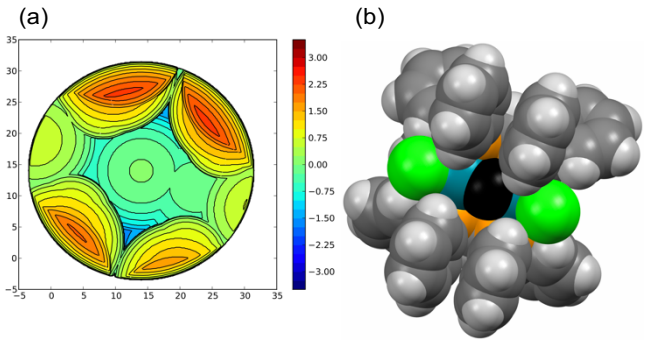


Figure 4. Alternative representations of the steric profile of **3**. (a) Steric map.[21] (b) Space-filling with μ-carbido shown as black.

In conclusion, the reaction of a class **A** dimetallacumulenic μ-carbido has provided the first isolable example of a bent μ-carbido ligand. Structural, spectroscopic and computational interrogation point to an analogy with *N*-heterocyclic carbenes or perhaps carbodicarbenes, which could be experimentally demonstrated by coordination to extraneous metals.

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Keywords: carbone • carbido • carbodicarbene • metalla-aromaticity • heterocyclic carbene

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[14] Herein we consider the μ-carbido ligand as a neutral carbon atom providing two valence electrons to each rhodium(I) centre. An alternative, description would envisage a tetranionic (C^{4-}) ion between two Rh(III) centres, although this is implausible in terms of electroneutrality arguments.

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