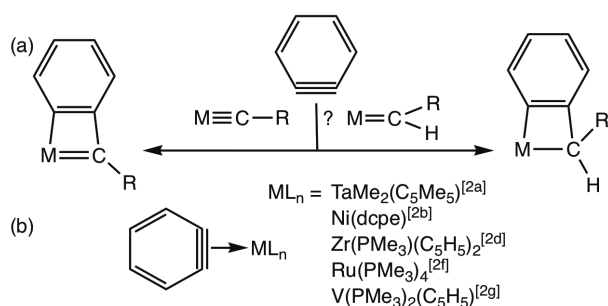


## Benzynes addition to a metal-carbon multiple bond.

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The linear  $\mu$ -carbido complex  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\text{dppm})_2]$  ( $\text{dppm}$  = bis(diphenylphosphino)methane) reacts with a benzyne equivalent ( $\text{Me}_3\text{SiC}_6\text{H}_4\text{OTf-2/F-}$ ) to afford  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4)(\mu\text{-Cl})(\text{C}_6\text{H}_5)\text{Cl}_2(\mu\text{-dppm})_2]$ , in which the benzyne moiety adds across one of the two metal-carbon double bonds.

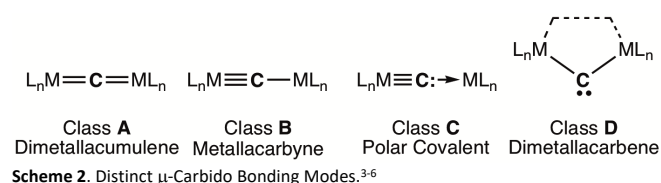
Metallacyclobutadiene formation *via* the formal cycloaddition of metal-carbon and carbon-carbon triple bonds provides the central mechanistic tenet of alkyne metathesis.<sup>1</sup> Arynes (1,2-dehydroarenes) constitute an exceedingly reactive class of alkynes and whilst the free molecules have never been isolated their coordination complexes display a rich organometallic chemistry (Scheme 1). A question yet to be considered is whether benzyne might also participate in [2+2] cyclo-addition reactions with metal-carbon multiple bonds in a manner akin to conventional alkynes (Scheme 1a). Herein we address this question by describing the addition of benzyne to the metal-carbon multiple bond of a dimetallacumulenic  $\mu$ -carbido complex.



Scheme 1. (a) Putative Cycloadditions of Benzyne with Metal-Carbon multiple bonds and (b) Selected Archetypal  $\eta^2$ -Benzyne Complexes.<sup>2</sup>

The bonding of bimetallic  $\mu$ -carbido complexes may be described by one of four bonding scenarios (Scheme 2)<sup>3-6</sup> that vary in the number of valence electrons (1, 2 or 3) required by each of the similar (Classes **A**<sup>3</sup> and **D**<sup>6,7</sup>) or disparate (Classes **B**,<sup>4</sup> and **C**<sup>5</sup>) metal termini, so as to acquire satisfactory effective atomic numbers (16 or 18 valence electrons). As examples from each class have been sporadically identified, an understanding of the more complex bonding within 'MCM' spines has begun to emerge.<sup>3n,5g,6a,b</sup> The reactivity of binuclear  $\mu$ -carbido complexes however remains essentially uncharted, being limited to various co-ligand substitutions,<sup>3i,3m,4b,4g,5e,6a</sup> oxidation to CO,<sup>3l</sup> CS or CSe<sup>7</sup>

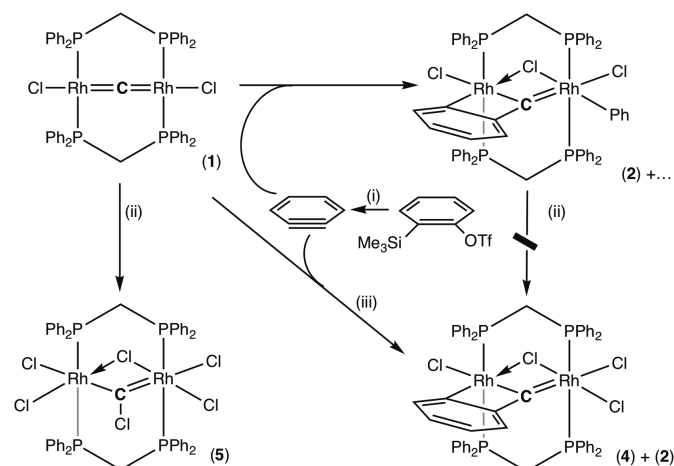
ligands, protonation to afford  $\mu$ -methyldiyne ( $\mu\text{-CH}$ ) ligands,<sup>4b</sup> coupling with  $\text{CS}_2$ ,<sup>4b,7</sup> halogenation to afford  $\mu$ -halocarbynes<sup>3m</sup> and interconversion of bonding classes (Classes **C**  $\rightarrow$  **B**<sup>5e,f</sup> and **A**  $\rightarrow$  **D**<sup>6a</sup>). In the case of Class **D**  $\mu$ -carbidos, the bent geometry at carbon renders it nucleophilic in reactions with a range of electrophiles ( $\text{CO}_2$ ,  $\text{MeOH}$ , chalcogens, metals).<sup>6</sup>



Recently, the activated alkyne dimethylacetylene dicarboxylate (DMAD,  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ ) was unexpectedly found to undergo formal [3+2] cycloaddition of the  $\text{C}\equiv\text{C}$  bond across the initially linear  $\text{Rh}=\text{C}=\text{Rh}$  spine of  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\mu\text{-dppm})_2]$  (**1**:  $\text{dppm}$  = bis(diphenylphosphino)methane), to provide the first structurally authenticated bent ( $124.7(10)^\circ$ )  $\mu$ -carbido complex  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\mu\text{-DMAD})(\mu\text{-dppm})_2]$ .<sup>6a</sup> The carbido ligand displays nucleophilic character substantiating its description as a *Dimetalla*-Heterocyclic Carbene (MHC).<sup>6a,7</sup> Whilst similar MHCs could be obtained with other highly electrophilic alkynes ( $\text{RC}\equiv\text{CCF}_3$ ,  $\text{R} = \text{CF}_3$ ,  $\text{CO}_2\text{Me}$ ),<sup>8</sup> attempts to extend this to simple non-activated alkyl, aryl or terminal alkynes failed. We have therefore turned our attention to highly reactive but transient benzyne with a view to perhaps constructing *benzo*-MHC derivatives. For the purpose of installing a benzyne ligand, we adopted the Kobayashi protocol by which fluoride-mediated desilylation of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate ( $\text{Me}_3\text{SiC}_6\text{H}_4\text{OTf-2}$ ), affords a benzyne equivalent under mild conditions.<sup>9</sup>

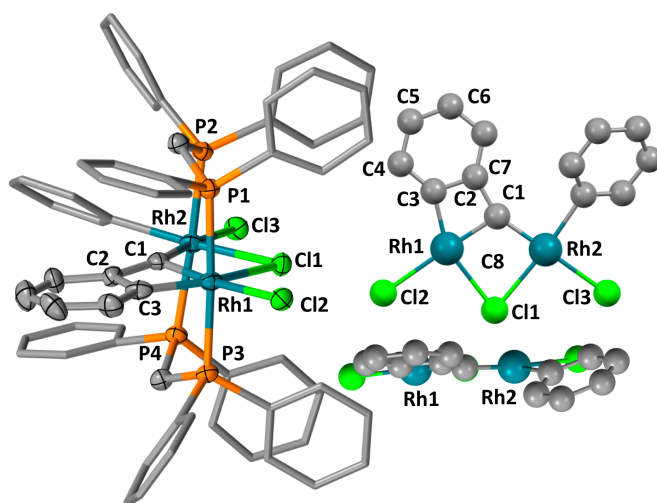
Treating the  $\mu$ -carbido complex **1** with  $\text{Me}_3\text{SiC}_6\text{H}_4\text{OTf-2}$  resulted in no discernible reaction prior to the subsequent addition of fluoride ( $[\text{t}^n\text{Bu}_4\text{N}]\text{F} = \text{TBAF}$ ) which resulted in an instant colour change to a dark red solution. Chromatographic purification afforded a pink/red product **2**, the spectroscopic data for which were however inconsistent with the formation of the desired  $\text{C}_{2v}$ -symmetric benzo-MHC complex  $[\text{Rh}_2(\mu\text{-C})\text{Cl}_2(\mu\text{-}\sigma\text{-}\sigma^1\text{-C}_6\text{H}_4)(\mu\text{-dppm})_2]$ . Specifically, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum indicated reduced symmetry ( $\text{C}_s$ ) and could be

modelled as an AA'BB'XY system ( $^{103}\text{Rh}$ ,  $^{31}\text{P}$   $I = \frac{1}{2}$  100%;  $\delta_{\text{P}} = 1.93, 6.92$ ,  $J_{\text{AB}} = 11$  Hz) with  $J_{\text{RhP}}$  values for the two chemically inequivalent rhodium centres (119, 125 Hz) being indicative of octahedral coordination. Furthermore, ESI-MS data ( $[\text{M}-\text{Cl}]^+$ :  $m/z = 1209.0574$ ) indicated addition of the elements of both benzyne and  $\text{C}_6\text{H}_5\text{Cl}$ . The identity of **2** as  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4)(\mu\text{-Cl})(\text{C}_6\text{H}_5)\text{Cl}_2(\text{dppm})_2]$  was established through single crystal X-ray diffraction analysis (Figure 1), which revealed that benzyne had added across one Rh=C bond rather than the Rh=C=Rh spine (Scheme 3). Furthermore, the two rhodium centres were bridged by a chloride with one also bearing a  $\sigma$ -phenyl ligand.



**Scheme 3.** Addition of benzyne to a  $\mu$ -carbido complex. (i) MeCN/THF,  $[\text{Bu}_4\text{N}]^+$  or  $[\text{Bu}_4\text{N}][\text{Ph}_3\text{SiF}_2]$ ,  $\text{Me}_3\text{SiC}_6\text{H}_4\text{OTf}$ -2. (ii) HCl in Et<sub>2</sub>O. (iii)  $[\text{NH}_4]\text{Cl}$ .

The two six-coordinate rhodium centres are symmetrically bridged by a chloride ligand and separated by 3.1760(7) Å. This exceeds the distance considered to indicate a formal bonding interaction ( $2r_{\text{cov}}(\text{Rh}) = 2.96$  Å), and indeed on the basis of effective atomic number (EAN) requirements there is no need to invoke metal-metal bonding. Despite presumed ring-strain, the Rh1-C3 bond (1.94(2) Å) of the rhodacycle is significantly shorter than that for the conventional  $\sigma$ - $\text{C}_6\text{H}_5$  ligand (2.19(2) Å), suggesting a degree of Rh-C multiple bond character. It is certainly appropriate to infer Rh-C multiple bonding to C1 (Rh1-C1 = 1.916(8), Rh2-C1 = 1.922(8) Å) given that complex **2** might be viewed as involving a cyclometallated  $\mu$ -benzylidyne ligand by analogy with the only known dirhodium  $\mu_2$ -carbynes  $[\text{Rh}_2(\mu\text{-CCl})\text{Cl}_5(\mu\text{-dppm})_2]$  (Rh-C = 1.948(6), 1.912(6) Å)<sup>3k</sup> and  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})(\eta\text{-C}_5\text{Me}_5)_2]\text{BPh}_4$  (Rh-C = 1.903(10) Å).<sup>10</sup> The ring-strain and geometric constraints that attend cyclometallation result in significant deviations from ideal  $sp^2$ -carbon geometries (Rh1-C1-Rh2 = 111.7(4)°, Rh1-C1-C2 = 93.6(4)°, C1-Rh1-C3 = 70.3(4)°), the most dramatic being the Rh2-C1-C2 angle of 153.3(4)° which also has spectroscopic ( $^{13}\text{C}$  NMR) implications.

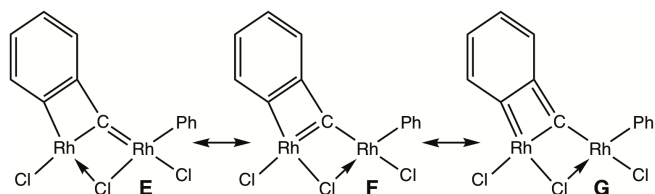


**Figure 1.** Molecular structure of **2** in a crystal (50% displacement ellipsoids, one of two positionally disordered metallacycle orientations shown, hydrogen atoms omitted and phenyl groups simplified). Selected bond lengths (Å) and angles (°): Rh1-C1 1.916(8), Rh2-C1 1.922(8), Rh1-C3 1.94(2), Rh2-C8 2.19(2), C1-C2 1.44(2), C2-C3 1.41(3), Rh1-Rh2 3.1760(7), Rh1-C1-Rh2 111.7(4), Rh1-C1-C2 93.6(4). Inset shows view orthogonal to the Rh-C-Rh plane with phosphine ligands omitted.

The ten aryl groups in **2** complicate the  $^1\text{H}$  NMR spectrum, however the shielding effect of the rhodium centre disperses the  $\text{RhC}_6\text{H}_5$  ( $\delta_{\text{H}} = 6.00, 6.22, 6.77$ ) and  $\text{Rh}_2\text{CC}_6\text{H}_4$  ( $\delta_{\text{H}} = 5.36, 6.66, 6.74, 7.60$ ) resonances sufficiently that these could be identified by a combination of  $^1\text{H}$ - $^1\text{H}$  COSY and ROESY experiments. The latter revealed a correlation between the resonances at  $\delta_{\text{H}} = 6.77$  and 5.36 due to the proximity of the *ortho* protons of the  $\text{RhC}_6\text{H}_5$  ligand with that bound to C7, which precludes coplanarity of these two rings in the solid state (Figure 1).

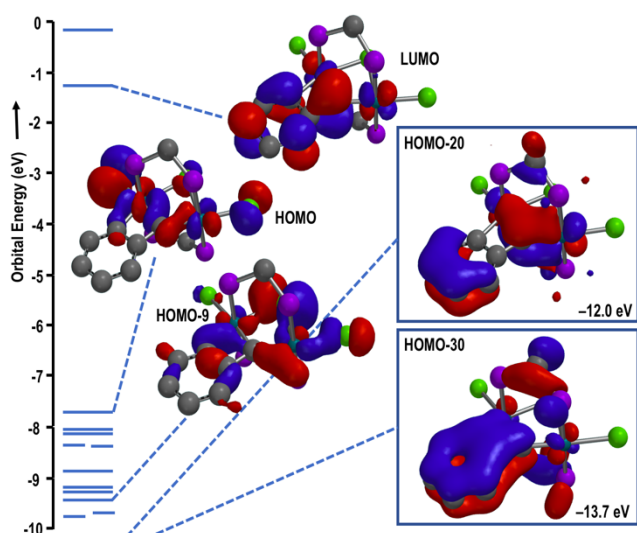
The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum revealed the resonances attributed to the two rhodium-bound aryl carbon nuclei shifted downfield ( $\delta_{\text{C}} = 171.3, 144.9$  ppm), however the resonance corresponding to the bridging carbonyl carbon could only be located with recourse to  $^{13}\text{C}$  enrichment (50%), at a remarkably low field ( $\delta_{\text{C}} = 394.8$ ,  $^1J_{\text{RhC}} = 35.6$  Hz).<sup>3j</sup> Once identified, the resonance was found to correlate ( $^1\text{H}$ - $^{13}\text{C}$  HMBC, see ESI Figure S13) with the resonances assigned to the benzo group.

The bonding within the dirhodium complex of **2** may be described *inter alia* by valence-bond forms (Scheme 4), however computational interrogation of the simpler model complex  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4)\text{HCl}_3(\mu\text{-dHpm})_2]$  (**3**: dHpm = bis(phosphino)methane, DFT:  $\omega\text{B97X-D/6-31G}^*/\text{LanL2DZ}\zeta(\text{W})$ ; Figure 3)<sup>11</sup> fails to reveal individual molecular orbitals that tidily adhere to such 2-centre-2-electron canonical depictions. Rather, components of the metallacycle  $\sigma$ -framework are apparent in a large number of occupied molecular orbitals, many of which also extend to the benzo unit and chloride co-ligands. It is noteworthy that none of the 25 highest occupied orbitals involve any direct Rh-Rh  $\sigma$ -bonding, substantiating inferences that follow from simple EAN considerations.



**Scheme 4.** Canonical Descriptions of the Metallacycle Bonding (dppm ligands omitted) in  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4)(\text{Ph})\text{Cl}_2(\text{dppm})_2]$  (**2**).

The issue of  $\pi$ -bonding is also less than clear, although the low-lying HOMO-20 corresponds to the fully  $\pi$ -bonding RhCRh unit. It is also significant that a number of orbitals comprise C1-C2 and Rh1-C3  $\pi$ -bonding, perhaps accounting for the shortness of this bond, as previously indicated. The *ortho*-quinoidal canonical form **G** (Scheme 4) provides an alternative means of envisaging this interaction and accounting for the chemical shifts noted above. As would be expected for a  $\pi$ -acceptor ligand bound to octahedral rhodium(III), the LUMO is significantly localised on C1 with some conjugation out to the benzo group.



**Figure 2.** Selected Molecular Orbitals of Interest for  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4)\text{HCl}_2(\text{dHpm})_2]$  (**3**) (DFT:  $\omega$ BP96X-D/6-31G\*/LANL2DZ; H-atoms omitted).

The formation of **2**, which proceeds in poor yield (32%), requires the addition of two benzyne units and one equivalent of HCl. This was initially suspected to arise from the decomposition of approximately one equivalent of **1** in combination with the 5% water content that may not be removed from commercial solutions of TBAF in THF.<sup>12</sup> Caesium fluoride proved ineffective as a fluoride source due to solubility incompatibilities, and by employing the anhydrous salt TBAT ( $[\text{t}^{\text{Bu}}_4\text{N}][\text{SiPh}_3\text{F}_2]$ ), the formation and yield of **2** was effectively unchanged, suggesting the hydrogen and chloride source is a second equivalent of **1** which undergoes decomposition. Attempts to increase the yield through provision of extraneous HCl resulted in no formation of **2**. Instead, isolation of the  $\mu_2$ -chlorocarbyne complex  $[\text{Rh}_2(\mu_2\text{-CCl})(\mu\text{-Cl})\text{Cl}_4(\mu\text{-dppm})_2]$  (**5**) was

observed which is also the product of the reaction of **1** with  $\text{PhCl}_2$ .<sup>3k</sup> Attempts to make use of a milder source such as  $\text{NH}_4\text{Cl}$  also failed to increase the yield of **2**, instead affording an approximately 1:1 inseparable mixture of **2** and  $[\text{Rh}_2(\mu\text{-CC}_6\text{H}_4)(\mu\text{-Cl})\text{Cl}_3(\text{dppm})_2]$  (**4**) for which limited spectroscopic and crystallographic data could be obtained (see Supporting Information). The possibility that **2** was a precursor to **4** could be excluded by the remarkable failure of the former to react with concentrated hydrochloric acid. This is in stark contrast to the high reactivity of Group 4 and 10 benzyne complexes<sup>2</sup> which readily react with acids,  $\text{CO}_2$  and halogens. The complex **2** was similarly unreactive towards  $\text{PhCl}_2$ . Repeating the synthesis of **2** in the presence of an aprotic chloride salt ( $[\text{t}^{\text{Bu}}_4\text{N}]\text{Cl}$ ) resulted in the formation of solely **2** in similar yields. Attempts to isolate **4** by increasing the amount of  $\text{NH}_4\text{Cl}$  present resulted in no observable reaction taking place. The efficacy of Kobayashi's benzyne equivalent arises from the rate of protonation of the 2-triflatophenyl anion obtained upon desilylation being slower than triflate dissociation to generate benzyne. In our case, the addition of HCl entirely quenches the benzyne manifold, whilst the weaker acid  $\text{NH}_4\text{Cl}$  allows the initial benzyne addition to occur across the Rh=C bond. It does however compete with the subsequent installation of the  $\sigma$ -phenyl ligand suggesting this step is slower. Mechanistic conjecture to account for these observations is presented in the Supporting Information with the caveat that the intimate mechanism remains frustratingly obscure.

In conclusion, benzyne equivalents have found utility in transition-metal mediated catalytic processes<sup>13</sup> including those that involve insertion into metal  $\sigma$ -bonds. We believe that we have now provided the first illustration that benzyne may add across a metal-carbon multiple bond. This occurs in a manner superficially reminiscent of metallacyclobutadiene formation which underpins alkyne metathesis. Metallacyclobutadienes remain comparatively rare, with most examples emerging from either alkyne metathesis studies<sup>1,14</sup> or from the coupling of alkynes with CO, CS or isonitrile ligands followed by *O*, *S* or *N*-alkylation.<sup>15</sup> Accordingly, none involve benzannulated cores as found in **2**. We are therefore exploring the reactivity of benzyne equivalents towards other metal-carbon multiple bonds.

## Acknowledgements

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## Conflicts of Interest

There are no conflicts to declare.

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