First Metallabenzenes and now a Stable Metallabenzyne

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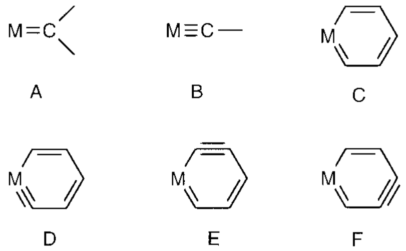
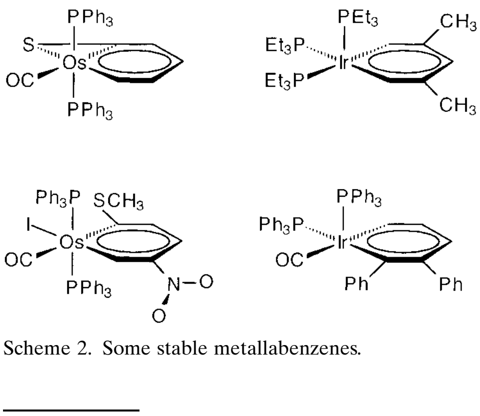
Many important examples of compounds with transition metal carbon multiple bonds can be derived, in a formal sense, by replacement of a carbon atom in an alkene or alkyne with a metal center and associated ligands. Thus in Scheme 1 we see that carbene complexes (A, or metalla-alkenes), are related to alkenes and that carbyne complexes (B, or metalla-alkynes) are related to alkynes. A particularly interesting example of cyclic carbene complexes are metallabenzenes (C) derived from replacement of one C–H group in benzene, the archetypal "aromatic" compound, by a metal center and associated ligands. The first example of such a compound was reported nearly twenty years ago[1] and numerous studies since then[2] have confirmed that metallabenzenes have all the attributes of conventional aromatic systems, that is: ring planarity, no bond length alternation, downfield chemical shifts for ring protons, and even in some cases that they undergo electrophilic aromatic substitution reactions.[3] Some representative examples of stable metallabenzenes are shown in Scheme 2.



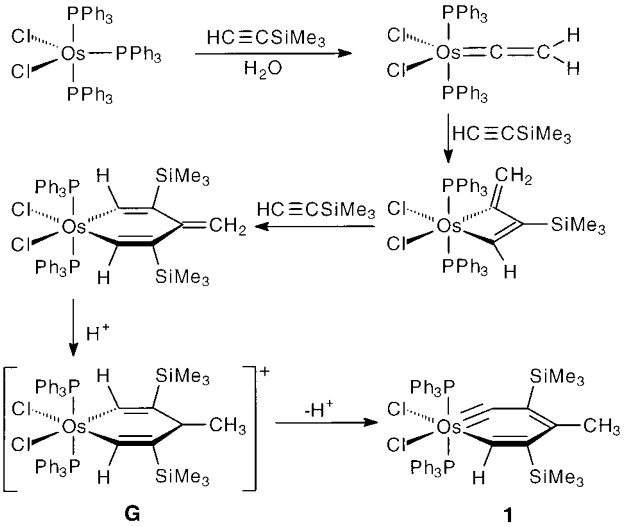
Scheme 1. Some known and unknown classes of compound with metal–carbon multiple bonds.

The possibility of obtaining isolable metal complexes from metal replacement of a C–H group in the reactive intermediate, *o*-benzyne, as illustrated by D, E, and F (Scheme 1), at first sight seems rather fanciful. Isomer D is related to a metal carbyne complex just as metallabenzene C is related to a metal carbene complex. Structural studies of many metal carbyne complexes[4] have revealed that the angle at the carbyne carbon atom is usually near to 180° (the mean is 173°) with a few exceptional cases having angles as low as 160°. Similar angles are also found for acetylenes. Therefore, considerable ring-strain would be expected in D, just as in E and F. However, any expectation that a complex of type D would be unstable is shattered by the recent report from Jia and co-workers[5] that reaction between $[OsCl_2(PPh_3)_3]$ and trimethylsilylacetylene leads to four products the major one of which is the stable, structurally characterized, metallabenzyne complex **1**.



Scheme 2. Some stable metallabenzenes.

Jia and co-workers propose the sequence of steps shown in Scheme 3 to account for the formation of **1**. Initially, reaction between $[OsCl_2(PPh_3)_3]$ and trimethylsilylacetylene (in the presence of H_2O) produces the coordinatively unsaturated vinylidene complex, $[Os(=C=CH_2)Cl_2(PPh_3)_2]$. This complex undergoes two successive cycloaddition reactions with further trimethylsilylacetylene to give first an osmacyclobutene and then an osmacyclohexadiene complex. The direction of each addition is probably dictated by steric factors. Protonation of the osmacyclohexadiene complex then gives **G** which is more reasonably depicted as **H** or **I** (see Scheme 4) and can be seen as a cationic osmabenzene complex. Loss of a proton from a metal-bound carbon atom then produces the observed metallabenzyne product **1**. The experimental data for **1** is convincing, the ^{13}C NMR spectrum shows signals corresponding to two metal-bound carbon atoms, one of which is carbene-like and one carbyne-like, and the X-ray crystal structure shows



G

1

Scheme 3. Proposed route to **1**.[5]

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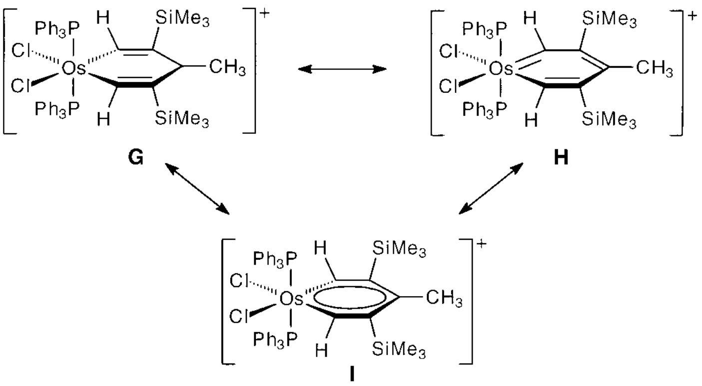

Scheme 4. Valence bond representations of the intermediate metallabenzene.

one Os–C bond of 1.815(4) Å (at the high end of observed Os≡C bonds[6]), and another Os–C bond of 1.939(5) Å (slightly shorter than observed in other osmabenzenes[3]). Other ring C–C distances are typical of regular aromatic systems. The angle at the carbyne carbon atom is 148.7(3)°, considerably larger than the angle at the other metal-bound carbon of 138.6(5)°. These very large ring angles are accommodated partly by the angle at osmium closing to 78.1(2)°.

So why is metallabenzyne **1** a stable isolable complex? The reactivity of **1** will certainly be reduced by the steric protection of the strained Os≡C bond provided by the ligands at the osmium center and the nearby trimethylsilyl group on the adjacent carbon atom. Simple protonation back to the precursor **G** (or **H**, **I**) will not be favored because the cationic osmabenzene so formed will have the acidity of what is already an acidic α-CH group enhanced. However, it may also be that the ring strain is not as great as might have been expected. The angle at the carbyne carbon atom is only 12° less than that observed in some noncyclic carbyne complexes. Metallabenzyne **1** will certainly not be unique. We must await with interest reports of the reactivity of **1**, the syntheses of other metallabenzynes, and possible interconversions of metallabenzenes and metallabenzynes. Organometallic chemistry can still provide some startling surprises!

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