Metallabenzenes

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Recent Advances in Metallabenzene Chemistry

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Research into aromatic metallacycles, though discussed in the literature over the last quarter century, has undergone a major expansion since 2000. A wide variety of new metallabenzenes, encompassing new synthetic methods and new metal centers, is now available. New aromatic metallacycle topologies (iridanaphthalene, osmabenzynes) have been isolated and characterized. The first metallabenzene valence isomers (iridabenzvalenes, rhodabenzvalenes) and constitutional isomers (isoosmabenzenes) are now known. This review discusses the synthesis, chemistry, and physical properties of these intriguing aromatic compounds.

1. Introduction

Ever since Kekulé proposed a cyclic six-membered ring with rapidly alternating single and double bonds to describe the structure and stability of benzene, chemists have been debating the nature of aromaticity and "aromatic" molecules.^[1,2] New aromatic molecules are constantly being synthesized, some of which continue to stretch and expand our definition of this concept. How does one qualify an aromatic compound?^[1-3] An undergraduate chemist is usually taught that a compound is either aromatic, antiaromatic, or non-aromatic based on the Hückel $[4n+2]\pi$ -electron rule, but it does not take much imagination to think of a compound that does not neatly fall into one of these categories. These "intermediate" compounds may exhibit some properties normally associated with aromaticity, such as downfield ¹H NMR signals, but completely lack other facets, such as stability towards dienophiles. For these reasons, it is risky to attempt to define aromaticity in fixed terms. Instead, it may be best to remove arguments that attempt to rigidly define the concept of "aromaticity" by considering the characteristics commonly attributed to aromaticity separately.^[3]

The replacement of a CH group within a benzenoid ring with an isolobal heteroatomic fragment is well-known and exemplified by molecules such as pyridine, phosphabenzene, pyrillium, and thiabenzene.[4-6] Benzenoid aromatic compounds of even heavier elements such as silicon and gallium are also known.^[5–8] Where the lines begin to blur is with one of these classes of "intermediate" compounds known as metallabenzenes. Metallabenzenes are six-membered metallacycles analogous to benzene for which one CH unit has been replaced by an isolobal transition-metal fragment $\{ML_n\}$.^[9,10] These metallacycles differ from regular aromatic compounds in that the π bonding requires involvement of the metal d orbitals since the metal p orbitals participate in σ bonding to the ligands. Thorn and Hoffmann were the first to consider the application of the Hückel rule to metallabenzenes.^[11] In their analysis, four electrons come from the p orbitals in the five-carbon backbone, while two electrons come from the filled d_{xz} orbital of the metal fragment; therefore, metallabenzenes obey the Hückel definition of aromaticity. Nonetheless, with such a fundamental difference in bonding, one cannot but wonder how incorporation of the d orbitals might ity and thus stability, reactivity, properties, etc. of the resultant compounds.

affect the aromatic-In the quarter century since Thorn and Hoffmann's initial proposal, over 30 varieties of metalla-aromatic species have been synthesized and/or characterized. Although most of these metallacycles have been isolated examples, a majority exhibit properties normally associated with aromatic systems, such as relatively deshielded proton resonances in the

¹H NMR spectrum.^[12] Whereas the ring protons in metallabenzenes are also deshielded, the anisotropy of the metal center can severely affect this analysis, especially at the position ortho to the metal.^[9] NICS (Nucleus Independent Chemical Shift) calculations have often been invoked to determine the aromaticity of a compound;^[13] however, NICS values are also subject to the anisotropy of metal centers.^[14]

Structurally, bond lengths and ring planarity can be analyzed to determine if the molecule in question is aromatic.^[15] An aromatic ring typically exhibits bond lengths intermediate between a single and double bond, and this property holds true to a reasonable extent for all metallabenzenes characterized to date. The bulkiness of the metal fragment, however, tends often to distort the six-membered ring from planarity.

Unique reactions such as electrophilic aromatic substitution (EAS) are occasionally invoked to demonstrate aromaticity. Owing in part to the reactivity of the metal center, EAS reactions have rarely been observed for metallabenzenes.^[9,16] Another reaction unique to aromatic compounds is the formation of arene-coordination complexes. For metallabenzenes, these complexes are formed readily and often stabilize metallacycles that would otherwise be too short-lived to be observed.^[9,17,18]

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Aromatic compounds are often noted for their stability and lack of reactivity under ordinary conditions. Metallabenzenes, however, undergo some very unusual reactions that are unheard of for classically aromatic compounds. For example, cycloadditions with dienophiles and rearrangements to form cyclopentadienyl complexes suggest that these molecules are not as aromatic—that is, as stable—as their all-carbon analogues.^[9,17,19-22]

While metallabenzenes have been known since 1982^[23] and were the subject of an excellent review in early 2001,^[9] these metallacycles have been synthesized at an ever-increasing pace over the last few years. More importantly, new aromatic topologies (metallabenzynes, metallanaphthalenes) as well as new, versatile syntheses of such metallacycles have begun to emerge. As opposed to being an all-encompassing document, this review will highlight the numerous advances from 2000 on. We will focus predominantly on the syntheses and properties of metallabenzenes and related aromatics where one metal atom and five carbon atoms comprise the metallacycle. Some attention will be paid to metal-coordinated metallabenzenes, for which the uncoordinated metallabenzenes, specifically of the 4d metals, were until very recently not known. Although there are numerous examples of hetero-metallabenzenes, such as a metallathiabenzene, that are worthy of inclusion, they do not fall under the scope of this review.[24,25]

2. Historical Perspectives

Originally postulated to be a stable species by Thorn and Hoffman in their seminal paper in 1979,^[11] the first unambiguous isolation of a metallabenzene was reported by Roper and co-workers in 1982.^[23,26] Through inspiration from the synthesis of metallacyclopentadienes from the [2+2+1] cycloaddition of alkynes with transition-metal complexes, arene **1** was isolated from the formal [2+2+2] cycloaddition of two ethyne molecules to $[Os(CO)(CS)(PPh_3)_3]$. The ¹H NMR spectrum of the resulting six-membered metallacycle exhibited a peak at $\delta = 13.95$ ppm and several overlapping peaks at $\delta = 7.28$ ppm. The unusual peak at $\delta = 13.95$ ppm was attributed to the proton *ortho* to the metal, and its deshielding was attributed to the anisotropy of the metal. Since the effects of the metal are expected to drop sharply as the distance from



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the metal center increases, the three peaks at $\delta = 7.28$ resonated in the typical range for aromatic protons. Additionally, C–C bond-length alternation was shown to be negligible by X-ray crystallography.

Work reported by Hughes and co-workers in 1986 demonstrated the first use of vinylcyclopropenes to give sixmembered metallacycles. Platinacyclohexadiene **2** could be made from treating [Pt(η^2 -C₂H₄)(PPh₃)₂] with 1,2,3-triphenyl-3-vinylcycloprop-1-ene.^[27] A year later this group reported that reaction of the same vinylcyclopropene with [MCl-(PMe₃)₂] (M=Rh, Ir) also produced the corresponding metallacyclohexadienes, one of which was crystallographically characterized as the acetylacetonate (acac) complex **3**.^[28] On heating, these metallacyclohexadienes were found to generate 1,2,3-triphenylcyclopentadiene. Recent studies have demonstrated that elimination to form cyclopentadienyl complexes is a common decomposition pathway of metallabenzenes, although other pathways could be responsible for this transformation.^[22]

In 1989, Bleeke et al. reported the synthesis of the first stable iridabenzene **4** utilizing 2,4-dimethylpentadienide as a source for the carbon backbone.^[17,29] Using the resultant iridabenzene as a starting point, the Bleeke group extensively examined the chemistry of such complexes.^[17] When exposed to EAS conditions, it was found that the electrophiles react preferentially with the electron-rich metal center. Additionally, it was found that when exposed to dienophiles, these iridabenzenes behave more like cyclohexatrienes and undergo cycloaddition reactions.^[19,20,30]

The first ruthenabenzene **5** to be observed spectroscopically was reported by Jones, Allison, and co-workers in 1995.^[31] Utilizing a method similar to what Ferede and Allison had previously reported for a suspected ferrabenzene,^[32] a



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3. Osmium

3.1. Osmabenzenes

The first metallabenzene to be isolated and characterized was osmabenzene 1.^[23,26] Recently, van der Boom, Martin, and co-workers calculated the energies of the various transition states in the formation of 1 by using model 6 as the starting complex to prepare 7 (Scheme 1).^[33] Their study



Scheme 1. Calculated pathway to osmabenzene by Roper and co-workers. ^[23, 26] Energies are given in kcalmol⁻¹. TS = transition state.

revealed that the first step in osmabenzene formation is loss of a phosphine ligand, followed by coordination to an acetylene molecule. The lowest-energy pathway was found to proceed by migratory insertion of the CS ligand into the σ bond of the osmacyclopropene (Dewar-Chatt-Duncanson model).^[34] The first insertion step opens up another coordination site for a second equivalent of acetylene, but the pathway leading to the resulting osmabenzene requires that the CO ligand rearranges to a position cis to the thiocarbonyl ligand prior to coordination with a second equivalent of acetylene. Coordination followed by insertion leads to the 2osma-3,5-cyclohexadiene-1-thione, which then rearranges to afford osmabenzene 7.

The hypothetical reaction involving migratory insertion of CO instead of CS was also studied.^[33] In addition to higher transition-state energies, it was found that the final step, rearrangement of the 2-osma-3,5-cyclohexadiene-1-one to the osmabenzene, would not take place owing to the strain in the resulting three-membered ring. The larger size of the sulfur atom reduces the ring strain sufficiently to allow formation of

While the structural properties of metallabenzenes are clearly consistent with the "aromatic" label, it is less clear with regard to the chemistry of these compounds since most metallabenzenes tend to react in ways that are atypical of conventional aromatic molecules.^[9,17] Recently, however, the first demonstration of electrophilic aromatic substitution was observed for osmabenzene 8 (Scheme 2).^[16] The nitration of 8



Scheme 2. Electrophilic aromatic substitution of osmabenzene 8.

was achieved with a solution of Cu(NO₃)₂ in Ac₂O. Analysis of the resultant purple crystals showed that nitration had occurred on the position para to the thioether to give 9. Similarly, the addition of Br_2 and Fe powder to a solution of 8 resulted in bromination at the para position of the metallacycle to give 10 (partial exchange of the osmium-bound iodide was also observed). Chlorination of $\mathbf{8}$ with PhICl₂ gave the corresponding metallacycle 11. Since electrophilic substitution occurred at the position predicted by the directing effects of the thioether, it is unclear what, if any, the directing effects of the metal fragment are.

A second pathway to stable osmabenzenes was reported by Jia and co-workers in 2004.^[35] This group found that reaction of [OsCl₂(PPh₃)₃] with 1,4-pentadiyn-3-ol led to the isolation of metallacycle 12, the phosphonium salt of an osmabenzene. The mechanism proposed for formation of this unusual species involves the substitution of a coordinated phosphine ligand with an η^2 -coordinated alkyne to give species 13 (Scheme 3). This step is followed by addition of the phosphine at the 2-position on the coordinated alkyne to afford intermediate 14, which could be isolated. A second molecule of PPh3 then attacks the resulting coordinated alkyne to give intermediate 15, which then eliminates a hydroxide ion to yield osmabenzene 12. Treatment of 12 with excess PMe₃ and Bu₄NCl furnished osmabenzene 16.

Spectroscopic characterization of 12 displayed the characteristic downfield shift of the ortho proton in the ¹H NMR spectrum at $\delta = 23.13$ ppm. This shift is significantly farther



Scheme 3. Synthesis of osmabenzene 12.

downfield from the *ortho* proton in **1**, which resonates at $\delta = 13.95 \text{ ppm}.^{[23,26]}$ The lower-field signal in **12** could, in part, be explained by the electron-deficient phosphonium substituents on the ring. The *para* proton gave a signal at $\delta = 8.57 \text{ ppm}$. Once again, compared to **1** ($\delta = 7.28 \text{ ppm}$), the shift is comparatively deshielded. A similar trend was observed for the *ortho* and *para* carbons in the ¹³C NMR spectrum, in which the respective signals were observed at $\delta = 239.7$ and 160.5 ppm. The *meta* carbon is shifted upfield ($\delta = 112.7 \text{ ppm}$) relative to benzene ($\delta = 128.4 \text{ ppm}$).

An X-ray diffraction analysis of **12** revealed that the metallacycle is a planar ring structure similar to osmabenzene **1**, except that the Os–C bond lengths are shorter than in **1** (1.97 Å vs. 2.00 Å). Contributing resonance structures **12c** and **12d** may explain this difference (Scheme 4). The mean



Scheme 4. Resonance contributors for osmabenzene 12.

deviation from the least-squares plane of the ring is 0.075 Å. All C–C bond lengths are intermediate between bond lengths typical for single and double bonds, which range from 1.363 Å to 1.448 Å. Two of the contributing resonance structures (**12 c** and **12 d**) are not cyclically conjugated. Comparison of the P–C bond lengths, however, shows that the P–C_{osmabenzene} and P–

C_{phenyl} bond lengths are similar, thus indicating that these two resonance structures are not major contributors to the overall structure.

Nucleophiles other than PPh₃ were also found to react with intermediate **14** to produce osmabenzenes.^[35] Addition of NaI to a solution of **14** gave iodobenzene **17** (Scheme 5).



Scheme 5. Synthesis of iodoosmabenzene 17.

The ortho protons of **17** resonate at $\delta = 20.1$ ppm (OsCHCI) and $\delta = 19.0$ ppm (OsCHCPPh₃) and the *para* proton resonates at $\delta = 8.1$ ppm in the ¹H NMR spectrum. This upfield shift in resonances in comparison to analogous protons in cationic **12** reflects the electronic effects of having one phosphonium group fewer.

Similar reactivity was observed upon treatment of $[OsBr_2-(PPh_3)_3]$ with 1,4-pentadiyn-3-ol, which formed intermediate **18**. Subsequent treatment with PPh₃ produced osmabenzene **19** after metathesis with Bu₄NBr (Scheme 6).^[35]



Scheme 6. Synthesis of osmabenzene 19.

3.2. Osmabenzynes

Addition of strong bases such as KNH₂ to a solution of chlorobenzene produces benzyne, a well-known but transient species.^[3a,36] Benzyne is a relative of benzene with two neighboring sp-hybridized carbons. The six-membered ring puts enormous strain on the ordinarily linear carbon–carbon triple bond, thus making this species extremely unstable.^[37] For this reason, it seems almost unthinkable that a metal-labenzyne could be isolated and fully characterized.

In 2001, the Jia group was able nonetheless to isolate the first stable osmabenzyne **20** (Scheme 7).^[38-40] Treatment of $[OsCl_2(PPh_3)_3]$ with an excess of trimethylsilylacetylene in wet benzene produced a brown solution, from which **20** was isolated in 30% yield. As confirmed by X-ray structural analysis, **20** contains an essentially planar six-membered metallacycle with a maximum deviation from the least-squares plane of 0.047 Å. The Os–C(sp) bond length is



Scheme 7. Proposed mechanism for the synthesis of osmabenzyne 20.

1.815 Å, shorter than that observed in both **1** and **12**, but longer than that for typical osmium–carbyne complexes. The ring C–C bond lengths range from 1.376 to 1.420 Å. Not surprisingly, the Os–C(sp²) bond length is 1.939 Å, only slightly shorter than those in the osmabenzenes (see Section 3.1).

A possible mechanism for the formation of osmabenzyne **20** is given in Scheme 7. Initial formation of a vinylidene complex followed by hydrolysis of the trimethylsilyl group should produce **21**. Subsequent [2+2] cycloaddition with a second equivalent of trimethylsilylacetylene would afford cyclobutene **22**. The remaining ring carbons then come from insertion of a third equivalent of trimethylsilylacetylene to give the six-membered metallacycle **23**, which aromatizes by protonation at the terminal methylene group and subsequently loses a proton at the carbon atom *ortho* to the Os center to furnish aryne **20**.

The sole aromatic proton on the benzyne ring of **20** resonates at $\delta = 13.83$ ppm, a value very similar to those of the osmabenzenes.^[9,23,38] In the ¹³C NMR spectrum, the sp carbon atom resonates at $\delta = 306.6$ ppm. The remaining *ortho* carbon atom produces a signal at $\delta = 227.8$ ppm. The carbon atoms *meta* to the metal center produce signals at $\delta = 136.1$ and 113.0 ppm, and the *para* carbon atom resonates at $\delta = 188.6$ ppm.

Initially, it may seem surprising that such a metallacycle might be stable; however, there are several factors that likely contribute to the stability of this species. The main reason for the instability of benzyne is the strain placed on the two sp carbon atoms by constricting the bond angles from 180° to 127°.^[41,42] With 2-butyne as a model, calculations showed that going from linear **24** to constrained **25** leads to a 51.8 kcal mol⁻¹ increase in energy. In a metallabenzyne, one of the sp-hybridized carbon atoms is replaced by a 14-electron transition-metal fragment. For this metal unit, the optimized Me[Os]=CMe angle in the acyclic fragment **26** ([Os]=OsCl₂-(PH₃)₂) was calculated to be 93.8°. In the osmabenzyne model



27 ([Os] = OsCl₂(PH₃)₂), this angle is constricted to 79.8°, and the optimal [Os]=C-C_{Me} angle of 180° is constricted to 148.3°. The resulting increase in energy on going from **26** to **27** was only 9.6 kcal mol⁻¹.

Several additional osmabenzynes have been synthesized by derivatizing **20** (Scheme 8).^[43] Reaction with two equivalents of aqueous HBF₄ first led to substitution of one chloride



Scheme 8. Derivatization of osmabenzyne 20.

ion with water to produce the osmabenzyne salt **28**. The mechanism probably involves loss of one of the chloride ligands followed by trapping of the resultant cation with water. Reaction of the salt with six equivalents of acid resulted in hydrolysis of the trimethylsilyl groups to give cationic complex **29**. When **20** was treated with acid and NaCl, or when NaCl was added to the hydrolyzed complex **29**, the neutral species **30** was produced. Reaction of either **20** or **30** with deuterated triflic acid resulted in quantitative, regiospecific deuteration of the β -carbon atoms. Similarly to normal silylarenes, treatment of **20** with Br₂ resulted in bromodesilylation to give tetrabromide **31**.^[43]

Attempts to synthesize osmabenzynes directly from $[OsCl_2(PPh_3)_3]$ and other terminal alkynes have not been successful.^[44,45] The proposed intermediate metallacyclobutene **22** (Scheme 7) was not isolable; however, cycloaddition of vinylidene **32** with phenylacetylene produced the related compound **33** (Scheme 9).^[46] Based on NMR and structural data, this compound is best described as an η^3 -allenylcarbene complex with three contributing resonance forms.

Reaction of **33** with phenylacetylene resulted mainly in polymerization and/or produced a mixture of species. Only a



Scheme 9. Synthesis and contributing resonance structures of allenylcarbene complex 33.

trace of osmabenzyne could be observed. Interestingly, when the reaction was carried out in the presence of NEt₃, osmabenzyne **34** was produced as the major product after a day, thus suggesting that an acetylide intermediate may be involved in the formation of the osmabenzyne. This hypothesis was tested by treating **33** with [(PPh₃)AuC=CPh] in the presence of HNEt₃Cl, which quickly proceeded to form osmabenzyne **34**. Exposure of **33** to three other gold acetylides under analogous conditions produced metallabenzynes **35–37** (Scheme 10).^[46]



Scheme 10. Synthesis of a series of osmabenzynes.

The mechanism for formation of these complexes is still not completely known.^[46] Reaction of **33** with [(PPh₃)AuC= CR] may initially produce the osmium–acetylide complexes [OsCl(C=CR)(=CPh- η^2 -CH=C=CHPh)(PPh₃)₂]. Alternatively, the gold acetylide may coordinate to the osmium– allenylcarbene complexes. The β -carbon atom of the acetylide attacks the γ -carbon atom of the allenyl carbene in the cyclization reaction. It is unclear if the cyclization reaction takes place before or after protonation of the terminal CHPh group. This newer work calls into question the mechanism outlined in Scheme 7; however, direct comparison may not be valid, as phenylacetylene and trimethylsilylacetylene can often exhibit different modes of reactivity with metal complexes.

3.3. Isoosmabenzene

The tautomer of benzene 1,2,4-cyclohexatriene (isobenzene) is a highly reactive, short-lived species proposed as a key intermediate in Diels–Alder reactions of enynes.^[47] Interestingly though, like the metallabenzynes, isometallabenzenes have proven to be isolable compounds. Reaction of **38** with phenylacetylene and HBF₄·OEt₂ produces the alkenyl–alkynyl–carbyne complex **39** (Scheme 11), which



Scheme 11. Synthesis of isoosmabenzene 40.

decomposes in solution at temperatures above -30 °C. In the presence of excess NaCl, the decomposition process is controlled and produces isoosmabenzene **40** in 64% yield.^[48]

The mechanism involved in producing **40** probably starts with migration of the α -alkenyl carbon atom to the α -carbyne carbon atom. Next, the β -alkynyl carbon atom couples with the β -alkenyl carbon atom. In the presence of CO instead of Cl⁻, it was found that the carbyne is destabilized so that (E,Z)- and (E,E)-1,4-diphenyl-1,3-butadiene and the alkynyl-tricarbonyl osmium complex **41** are isolated.

3.4. Osmabenzofuran

Consistent with the mechanism calculated by Martin, van der Boom, and co-workers,^[33] Elliott and Roper have found that the reaction of diphenylacetylene with [Os(CS)(CO)- $(PPh_3)_3$ produces the alkyne-substituted complex 42 and an osmacyclohexadienethione.^[49] Unlike in the case calculated for acetylene, a second equivalent of diphenylacetylene does not add to generate the osmabenzene. Reaction of 42 with methyl propiolate, an activated acetylene, does indeed afford a metallacycle.^[50] Interestingly, an osmabenzene did not result from insertion of the thiocarbonyl into the ring, but instead a second equivalent of methyl propiolate inserted to create the bicyclic species 43 (Scheme 12; the numbering scheme is used in Table 1). This molecule is best described as an osmabenzofuran in which the Os center is shared by both rings. Reaction of 43 with ethanolic HCl results in transesterification of the free ester functionality to afford 44 while leaving the metal-bound ester unchanged. Reaction of 43 with pyridinium tribromide results in bromination at C6 to give



Scheme 12. Synthesis of osmabenzofurans **43–45** and osmabenzenes **46–47**.

45. Finally, C6 can also be protonated with either trifluoroacetic acid or HI/I_2 to generate complexes **46** and **47**, respectively. While the triiodide salt **47** could be isolated, attempts to isolate **46** only resulted in regeneration of **43**. The reversible nature of this reaction at C6 is strikingly similar to recent iridabenzene chemistry reported by Chin et al. (see Section 5.2).^[51,52]

Three resonance structures account for the overall bonding picture in these complexes. Structures **43a** and **43b** (Scheme 13) account for the aromatic character of these



Scheme 13. Contributing resonance structures of 43.

molecules, while structure 43c contains an osmacyclohexadiene system.^[50] The crystal structures of compounds 43-45show, unlike in other metallabenzenes, that there is some apparent bond alternation (Table 1). The C1–C2, C3–C4, and C5–C6 bonds are all shorter than the C2–C3 and C4–C5 bonds. This bond alternation suggests that the dominant contributing resonance structure may be 43c; however, the C5–C6 and the C6–C7 bonds are similar enough in length to suggest that resonance forms 43a and 43b also contribute

Table 1: Bond lengths for osmabenzofurans 43–45, osmabenzene 47, and structurally related Ru (48) and Fe (49) complexes.

М	43 Os	44 Os	45 Os	47 Os	48 Ru	49 Fe
M-C1	2.068	2.068	2.055	1.996	2.003	1.908
M-C5	2.142	2.162	2.135	2.103	2.107	1.994
M-O	2.218	2.232	2.234	2.221	2.26	2.073
C1-C2	1.367	1.406	1.389	1.45	1.367	1.364
C2-C3	1.442	1.45	1.433	1.374	1.448	1.43
C3-C4	1.359	1.38	1.368	1.438	1.34	1.366
C4-C5	1.436	1.466	1.438	1.375	1.477	1.467
C5-C6	1.371	1.375	1.363	1.507	1.369	1.363
C6-C7	1.416	1.424	1.438	1.495	1.442	1.421
C7-O	1.333	1.264	1.244	1.226	1.239	1.242

significantly. In all of these complexes, the *trans* influence of the thiocarbonyl ligand lengthens the Os-C5 bond.

The X-ray structure for cationic complex **47** reveals deviations from the trends in the neutral series. In this structure, C1–C2, C3–C4, and C5–C6 have bond lengths that are larger than the C2–C3 and C4–C5 bond lengths (Table 1). Additionally, the Os–C5 bond is slightly shortened. This combination of structural features suggests that **47** has significantly more delocalization than **43–45**. Consistent with this observation is the downfield shift of the ¹H NMR resonance signal of the *ortho* proton upon acidification with HI/I₂ or CF₃CO₂H (from $\delta = 6.99$ ppm for **43** to $\delta = 8.36$ ppm for **46**).

Similar Ru(48) and Fe(49) complexes have been reported previously but were not initially recognized as



metallabenzofurans.^[53-56] These molecules are structurally quite similar to **43–45**. It is interesting to note that the authors did not report these complexes as aromatic, though they do have some characteristics suggesting that delocalization is present. Nonetheless, bond alternation is more pronounced in **48** and **49** (Table 1) and thus these may be borderline cases of metalla-aromatic compounds.

4. Ruthenium

While osmium has been shown to be involved in a number of thermally stable metalla-aromatic compounds, the same cannot be said about chemically similar ruthenium. Most of the ruthenabenzenes that have been synthesized are either short-lived at room temperature or can be isolated only if coordinated to a transition-metal center to which some of the electron density can be donated.^[18,31] This stability trend between the 4d and 5d metallabenzenes is generally true, in

that the 4d metals do not usually produce isolable metallabenzenes while the 5d metals do.

4.1. Coordinated Ruthenabenzenes

One recent example of a metal-coordinated ruthenabenzene was reported by Bruce et al.^[57] The authors found that when the Ru cluster 50 was mixed with two equivalents of HC=CFc in CH₂Cl₂ (Scheme 14), complex 51 was formed in 10% yield, as identified by X-ray crystallography. The Ru–C(sp²) bond lengths in the metallacycle are 2.083 and 2.054 Å, and the C-C bond lengths within the ring range from 1.407 to 1.437 Å. The C-Ru-C angle is 88.4°, and the remaining ring angles lie between 120.8 and 128.4°. Despite the structural similarities to previous metallabenzenes, the two protons meta to the metal resonate as a singlet at 5.31 ppm in the ¹H NMR spectrum. Similar upfield shifts for metalcoordinated arenes are commonly observed.^[9,34] The mechanism for formation of ruthenabenzene 51 probably involves double insertion of HC=CFc into the Ru-C bonds of the complex and subsequent loss of water.



Scheme 15. Synthesis of triple-decker ruthenabenzene 52.



Scheme 14. Synthesis of ruthenium-coordinated ruthenabenzene 51. Fc = ferrocenyl.

Jia obtained the triple-decker ruthenabenzene **52** by treating [Cp*Ru(H₂O)(nbd)]BF₄ (**53**; nbd = norbornadiene) with sodium formate to produce first the binuclear Ru cluster **54** (Scheme 15). This cluster was then treated with HBF₄, and the resultant solution was allowed to stand for several days at room temperature to give ruthenabenzene **52**.^[58] The initial complex **54** is probably produced by C–C bond cleavage of the norbornadiene ligand and subsequent elimination to produce the bridging vinylcyclopentadiene ligand. Protonation of **54** leads to the intermediate complex **55**, which rearranges to form the triple-decker ruthenabenzene **52**, as well as ruthenacene **56** and the triple-decker complex **57**. While the details of these rearrangements are not well understood, it is interesting since it must involve C–C bond activation under mild conditions.

X-ray diffraction revealed that the six-membered ruthenacycle of **52** is η^6 -bonded to the lower Ru center but only η^5 bonded to the upper Ru center. The bridging hydride ligand allows the Ru center of the ring to maintain its 18-electron count. The C–C bonds of the metallacycle range between 1.358 and 1.463 Å with no significant bond alternation while the Ru-C(sp²) bond lengths are 2.043 and 2.055 Å. The C(sp²)-Ru-C(sp²) angle is 82.2°, and the remaining ring angles range between 120.4 and 132.9°. As in the previously described coordinated ruthenabenzene **51**, the ¹H NMR spectrum of **52**, with signals ranging from $\delta = 5.26$ to 8.20 ppm, exhibits signals shifted upfield from those of other metallabenzenes.

Other examples of metal-coordinated ruthenabenzenes are the homoleptic Ru sandwich complexes 58 and 59 reported by Salzer, Kaupp, and co-workers (Scheme 16).^[59] These complexes were produced by treating pentadienyl sandwich complexes with two equivalents of $[Ru_3(CO)_{12}]$. Interestingly, reaction with only one equivalent of $[Ru_3(CO)_{12}]$ afforded pentadienyl ruthenabenzene complex 60 in very low yield. Complex 58 produced signals at $\delta =$ 6.23 ppm (*para*) and $\delta = 5.62$ ppm (*ortho*) in the ¹H NMR spectrum. The related complex **59** produced a signal at $\delta =$ 5.39 ppm for the protons ortho to the metal center. In both 58 and 59, the most stable conformation is fully eclipsed with the ring plane tilted 18.2° (58) toward one another at the side of the metals, such that the ring plane is defined by the four ortho and meta carbon atoms. The Ru atoms in the metallacycles of 58 are bent slightly away from each other by 14.3° and 16.3° with Ru-Ru distances (3.38 Å) between the rings that are smaller than the sum of the van der Waals radii. These structural features indicate that there is more than a superficial relationship between them. Reaction of 58 with HBF_4 produced unstable complex **61**, which revealed a ¹H NMR resonance ($\delta = -16.89$ ppm) typical for a metal hydride.



Scheme 16. Synthesis of ruthenabenzene complexes 58-61.

4.2. Ruthenabenzenes Revisited

Early work by Hughes and Robinson suggested that ruthenium would be a good candidate for producing metallabenzenes from vinylcyclopropene derivatives.^[60] The Dartmouth group demonstrated that mixing 3-vinylcyclopropenes with either [Cp*RuCl(cod)] or [{Cp*Ru(μ^3 -Cl)}₄] produced ruthenacenes such as **62** (Scheme 17) which are potential



Scheme 17. Reactions of vinylcyclopropenes with ruthenium complexes. cod = cyclooctadiene; $Cp* = C_5Me_5$.

decomposition products of ruthenabenzenes. It was presumed that these complexes were formed by loss of HCl from the intermediate olefin complexes such as **63** and subsequent carbene insertion to produce the new cyclopentadienyl ligands. Our group has recently generated a similar result via a lithiated vinylcyclopropene.^[61] Based on related chemistry from our lab (see below), ruthenabenzene **64** is presumed as an unstable intermediate which undergoes facile carbene insertion to give **65**.

Given the instability of **5** and the elusiveness of **64**, it would seem that synthetic efforts to prepare an isolable metallabenzene of a 4d metal which is not coordinated to another metal fragment would be futile. Very recently, Jia, Xia, and co-workers proved this theory wrong by isolating the first stable ruthenabenzene by a method analogous to the synthesis of **12**. Treatment of $[RuCl_2(PPh_3)_3]$ with 1,4pentadiyn-3-ol, PPh₃, and Bu₄NCl afforded cationic ruthenabenzene **66** in 55% yield (Scheme 18).^[62] This complex can



Scheme 18. Synthesis and derivatization of stable ruthenabenzene **66**. 2,2'-bipy=2,2'-bipyridine.

also be produced directly from $RuCl_3 \cdot 3H_2O$, PPh₃, and 1,4pentadiyn-3-ol in 20% yield. Metallacycle **66** is stable in air at temperatures up to 100 °C. The authors attribute this unusual stability to the bulky phosphine substituents and/or ligands.

Complex **66** has similar spectral characteristics to other metallabenzenes. The *ortho* proton resonates in the ¹H NMR spectrum at $\delta = 17.5$ ppm, which is reasonably expected for a Ru carbene. The *para* proton appears in the aromatic region at $\delta = 8.2$ ppm. The carbon atoms *ortho*, *meta*, and *para* to the metal center resonate at $\delta = 284.3$, 108.3, and 146.0 ppm, respectively, in the ¹³C NMR spectrum. Confirmation of this structure was provided by X-ray diffraction, which showed that **66** is basically planar with only small deviations (0.043 Å) from the root-mean-square plane defined by the six-membered metallacycle. The electrons in the ruthenacycle are fully delocalized with the C–C bond lengths ranging from 1.378 to 1.395 Å, thus showing no significant bond alternation.

Derivatization of **66** afforded three additional ruthenabenzene complexes (Scheme 18). Reaction with PMe₃ resulted in substitution of the metal-bound phosphines to produce **67**. The ligand sphere could also be modified by reaction of **66** with *t*BuNC, resulting in **68** in which one chlorine ion is exchanged for the isonitrile. Complex **69** could be produced by reaction of **66** with 2,2'-bipyridine. The structural and spectroscopic properties of **67** and **68** are analogous to those of **66**; however, the solid-state structure of **69** reveals that the Ru atom is situated outside of the plane of the ring (defined by the five carbon atoms) by 0.672 Å. Nonetheless, **69** retains its aromaticity, as the *para* proton resonates at $\delta = 8.2$ ppm and the C–C and Ru–C bond lengths indicate delocalization.

5. Iridium

One of the earliest metallabenzenes to be isolated and characterized was iridabenzene **4**, which Bleeke et al. synthesized by the reaction of 2,4-dimethylpentadienide with $[IrCl(PEt_3)_3]$.^[17,29] A number of iridabenzene derivatives could be prepared from **4**; for example, reactions with phosphines that are more electron-rich usually resulted in substitution of one or more PEt₃ ligand, depending on the sterics of the ligand. Carbon monoxide could substitute one ligand at room temperature, while at reflux a second equivalent would insert into the metallacycle to produce an iridium–phenoxide complex. Reaction with bromine or iodine resulted in oxidation of the Ir center rather than electrophilic aromatic substitution.^[9,29]

A key step in the synthesis of **4** is deprotonation of an intermediate iridacyclohexadiene.^[17,29] This deprotonation was not found to occur when using $[IrCl(PMe_3)_3]$ as the metal source.^[63] As a result, synthesis of an iridabenzene was only feasible from $[IrCl(PEt_3)_3]$, such that all additional metallacycle examples must be derived from **4**.

5.1. Iridabenzenes from Nucleophilic 3-Vinylcyclopropenes

Recently, our group reported the direct synthesis of a series of iridabenzenes from nucleophilic 3-vinylcyclopropenes.^[64-68] In this case, several different ligands and metal complexes were used to produce a variety of structurally related iridabenzenes. This method of synthesis, which was inspired by the aforementioned studies from Hughes and coworkers, is derived from the well-known reactivity of cyclopropenes to form vinyl carbenes.^[69] For a bond-fixed "Kekulé" structure of a metallabenzene, the ring can be seen as a vinyl carbene that is tethered to the metal center by a vinyl σ bond. Retrosynthetic analysis suggested that a (Z)-3-(2-iodoethenyl)cyclopropene such as 70 would be a good synthon for iridabenzenes like 71 (Scheme 19). Lithiumhalogen exchange of vinyl iodide 70 and subsequent addition of Vaska's complex resulted in the isolation of iridabenzene 71 a (R = Ph).^[64] When less bulky phosphines were used, the σ -vinyl/ η^2 -cyclopropene complex 72 (for example, R = Me) was isolated. This "iridabenzvalene", a valence isomer of 71, then could be converted into the corresponding iridabenzene in nearly quantitative yield either by heating in solution or by treatment with Ag^I salts.^[65]

Varying the phosphine ligand gave insight into the factors determining which isomer would be isolated (Table 2).^[67]



Scheme 19. Iridabenzene synthesis from a nucleophilic 3-vinylcyclopropene.

Table 2: Product ratios for the synthesis of iridabenzenes **71** with various phosphines.

Cmpd	Phosphine	≮ [°] ^[a]			Yield	[%]
-			71:72 ^[b]	71	72	72 → 7 1
71 a	PPh ₃	145	100:0	66	-	-
71 b	PMe ₃	118	0:100	-	54	97
71 c	PMe₂Ph	122	2:98	58	-	-
71 d	PEt ₃	132	0:100	-	51	95
71 e	$PMePh_2$	136	30:70	56	-	-
71 f	PiBu₃	143	35:65	49	-	-
71 g	$P(p-MeOC_6H_4)_3$	145	100:0	61	-	-

[a] Cone angle, reference [70]. [b] Initial product ratio, determined by ¹H NMR spectroscopy.

Phosphines with smaller cone angles^[70] tended to afford more of the iridabenzvalene product. Comparison of PMe₃ and PiBu₃ shows that the smaller PMe₃ ligand forms 100% iridabenzvalene, while the larger PiBu₃ forms only 65%. Additionally, ligands possessing electron-rich groups resulted in an initial product ratio favoring the iridabenzvalene. For example, while PPh3 led to exclusive formation of the iridabenzene, PiBu3 led to an initial product ratio of about 2:1 iridabenzvalene to iridiabenzene. Since the cone angles on these two ligands are 145 and 143°, respectively, it is likely that electronic effects are primarily responsible for this difference. Steric effects, which seem to be secondary in this study, do eventually come into play as a solution of the PiBu₃ product mixture in C₆D₆ does convert to all iridabenzene over eight hours at room temperature, while a solution of the PMe₃ iridabenzvalene in C_6D_6 is stable indefinitely at room temperature.

There are two potential mechanisms for the formation of iridabenzene **71** from iridabenzvalene **72** (Scheme 20).^[33,67,68] One pathway begins by dissociation of the cyclopropene from the metal center and subsequent oxidative addition to generate Dewar benzene **74**, which quickly rearranges into **71**. Evidence for this pathway lies in the ability of donor solvents to rapidly increase the rate of isomerization. Similar types of reactivity with cyclopropenes have been reported by Hughes and co-workers.^[71,72] In these cases the intermediate metallacyclobutenes were isolated from the reaction of perfluorinated cyclopropenes with transition-metal complexes. Additionally, a metal-assisted mechanism has been proposed for the opening of 3,3-diphenylcyclopropenes, as based on the isolation of an iridium-coordinated iridacyclobutene.^[73]



Scheme 20. Proposed mechanisms for formation of iridabenzenes and valence isomers from a nucleophilic 3-vinylcyclopropene (R' = Ph). For the purpose of calculations, R = R' = H. The numbering scheme is used in Table 3.

Recent DFT calculations reported by van der Boom, Martin, and co-workers, however, suggest that the more feasible pathway is through direct rearrangement of the iridabenzvalene by twisting of the iridacyclopropane ring into the planar metallacycle.^[33] For the purpose of these calculations, an Ir complex 73 for which R = R' = H was used. Under these circumstances, two isomers of 73 were distinguishable by the orientation of the cyclopropene ring. The syn isomer, in which the cyclopropene ring is oriented towards the Ir center, gave a calculated energy of 1.8 kcal mol⁻¹ higher than the *anti* isomer. When this lower-energy σ complex is defined as having an energy of zero, the transition state to iridabenzvalene 72 carries an energy of only 3.5 kcalmol⁻¹. The iridabenzvalene itself lies in an energy well at -23.1 kcalmol⁻¹. From the iridabenzvalene, a barrier of 39.5 kcalmol⁻¹ was found in forming the iridabenzene 71 directly. While no transition state was found for the formation of Dewar benzene 74, its energy was calculated to be 38.3 kcal mol⁻¹ above the iridabenzvalene, thus suggesting that the Dewar benzene model would be considerably higher in energy.

None of the experimental evidence so far indicates definitively either the Dewar benzene or the direct-insertion pathway. While the calculations are generally reliable, they may not take into account any associative mechanism(s) in which the solvent may play a role. Since the calculations were only able to approximate solvation effects by using the polarized continuum model, no direct interactions such as solvent coordination or a metal-assisted mechanism would be predicted. It is also possible that no one of these mechanisms operates to the exclusion of the others.

In addition to isolating iridabenzenes with different phosphine ligands, we have successfully synthesized a number of iridabenzenes with different ring substituents from unsymmetrically substituted cyclopropene precursors.^[66,68] As in the previous work, iridabenzvalenes such as **75** and **79** are formed in addition to iridabenzenes depending not on the phosphine, but on the nature of the R group. In certain cases, isomerization to the iridabenzene was found to be highly regioselective, forming the *ortho*-phenyl isomer **76**



over the *meta*-phenyl isomer **77**. In addition to the iridacycles, cyclopentadienyl complexes such as **78** and **81** were also isolated. As in previous examples, these complexes are thought to come from migratory carbene insertion of the corresponding iridacycle.

The series derived from 1-alkyl-2-phenylcyclopropenes **82 a–d** proved to be the best "behaved" of the various systems explored, with **82 d** allowing easy access for complete study of the iridabenzene manifold.^[68] Reaction of lithiated **82 d** with Vaska's complex furnished iridabenzvalene **75 d** (Scheme 21).



Scheme 21. Synthesis of tBu/Ph-substituted iridacycles.

Although stable in the solid state, solutions of **75 d** in C_6D_6 at 20 °C immediately began to isomerize, which after four days afforded a 3:1 mixture of iridabenzene **76 d** and cyclopentadienyl complex **78 d** in 94% combined yield. The regiochemistry of **76 d** was confirmed by X-ray analysis to be the *metat*Bu isomer, and none of the corresponding *ortho-t*Bu regioisomer **77 d** was detected. Unlike **71 a–g**, **76 d** proved to be extremely labile as it converted quantitatively into **78 d** in C_6D_6 solution at 50°C. The kinetics of the rearrangement were shown to be first-order with respect to **76 d**.

Initially, it was presumed that the *ortho-t*Bu regioisomer **77 d** had quickly rearranged and thus was the source of **78 d**. To test this theory, kinetic studies on the isomerization of **75 d** and **76 d** to the cyclopentadienyl complex **78 d** were performed. The data showed that at 20°C the rate of isomerization of **76 d** to **78 d** was faster than the corresponding rate of isomerization of **75 d** to **78 d**. This was taken to mean that the

cyclopentadienyl complex **78 d** originated by the rearrangement of the *meta-t*Bu isomer **76 d** and not from *ortho-t*Bu isomer **77 d**. It therefore appears that the valence isomerization of unsymmetrical iridabenzvalene **75 d** to iridabenzene **76 d** is highly regioselective.

Reactions of Vaska's complex with cyclopropenes 82 a–c showed the influence of alkyl substituent on both the formation of 75 and its transformation to 76. ¹H NMR spectroscopy showed that each crude reaction mixture was composed of the corresponding iridabenzvalene and iridabenzene. Iridabenzvalenes 75 a–c were not isolated from the reaction mixture because of their relatively rapid isomerization to 76 a–c, which were isolated in about 25–30 % yield. After eight hours and 30 hours at 20 °C in C₆D₆ solution, 75 a,b and 75 c, respectively, had isomerized completely to 76 a–c, and very minor amounts of the *ortho*-alkyl regioisomer 77 a–c were detected by NMR spectroscopy of the crude reaction mixtures. Unlike 76 d, solutions of 76 a–c were stable for over 48 hours at 75 °C.

In contrast, reaction of vinylcyclopropenes 82 b,d with the less bulky and more electron-rich complex [IrCl(CO)-(PMe₃)₂] yielded the corresponding iridabenzvalenes **79b,d** as the only products, which were stable at 20 °C. Isomerization at 75°C converted 79b completely into the meta-Et regioisomer 80b over four hours. Under the same conditions, however, the tBu analogue 79d gave a mixture composed of unreacted iridabenzvalene, iridabenzene 80d, and cyclopentadienyl complex 81d in a ratio of 5:10:1, as well as partial decomposition. Prolonged heating of this mixture led to complete decomposition to unidentified materials. Interestingly, evidence for formation of the ortho-alkyl regioisomer of 80 was never observed; thus, the lower steric hindrance of PMe₃ than PPh₃ does not decrease the regioselectivity of the isomerization. The influence of the Et and tBu substituents on the stability and isomerization rate of 79 is similar to that observed for the corresponding PPh₃ analogues 75. Additionally, the greater stability of meta-tBu substituted 80d compared to the corresponding PPh₃ analogue **76d** indicates that the PMe₃ ligand does stabilize the iridabenzene. Regarding the whole "alkyl" series, the trend of the isomerization rate of alkyl-substituted iridabenzvalenes to iridabenzenes is 75 a = $75\,b>75\,c>75\,d>79\,b>79\,d,$ which is in agreement with the increase in both electronic-donating ability and steric hindrance of the alkyl group as well as with increased electronicdonating ability and/or reduced steric hindrance of the phosphine ligand. On the other hand, iridabenzene stability is ordered as 80b > 76a = 76b = 76c > 80d > 76d, indicating that a decrease in steric hindrance of the alkyl group as well as a decrease in electronic-donating ability and/or sterics of the phosphine ligand enhance the stability of the iridabenzene.

Replacement of the alkyl group with a trimethylsilyl unit, as in 82 e, furnished interesting but more perplexing results. In this case, the reaction of the lithiated vinylcyclopropene with Vaska's complex furnished a 47 % yield of a mixture of 75 e, 77 e, and 78 e in a 10:2:3 ratio (Scheme 22). Iridabenzvalene 75 e and cyclopentadienyl 78 e were isolated cleanly by treatment of the purified mixture with MeI or by heat, respectively; unfortunately, pure iridabenzene 77 e could not be isolated. In contrast to 75 a–d, the Ph/SiMe₃-substituted



Scheme 22. Synthesis of Ph/SiMe₃-substituted complexes 75 e-78 e.

iridabenzvalene **75 e** is stable at room temperature. Heating a solution of pure **75 e** to 75 °C, however, did not lead to isomerization of **77 e** as expected, but instead afforded the *meta*-silyl regioisomer **76 e** (confirmed by ¹H,²⁹Si gHMQC NMR experiments). While **76 e** is more stable than the *ortho*-silyl isomer **77 e**, it also undergoes carbene migratory insertion to give complex **78 e**. It is reasonable to suspect that the *ortho*-silyl isomer **77 e**; however, **77 e** was not detected by ¹H NMR during the isomerization of **75 e**.

These results suggest that regioisomers 76 and 77 are formed by different mechanisms. One possible pathway is that the initial σ -vinyl complex 83 forms an intermediate such as **84** (Scheme 23, $R = SiMe_3$). This intermediate is plausible for $R = SiMe_3$ since the carbocation would be stabilized by both the α -Ph and the β -SiMe₃ moieties. Subsequent cleavage of the three-membered ring could then lead to the selective formation of iridabenzene 77e. Possibly a result of steric congestion by the bulky trimethylsilyl group, 77e easily undergoes carbene migratory insertion and subsequent dissociation of PPh₃ to give cyclopentadienyl complex 78 e. The lower stability to 84 which results from the corresponding alkyl groups essentially shuts down this pathway and thus leads to detection of 77 a-c only by NMR. Instead, the major pathway consists of concerted opening of 75 to yield 76. Nonetheless, the exact origin of this preferential pathway to furnish regioisomer 76 is still uncertain and is subject to further interpretation and debate.

One additional system studied by our group is derived from the bis(trimethylsilyl)cyclopropene **85**. By employment of the usual synthetic method with Vaska's complex, **86** could be isolated in 40 % yield (Scheme 24).^[74] Compound **86** has proven to be one of the most stable iridabenzvalenes isolated to date, requiring prolonged heating at 75 °C to isomerize/ rearrange to cyclopentadienyl complex **87** in essentially quantitative yield. Unfortunately, iridabenzene **88** has not been detected in this process, though its intermediacy is presumed based on the related studies. Incorporation of two trimethylsilyl groups seems to have two effects: the σ -



Scheme 23. Proposed mechanism for isomerization/rearrangement to 78.



Scheme 24. Synthesis of bis(trimethylsilyl) complexes 86 and 87.

donating ability of the Si atoms appears to stabilize the formation of iridabenzvalene, yet the π -accepting nature of the Si atoms destabilizes the corresponding iridabenzenes. Ongoing computational efforts tend to support this hypothesis.^[75]

5.1.1. Spectroscopic Properties

The synthesis of a family of structurally related iridabenzenes has allowed for detailed comparison of their spectro-

Table 3: Selected NMR data for iridabenzenes 71, 76, and 80.[a]

scopic properties. All the iridabenzenes are easily identified by the NMR resonance of the proton *ortho* to the metal, which varies between $\delta = 10.41$ ppm for **71a** and $\delta =$ 11.30 ppm for **71d** (Table 3).^[67] The downfield shift of these characteristic resonances is attributed to the anisotropy of the neighboring metal. This effect quickly dissipates for the protons *meta* and *para* to the metal center ($\delta = 7.38-7.90$ ppm and $\delta = 7.69-8.78$ ppm, respectively). These latter two resonances are more in line with aromatic ring currents in electron-withdrawn systems such as pyridine. Interestingly, in C₆D₆ the *meta* and *para* protons are 0.1–0.5 ppm downfield compared to the same protons in CD₂Cl₂, but the analogous comparison of the *ortho* proton shows that it generally resonates 0.1–0.2 ppm upfield in C₆D₆.

The ¹³C NMR spectra demonstrate similar anisotropy trends (Table 3). Carbon atoms neighboring the Ir center resonate between $\delta = 174$ and 190 ppm with the resonance of the phenyl-substituted carbon atom C1 appearing generally downfield from unsubstituted C5. The remaining carbons resonate in the standard aromatic region. While the resonating frequency of the carbon atom *meta* to the metal center remains relatively unaffected by changes to the ligand sphere of **71** ($\Delta \delta < 1.4$ ppm), carbon atoms C5 (*ortho*) and C3 (*para*)

Compound	Phosphine	Substituent	δ	(¹ H) [p	om]			δ(¹³ C)	[ppm]			δ (³¹ P) [ppm]
		R	H3	H4	H5	C1	C2	C3	C4	C5	C6	
71 a ^[b]	PPh ₃	Ph	7.99	7.69	10.41	187.60	141.93	139.99	127.76	187.43	201.09	16.44
71 a ^[c]	PPh ₃	Ph	8.44	7.79	10.79	187.74	142.83	141.16	127.64	187.49	203.26	17.88
71 b ^[b]	PMe ₃	Ph	7.75	7.49	11.10	189.25	140.49	135.53	128.65	176.58	189.44	-40.54
71 b ^[c]	PMe ₃	Ph	8.25	7.91	11.00	189.95	141.49	136.74	129.06	176.04	189.44	-40.27
71 c ^[b]	PMe ₂ Ph	Ph	7.82	7.53	11.05	188.56	140.53	136.49	128.85	179.68	190.77	-26.90
71 d ^[b]	PEt ₃	Ph	7.69	7.40	11.30	189.87	140.53	135.67	128.07	176.45	192.36	-2.08
71 e ^[b]	PMePh ₂	Ph	7.98	7.66	10.93	187.36	141.47	137.61	128.37	181.93	197.14	-5.20
71 f ^[b]	PiBu ₃	Ph	7.71	7.51	10.89	190.54	141.45	136.14	128.01	177.28	194.09	-0.29
71 g ^[b]	$P(p-MeOC_6H_4)_3$	Ph	7.96	7.38	10.43	188.51	141.70	138.92	128.50	187.11	198.18	13.01
76 a ^[c]	PPh ₃	Me	8.30	7.75	10.62	187.46	140.47	133.93	129.07	183.92	204.97	18.03
76 b ^[c]	PPh	Et	8.29	7.79	10.61	187.31	140.84	139.99	129.48	184.95	204.17	18.65
76 c ^[c]	PPh	<i>i</i> Pr	8.41	7.86	10.60	187.65	145.52	_[d]	129.85	185.52	203.90	18.79
76 d ^[c]	PPh ₃	<i>t</i> Bu	8.69	7.83	10.54	186.68	145.61	138.89	129.63	186.55	208.32	18.24
76 e ^[c]	PPh ₃	$SiMe_3$	8.78	_[d]	10.85	188.00	141.37	137.15	128.95	188.93	_[e]	17.13
80 b ^[c]	PMe ₃	Et	8.13	7.90	10.92	188.83	138.55	135.38	129.70	174.20	181.02	-38.56
80 d ^[c]	PMe ₃	tBu	8.46	7.88	10.87	_[e]	_[e]	_[e]	_[e]	_[e]	_ ^[e]	-38.79

[a] Atom labeling as shown in Scheme 20. [b] In CD₂Cl₂. [c] In C₆D₆. [d] Resonance obscured by other signals. [e] Resonance not assigned.

vary considerably. Replacement of an alkyl group with a phenyl group on the phosphine results in a deshielding of the *para* carbon atom C3 ($\Delta \delta = 4.5$ ppm) and the *ortho* carbon atom C5 ($\Delta \delta = 11$ ppm). The resonance of the carbonyl group varies in a similar way (C6: $\Delta \delta = 11.5$ ppm). The substituted carbon atom C1 does not show this dependence on the ligand sphere ($\Delta \delta = -1.4$ ppm) and actually shifts in the opposite direction. For the "alkyl" series 76/80, replacement of PPh₃ with PMe₃ on the Ir center leads to an upfield shift of the resonances for C3 ($\Delta \delta = -5.5$ ppm), C5 ($\Delta \delta = -10.8$ ppm), and C6 ($\Delta \delta$ = -23.2 ppm), which can be rationalized in terms of electronic influences. The stronger donating ability of PMe₃ compared to PPh₃ results in a more electron-rich metal center, which in turn increases the electron density of the iridabenzene ring and thus results in the upfield carbon shifts. On the other hand, these effects are much smaller for C1 $(\Delta \delta = -1.5 \text{ ppm})$, C2 $(\Delta \delta = -1.4 \text{ ppm})$, and C4 $(\Delta \delta =$ -0.2 ppm).

The ³¹P NMR spectra reveal sharp singlets for the phosphines, even when samples were cooled to -80 °C, thus demonstrating that the axial and basal phosphines exchange rapidly in solution by the well-known Berry pseudorotation process. ³¹P-¹³C coupling is observed for the substituted carbon atom C1 but not for the unsubstituted C5. This observation demonstrates that while the ligand sphere in solution is dynamic, the smaller CO ligand spends a disproportionate amount of time near substituted C1, probably as a result of steric crowding. Analogous behavior was demonstrated previously by Bleeke et al. through careful correlation of ³¹P-¹H coupling constants in a similar system.^[17]

The ¹H NMR signals of the other species observed in these studies offer a quick and easy diagnostic handle. For the iridabenzvalenes, the bridgehead cyclopropyl proton appears as a characteristic broad singlet in the range of $\delta = 3.2$ -3.8 ppm. Two complex multiplets in the ranges $\delta = 6.0$ -6.8 ppm and $\delta = 6.7$ -7.2 ppm (the latter was sometimes obscured by additional peaks from Ph groups) correspond to the alkene resonances H4 and H5, respectively. For cyclopentadienyl complexes, sharp signals for the three ring hydrogens appear around $\delta = 4.2$ -5.4 ppm. The unreacted lithiated vinylcyclopropene that is protonated in the reaction work up has a characteristic signal (ddd) that appears at about $\delta = 6.0$ -6.2 ppm. Thus, by ¹H NMR analysis, it is relatively easy to ascertain what products are present in the crude reaction mixtures.

5.1.2. Solid-State Structures

X-ray diffraction studies of five iridabenzenes synthesized in our group illustrate some key structural features of metallabenzenes. The molecular structure of **76b** is shown in Figure 1. Comparison of the bond lengths and bond angles of **71a,d** and **76a,b,d** is given in Table 4. The metallacycles possess a distorted coordination geometry that can be classified as somewhere between square pyramidal and trigonal bipyramidal. The C–C bond lengths in the central ring (1.334–1.427 Å) are essentially equal and thus can be regarded as evidence of delocalization of the π -electrons. The mean C–C bond lengths are very close and range from 1.383



Figure 1. Molecular structure of iridabenzene **76b**. The thermal ellipsoids are set at 25% probability.

Table 4: Selected bond lengths [Å] and bond angles [°] from X-ray structural analyses of iridabenzenes.

Ir-C1 2.021 Ir-C5 2.025 C1-C2 1.409 C2-C3 1.410 C3-C4 1.377 C4-C5 1.334 \emptyset (C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	2.047 2.004 1.427 1.372 1.386 1.381 1.392 127.1 123.1	2.020 2.012 1.423 1.335 1.382 1.408 1.387 129.1 123.5	2.029 2.023 1.413 1.390 1.393 1.360 1.389 130.0 122 1	2.054 2.000 1.407 1.382 1.427 1.343 1.390 130.8
Ir-C5 2.025 C1-C2 1.409 C2-C3 1.410 C3-C4 1.377 C4-C5 1.334 Ø(C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	2.004 1.427 1.372 1.386 1.381 1.392 127.1 123.1	2.012 1.423 1.335 1.382 1.408 1.387 129.1 123 5	2.023 1.413 1.390 1.393 1.360 1.389 130.0 122 1	2.000 1.407 1.382 1.427 1.343 1.390 130.8
C1-C2 1.409 C2-C3 1.410 C3-C4 1.377 C4-C5 1.334 \emptyset (C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	1.427 1.372 1.386 1.381 1.392 127.1 123.1	1.423 1.335 1.382 1.408 1.387 129.1 123 5	1.413 1.390 1.393 1.360 1.389 130.0 122 1	1.407 1.382 1.427 1.343 1.390 130.8
C2-C3 1.410 C3-C4 1.377 C4-C5 1.334 $ \emptyset$ (C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	1.372 1.386 1.381 1.392 127.1 123.1	1.335 1.382 1.408 1.387 129.1 123 5	1.390 1.393 1.360 1.389 130.0 122 1	1.382 1.427 1.343 1.390 130.8
C3-C4 1.377 C4-C5 1.334 ∅(C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	1.386 1.381 1.392 127.1 123.1	1.382 1.408 1.387 129.1 123 5	1.393 1.360 1.389 130.0 122 1	1.427 1.343 1.390 130.8
C4-C5 1.334 ∅ (C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	1.381 1.392 127.1 123.1	1.408 1.387 129.1 123 5	1.360 1.389 130.0 122 1	1.343 1.390 130.8
Ø (C-C) 1.383 Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	1.392 127.1 123.1	1.387 129.1 123 5	1.389 130.0 122 1	1.390 130.8
Ir-C1-C2 128.8 C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	127.1 123.1	129.1	130.0 122 1	130.8
C1-C2-C3 123.6 C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	123.1	123 5	122 1	110 5
C2-C3-C4 124.2 C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7		123.5	144.1	119.5
C3-C4-C5 125.5 C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	127.9	125.9	126.2	128.2
C4-C5-Ir 130.7 C1-Ir-C5 86.9 sum of angles 719.7	122.5	126.6	124.3	123.9
C1-Ir-C5 86.9 sum of angles 719.7	130.4	126.4	130.3	130.2
sum of angles 719.7	88.1	88.5	87.0	87.4
0	719.1	720.0	719.9	720.0
C5-lr-C6 165.0	167.8	172.5	171.8	172.1
P1-Ir-P2 99.2	104.8	102.5	102.4	105.6
P1-Ir-C1 112.6	101.9	119.8	121.0	137.5
P2-Ir-C1 148.2	153.0	137.7	136.3	116.5
tilt angle ^[a] 3.7	6.4	1.7	1.2	1.4

[a] The angle between the C1-Ir-C5 plane and the C1-C2-C3-C4-C5 plane.

to 1.392 Å. The Ir–C1 and Ir–C5 bond lengths (average: 2.02 Å) are intermediate between typical Ir–C single- and double-bond lengths. The metallacycles are basically planar (sum of bond angles: 719.1–720.0°) with the Ir center tilted out of the five-carbon backbone from 1.2° (76a) up to 6.4° (71d). The X-ray analyses verify that the alkyl groups of 76a,b,d are at the *meta* position to the Ir center, thus in agreement with the spectroscopic assignments. Contrary to our expectations based on reactivity, the bulky *t*Bu group does not induce greater torsion strain in the iridabenzene ring of 76d, at least not in the solid state.

The solid-state structures of the iridabenzvalenes are also of considerable interest. The molecular structure of 75 d is shown in Figure 2, and selected bond lengths and bond angles



Figure 2. Molecular structure of iridabenzvalene **75 d**. Thermal ellipsoids are set at 30% probability. Only the *ipso* carbon atoms of the PPh₃ ligands are shown.

of **72 b,d**, **75 d**, and **86** are given in Table 5. The iridabenzvalenes possess a torsion trigonal-bipyramidal coordination sphere composed of a carbonyl ligand, the cyclopropene double bond (bound in η^2 mode), two phosphine ligands, and

 $\ensuremath{\textit{Table 5:}}$ Selected X-ray bond lengths [Å] and bond angles [°] for iridabenzvalenes.

	72 b	72 d	75 d	86
Ir-P1	2.306	2.330	2.353	2.367
Ir-P2	2.318	2.326	2.353	2.381
lr-C1	2.146	2.172	2.189	2.173
lr-C2	2.143	2.159	2.220	2.189
lr-C5	2.095	2.092	2.184	2.074
C1-C2	1.447	1.440	1.405	1.446
C1-C3	1.529	1.519	1.555	1.539
C2-C3	1.526	1.533	1.566	1.543
C3-C4	1.466	1.481	1.401	1.457
C4-C5	1.322	1.328	1.375	1.330
C1-Ir-C2	39.4	38.8	37.1	38.7
C5-Ir-C6	178.9	176.5	174.0	172.6
P1-Ir-P2	104.1	109.4	110.4	106.5
P1-Ir-C1	109.4	106.5	100.5	105.0
P2-Ir-C2	105.9	104.0	109.8	109.2
dihedral angle ^[a]	110.4	109.9	108.8	108.4
dihedral angle ^[b]	116.3	116.2	120.2	129.6

[a] Angle between the C1-C2-C3 plane and the Ir-C1-C2 plane. [b] Angle between the C1-C2-C3 plane and the C7-C1-C2-C13 plane.

the σ -vinyl ligand around the Ir atom. The Ir–C1 and Ir–C2 bond lengths (2.143–2.220 Å) are typical of Ir–C single bonds. The C1–C2 bond lengths (1.405–1.447 Å) are characteristic of transition-metal–olefin complexes that have significant backbonding contribution from the metal center, that is, metallacyclopropanes. The longer Ir–C bond lengths, the shorter C1–C2 bond length, and the smaller C1-Ir-C2 bond angle in **75d** all suggest that the η^2 interaction of the cyclopropene π bond with the Ir center is considerably weaker than in the analogous complexes listed in Table 5. This weaker bonding is corroborated by the fact that **75d** isomerizes at room temperature to **76d** whereas the other iridabenzvalenes are stable under similar conditions (see Section 5.1).

5.2. Iridabenzenes by [2+2+1] Cycloaddition

C-C bond-forming reactions of alkynes with transitionmetal complexes is an area of considerable interest because of the synthetic utility in assembling highly conjugated organic products.^[76] One common intermediate in such reactions is a metallacyclopentadiene. During recent investigations, Chin et al. found that reaction of $[Ir(CO)(NCMe)(PPh_3)_2]^+$ with two equivalents of acetylene and subsequent addition of an equivalent of a terminal arylacetylene, produced alkynyl iridacyclopentadienes such as 89 (Scheme 25).^[77] Upon acidification with HBF₄, 89 rearranged cleanly into iridacyclohexadiene 90, the product of a formal [2+2+1] alkyne cyclization. Treatment of 90 with Lewis bases such as CO and MeCN caused the aryl group to rotate outward to a position trans to the Ir center to afford 91 and 92, respectively. Although zwitterionic iridabenzene resonance structures such as 90' and 91' were invoked to help explain these types of rearrangements. metalla-aromatic species were not observed.[76]

More recently though, Chin and Lee found that if MeCN is present during acidification of **90** with HBF₄, cationic iridabenzene **93** is then isolated.^[51] ¹H NMR analysis of **93** is consistent with the classification of this compound as an iridabenzene. The proton *ortho* to the Ir center in **93** (Ar = Ph) resonates at $\delta = 13.99$ ppm, considerably downfield from where the corresponding proton resonates in **90** (R = H, $\delta = 6.64$ ppm). On going from **90** (R = Me) to **93** (Ar = *p*-Tol), a similar trend is observed for the protons *meta* to the Ir center: from $\delta = 5.79$ ppm and $\delta = 5.55$ ppm to $\delta = 6.88$ ppm and $\delta = 7.3-7.6$ ppm (with overlapping signals from PPh₃), respectively.

Unique to 93 is its ability to reversibly react with weak Lewis bases such as CO and Et₃N to form iridacyclohexadiene complexes 91 and 92, respectively.^[51] It is particularly unusual that MeCN (ordinarily a more labile ligand) would replace the carbonyl ligand on conversion of 91 back into 93. The facile interconversion of cyclohexadienes 91 and 92 and iridabenzene 93 supports the presumed intermediacy of iridabenzenes in the original studies.^[76] This reactivity could be a result of the amphiprotic benzylic carbon atom connected to the carbon atom ortho to the Ir center. Resonance structures 90' and 91' could at least partly explain this behavior. While the ¹H NMR data of the iridacyclohexadienes suggest that 91' is not a dominant resonance structure, it may increase the lability of the CO ligand by reducing the ability of the Ir center to backbond efficiently. Additional evidence for the amphiprotic nature of the benzylic carbon atom is found on treatment of 90 with HCl, which protonates this carbon atom and cleanly produces iridabenzene 94.^[51] This unusual reactivity parallels that observed in the previously mentioned osmabenzofuran studies (see Section 3.4).[50]

The addition of an arylacetylene to (η^2 -acetato)iridacycle 95 produced an unexpected difference in the key intermediate that nonetheless led to iridabenzene synthesis.^[52] Unlike 89, the alkynyl(buta-1,3-dien-1-yl)iridium complex 96 was isolated in this experiment (Scheme 26). Addition of triflic acid to a CHCl₃ solution of 96 furnished cationic iridabenzene 97,



Scheme 25. Formation of iridabenzenes by [2+2+1] cycloaddition.



Scheme 26. Formation of iridabenzene **97**. Ar = Ph, *p*-Tol.

which was characterized as its OTf⁻ salt by NMR and IR spectroscopy and by elemental analysis. Iridabenzene **97** could also be produced by displacement of both MeCN ligands in complex **93** when it was treated with NaOAc.^[51,52]

The probable mechanism for the formation of **97** from **96** involves proton attack on the β -carbon atom of the alkynyl group in **96** to give a cationic alkylidene, which is then attacked at the α -carbon atom by the terminal diene. Tautomerization of the resulting iridacycle affords **97**. Deuterium-labeling studies corroborate this hypothesis. Reaction of **96** with D⁺ produces iridabenzene [6-D]-**97** (here, C6 is the benzylic carbon). Similarly, reaction of **95** with deuterated acetylene and subsequently with D⁺ produced [4,6-D₂]-**97**, thus confirming that it is the terminal carbon atom of the diene that attacks the α -carbon atom of the alkylidene complex. This chemistry is related to the known reactions of alkynyl complexes with H⁺ which lead to C–C coupling with neighboring unsaturated ligands.^[76,77]

Paneque, Poveda, and co-workers have recently reported an interesting variation of the [2+2+1] protocol by the coupling of an alkene and an iridacyclopentadiene.^[78] Reaction of diene **98** with propene at 60 °C furnished iridabenzene **99** (Scheme 27). It is believed that **99** results from the coordination of the alkene and subsequent isomerization to the propylidene species **100**, in which the propylidene ligand undergoes carbene migratory insertion into the iridacyclopentadiene moiety. Subsequent α -hydride elimination from **101** produces iridabenzene **99**. Support for this mechanism is provided by the reaction of **99** with MeCN to yield a 6:1 kinetic mixture of **102** and **103**. These two products are explained by hydride migration back to the six-membered ring. Upon heating, **102** rearranges to the more thermodynamically favored isomer **103**, likely via **99**, which is similar to reactivity first observed by Hughes et al. in their studies of the reaction of 3-vinylcyclopropenes with Ir complexes.^[79]

Replacement of **98** with the related diene complex **104** illustrates the subtleties of the system, as this analogous reaction affords iridabenzene **105**, which bears a Me group bound to the Ir center.^[78] As before, the first step in the mechanism is alkene coordination; however, to explain the different outcome, a 1-methylethylidene unit must be favored over the linear propylidene in the previous example. Carbene migratory insertion would then be followed by the unusual α -methyl elimination to give iridabenzene **105**. Even more surprisingly, the reaction with MeCN completely reverses the process, such that loss of propene regenerates the original iridacyclopentadiene ring in **106**.

X-ray structure analyses of **99** and **105** reveal two interesting features. First, the molecules are decidedly nonplanar, with the Ir centers deviating 0.57 and 0.70 Å out of the plane defined by the five C atoms of each iridacycle. Second, the molecules both exhibit a surprising degree of bond alternation. In contrast to most metallabenzenes, the differences between the "single" and "double" bonds in the two



Scheme 27. Formation of iridabenzenes 99 and 105.

structures are on the order of 0.040–0.057 and 0.21–0.36 Å for **99** and **105**, respectively. These features reflect the diminished aromaticity of these iridabenzenes and thus could explain in part the unusual reactivity noted above.

5.3. Iridanaphthalene

Although the existence of higher homologues of metallabenzenes had only been inferred from their decomposition products and the comparable reactivity of the metallabenzene analogues, one of the most exciting developments in recent vears is the isolation and characterization of iridanaphthalene 107 by Paneque et al.^[80] Synthesis of 107 begins by treating 108 with dimethyl acetylenedicarboxylate (DMAD), which yields isomeric iridacycloheptatrienes 109 and 110 (Scheme 28).^[81] Even though no intermediates could be detected, these products are likely produced by initial insertion of one molecule of DMAD into one of the Ir-Carvl bonds. C-H activation of the ortho proton in the resulting phenylalkenyl ligand and subsequent reductive elimination of benzene would lead to an iridacyclopentadiene complex. Insertion of a second equivalent of DMAD into either Ir-C bond and coordination of an adventitious water molecule would result in 109 or 110. Oxidation of isomer 109 with tBuOOH produces the coordinated oxoacetyl product 111. If excess tBuOOH is added, then iridanaphthalene 107 is produced.^[80] Conversion of 111 into 107 likely starts as a simple Baeyer-Villiger oxidation of the oxoacetyl group. The newly generated O-Caliphatic bond in 112 can then be cleaved irreversibly to form 107.

Structurally, the iridanaphthalene framework of **107** is similar to naphthalene in many respects. The bond lengths in the six-membered carbocycle are within 0.02 Å of those in

naphthalene. The Ir atom is tilted somewhat out of the plane of the metallacycle carbon atoms by 0.76 Å. The two Ir-C bond lengths (1.930 and 1.981 Å) are intermediate between single- and double-bond lengths and are in good agreement with those in Ir^{III} metallabenzenes. Spectroscopically, the aromatic protons of 107 resonate between $\delta =$ 6.60 and 8.12 ppm and are increasingly deshielded the nearer they are to the metal center. While no protons are attached directly to the primary metallacycle, ¹³C NMR spectroscopy demonstrates the typical anisotropic effects of the metal, as the outside C atom produces a signal at $\delta =$ 255.0 ppm, and the bridging C atom gives a signal at $\delta = 177.9$ ppm.

Column chromatography of **107** on silica gel results in the destruction of its aromaticity and affords **113**



Scheme 28. Synthesis of iridanaphthalene 107.

(Scheme 28),^[80] thus reminiscent of an internal "neutral" Jackson–Meisenheimer complex.^[82] Hydrolysis of the carboxylate ligand in **107** would result in an intermediate hydroxyl complex, which likely undergoes intramolecular nucleophilic attack at the γ -carbon atom to furnish **113**. Reaction of this new complex with ClC(O)CO₂Me in the presence of pyridine regenerates the iridanaphthalene, thus proving the viability of the proposed final step in the initial formation of **107**.

Similar to the method used to generate iridanaphthalene **107**, treatment of **114** with excess *t*BuOOH produced iridabenzene **115** (Scheme 29).^[80] When Thorn and Hoffman



Scheme 29. Synthesis of iridabenzene 115.

first predicted the stability of metallabenzenes, it was suggested that because of the low-lying LUMO of the $C_5R_5^-$ fragment, π donors, especially those *ortho* and *para* to the metal, would be most suited for stabilizing the metallabenzene.^[11] Although a number of metallabenzenes have been synthesized with π donors *ortho* to the metal fragment,^[23,31] iridanaphthalene **107** and iridabenzenes **99**, **105**, and **115** are the first examples of metalla-aromatic species substituted with electron-withdrawing groups, namely CO₂Me. Other examples of metallabenzenes bearing electron-withdrawing groups include the phosphonium-substituted osmabenzenes and ruthenabenzenes reported by Jia,^[35,62] but these moieties are located on the less influential *meta* positions.

6. Rhodium

As with other 4d transition metals, uncoordinated rhodabenzenes are probably unstable, and no rhodabenzene has yet been reported. Reaction of lithiated cyclopropene **70** with the Rh analogue of Vaska's complex provided spectroscopic evidence of a rhodabenzene, but all attempts to isolate the material furnished either uncharacterizable decomposition products or very low yields of cyclopentadienyl complexes similar to **78**.^[83] However, analogous reaction with [RhCl(CO)(PMe₃)₂] resulted in the isolation of rhodabenzvalene **116** (Scheme 30).^[84] Solutions of this complex decomposed at room temperature to an unidentified mixture of products, but at -30 °C are stable for several weeks.

X-ray data of a crystal of **116** which was kept at low temperature showed that, while most bond lengths and bonds angles were similar to those of **72b**, the main differences between the two structures were a consequence of the differing binding affinities for the cyclopropene π bond.





Second-row metals are known to backbond less efficiently. This was reflected in a shorter C1-C2 bond length (1.414 in 116 vs. 1.447 Å in 72b). The dihedral angle between the plane of the three-membered ring and the plane formed by the phenyl ipso carbon atoms and the cyclopropene double bond was greater (119.3° in 116 vs. 115.8° in 72b). The weaker coordination also translated into a much larger P1-M-P2 angle, which was nearly 7° larger in **116**. Formation of the η^2 cyclopropene-rhodium moiety was unique, as oxidative addition to the strained σ bond had been the exclusive reactivity observed in previous studies of cyclopropenes with Rh complexes. Equally rare was the σ-vinyl Rh^I linkage as such complexes generally display poor thermal stability and require sterically demanding ligands for stabilization. Given these facts, successful preparation of 116 was attributed to the synergistic combination of intramolecular π bonding of the cyclopropene unit and o-vinylic linkage to the Rh atom, both of which in turn inhibit decomposition of the other respective moiety.

In 1999, Hughes et al. reported the reaction of a 3-vinylcyclopropene with the $\{RhCl(PMe_3)_2\}$ fragment to furnish isomeric complexes **117** and **118**. In solution, a third



compound, **119**, was detected.^[85] There is a striking similarity between cation **119** and **120**,^[29] the precursor to Bleeke's iridabenzene **4**, which suggested that deprotonation may lead to a rhodabenzene. Complex **119**, however, either decomposed or failed to react with several strong bases.

The inability to isolate a rhodabenzene is congruent with the DFT calculations reported by van der Boom, Martin, and co-workers.^[22,33] According to their computations, after initial phosphine loss, the hypothetical rhodabenzene $[C_5H_5Rh-(PH_3)_3]$ has a barrier of 20.5 kcal mol⁻¹ for decomposition to the cyclopentadienyl complex, while the analogous decomposition of the corresponding iridabenzene gives a much higher barrier of 44.4 kcal mol⁻¹. For that reason it can be expected that, in the absence of stabilizing functionalities, rhodabenzenes are too reactive to be isolated.

7. Platinum

The most recent transition metal to be incorporated into stable metallabenzene complexes is platinum.^[86,87] Using the same chemistry that was used to prepare iridabenzenes, we reported the synthesis of platinabenzene **121** by the addition of lithiated **70** to [PtCl₂(cod)], albeit in only 7% yield (Scheme 31).^[86] One particularly intriguing aspect of this reaction is that both the metallacycle and cyclopentadienyl moiety are derived from the starting 3-vinylcyclopropene.



Scheme 31. Synthesis of the first platinabenzene 121.

Based on related experiments (see below), it is possible that formation of the cyclopentadienyl ligand results from the decomposition of an intermediate platinabenzene before addition of the second equivalent of lithiated **70**. In addition to being the first platinabenzene, this example demonstrates the versatility of the 3-vinylcyclopropene approach to metallabenzenes, as this is the first method that has produced stable metallabenzenes for more than one transition metal, while Jia's 1,4-pentadiyn-3-ol cyclization route now represents a second such method (see Sections 3.1 and 4.2).

After this initial success, attempts were made to synthesize platinabenzenes by using an "asymmetric" $[L_2Pt(X)Y]$ complex in which only ligand X would be substituted for the vinylcyclopropene unit while Y would remain unchanged. In the following step, Y could then be cleaved from the σ -vinyl compound, thus allowing for coordination of the cyclopropene double bond. Depending on stability, either the resultant cationic platinabenzvalene or rearranged products like a cationic platinabenzene would be expected. Addition of lithiated **70** to $[Pt(Me)I(PEt_3)_2]$ resulted in displacement of the primary leaving group, I⁻, and thus formation of σ -vinyl complex **122** (Scheme 32).^[88] Given that Pt^{II} is found preferentially in a square-planar geometry, it is not surprising that



the cyclopropene moiety does not coordinate to afford a platinabenzvalene. Protonolysis of 122 with HBF₄ opened a coordination site by removal of the secondary leaving group, Me⁻. Similarly, substitution with chloride to give 123 and subsequent Cl⁻ abstraction with TlPF₆ generated the analogous reactive 14-electon Pt^{II} species. In both cases, only complex 124 was isolated. This complex is an interesting molecule itself, which in the solid state possesses a slipped Cp ring with η^3 coordination. Since platinabenzene intermediates were suspected, protonolysis was performed at -60 °C with trifluoroacetic acid to yield the *cis* complex **125**. While 125 was stable at low temperatures, warming to room temperature resulted in the production of a 3:2 mixture of 124-O₂CCF₃ and the *trans* isomer of 125. Even though monitoring the reaction by ¹H NMR spectroscopy provided no direct evidence for a platinabenzene, it is reasonable to assume the intermediacy of unstable cationic platinabenzenes such as 126, which readily undergo carbene migratory insertion to give Cp complexes like 124.

The results of the above two studies suggested that the next set of experiments should begin with a Cp unit already affixed to the Pt center. Reaction of [Cp*Pt(CO)Cl]^[89] with the lithiated vinylcyclopropene 70 resulted only in trace amounts of platinabenzene, recovered Pt starting complex, and the protonated vinylcyclopropene. A more labile leaving group was next examined, and thus, the new complex [Cp*Pt(CO)I] was synthesized from the known platinum dimer [{Cp*Pt(CO)}2].[87,89] Reaction of lithiated 70 with [Cp*Pt(CO)I] afforded a mixture of σ complex 127a and platinabenzene 128a (Scheme 33). Solutions of pure 127a in C_6D_6 rearrange over 2–3 days at room temperature to give quantitative conversion to 128 a. Presumably, 128 a is formed by metathesis of the iodide with the lithiated vinylcyclopropene and subsequent loss of CO with fast rearrangement to the platinabenzene. Unlike in the case with iridium, monitoring this process by ¹H NMR spectroscopy did not provide evidence for an intermediate platinabenzvalene. Extension of this chemistry has also led to phenyl(alkyl)platinabenzenes



Scheme 32. Unsuccessful attempts at the synthesis of platinabenzenes.

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128b,c. Additional examples are currently under investigation along with general studies of platinabenzene reactivity.^[61]

The NMR spectroscopic data for **121** and **128** are similar to those of other metallabenzenes. The proton *ortho* to the Pt atom produces a ¹⁹⁵Pt-coupled signal at $\delta = 12.76$ ppm for **121** and in the range $\delta = 11.83-12.09$ ppm for **128a–c**. The upfield shift for the latter complexes illustrates the greater contribution of electron density by Cp* to the metal center. The *meta* and *para* protons produce signals in the ranges $\delta = 7.4-7.6$ and 8.2–8.5 ppm, respectively. Two ¹³C NMR signals in the ranges $\delta = 200-204$ and 188–195 ppm are attributed to the phenyl-substituted and unsubstituted *ortho* carbon atoms, respectively.

The solid-state structures of the platinacycles are of considerable interest. The molecular structure of **128b** is shown in Figure 3, and selected bond lengths and angles for



Figure 3. Molecular structure of platinabenzene **128b**. Thermal ellipsoids are set at 30% probability.

121 and **128 a,b** are given in Table 6. Unlike most metallabenzenes, the platinabenzenes have planar structures (for **121**: deviation from mean plane 0.02 Å, sum of angles 720°).

 $\mbox{\it Table 6:}$ Selected X-ray bond lengths [Å] and bond angles [°] for platinabenzenes.

	121	128 a	128 b
Pt-C1	1.959	1.951	1.975
Pt-C5	1.929	1.937	1.926
C1-C2	1.387	1.401	1.406
C2-C3	1.392	1.395	1.389
C3-C4	1.381	1.364	1.387
C4-C5	1.364	1.387	1.350
Ø(C-C)	1.382	1.387	1.383
Pt-C1-C2	129.2	129.2	129.8
C1-C2-C3	122.6	122.3	124.1
C2-C3-C4	124.8	125.2	126.9
C3-C4-C5	124.1	124.5	119.8
C4-C5-Pt	130.0	128.9	129.8
C1-Pt-C5	89.3	89.7	89.4
sum of angles	720.0	719.8	719.8

The Pt–C bond lengths are 1.926–1.937 and 1.951–1.975 Å, which compare well with Pt–C bond lengths in other Pt^{II} carbene complexes. The C–C bond lengths in the metallacycle have an average of 1.382–1.387 Å with no appreciable bond alternation. The Cp ring in each system is η^5 -coordinated to the Pt center (Pt–C_{cp} bond lengths: 2.257–2.342 Å).

Van der Boom, Martin, and co-workers also performed calculations on the stability of several platinabenzene complexes.^[22,33] Based on their results, the cyclopentadienyl ligand does stabilize the platinabenzene by increasing the energy barrier for the occurrence of carbene migratory insertion. In the case of $[C_5H_5Pt(PH_3)_2]^+$, the computational analogue of **126**, the transition state to forming $[(\eta^5-Cp)Pt(PH_3)_2]^+$ was only 24.0 kcalmol⁻¹, which corroborates the experimental results shown in Scheme 32. For the Cp complex [C₅H₅PtCp], the computational analogue of 121, the energy of the transition state for forming $[(\eta^3-Cp)_2Pt]$ was considerably higher (45.9 kcalmol⁻¹). De Proft and Geerlings recently utilized the isomerization method to predict the aromatic stabilization energy of the platinabenzene ring in the model system [Pt(C₅H₃Me₂)(η³-C₅H₃Me₂)].^[90] They obtained a calculated value of 23.4 kcalmol⁻¹, approximately two thirds of the aromatic stabilization energy calculated for benzene. Based on these computational results, it is not surprising that platinabenzenes such as 121 and 128 are stable even at elevated temperatures.

8. Conclusions

Aromaticity is a concept that many chemists take for granted as well-defined. In fact, like so many things in chemistry, the truth is multifaceted and thus considerably more complicated. Metallabenzenes and their higher analogues display a number of contradictory behaviors that place them in a delicate gray area between aromatic and nonaromatic. While their structures are in general planar and exhibit negligible bond alternation, they also undergo [4+2] cycloadditions as if they were simple metallacyclohexatrienes. The NMR spectroscopic properties suggest that the ring substituents are deshielded; however, this could simply be an effect of the transition metal. Unlike benzene, many metallabenzenes rearrange readily to form cyclopentadienyl complexes. Like benzene, they readily form η^{6} -metal complexes, through which the metallabenzenes are in fact clearly stabilized.

Over the last few years, the field of metalla-aromatics has expanded significantly. Several new methods to generate metallabenzenes have been developed. In addition to synthesis from nucleophilic 3-vinylcyclopropenes, they can be prepared from a number of alkyne precursors by generally unrelated mechanisms. For the first time, a metallanaphthalene has been isolated and characterized. Platinum has now been added to the list of transition metals capable of yielding a metallabenzene. At the current rate of progress, there is little doubt that the coming years will be equally exciting for metallabenzene chemistry. We would like to thank the University of Oregon graduate and undergraduate students and postdoctoral associates who made our work on metallabenzene chemistry possible. The National Science Foundation and the University of Oregon are gratefully acknowledged for support of this research. We also thank Profs. John Bleeke, Guochen Jia, Warren Roper, and James Wright, our colleagues in the field, for stimulating discussions and helpful advice, and for sharing results prior to publication.

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