Chinese Science Bulletin 2004 Vol. 49 No. 15 1543—1553

Progress in the synthesis and reactivity studies of metallabenzenes

HE Guomei[1], XIA Haiping[1] & JIA Guocheng[2]

1. College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China;
2. Department of Chemistry, The Hong Kong University of Science and Technology, Hong Kong, China

Correspondence should be addressed to Xia Haiping (e-mail: hpxia@xmu.edu.cn)

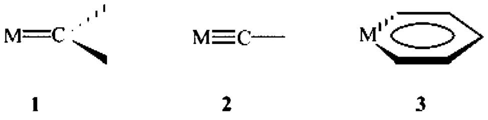
Abstract **Metallabenzenes are metallacyclohexatriene complexes that are derived by replacement of one of the CH groups in benzene with a transition-metal fragment. Their synthesis and aromatic properties have recently attracted considerable attention. This paper summarizes the progress in the synthesis, aromatic property, and reactivity studies of metallabenzenes. We will describe the synthesis and reactivity of typical metallabenzenes with various metals (e.g. osmium, iridium, and ruthenium, etc.), the synthesis and structure of a recent reported example of metallanaphthalene and several rare examples of novel and stable metallabenzynes. Finally, the possible future developments in this field have also been suggested.**

Keywords: aromaticity, metal-carbene, metal-carbyne, metallabenzene, metallanaphthalene, metallabenzyne.

DOI: 10.1360/04wb0005

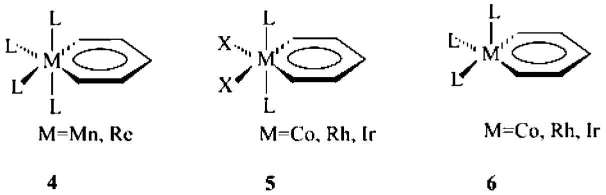
In 1865, Kekulé[1,2] introduced the term "aromaticity" to describe the unique properties of benzene. For over a century, the chemistry of aromatic compounds has been an active research topic for both theoretical and synthetic chemists. It is now well established that a large number of benzenoid hydrocarbons exhibits "aromatic" properties, including high thermodynamic stability, low chemical reactivity, delocalization of π bonds, and diamagnetic ring currents. Formal replacement of a CH group in benzene with an isoelectronic heteroatom (e.g. N, P, As, O^+, S^+) leads to heterocyclic compounds in which aromaticity is retained[3,4]. While detailed studies on these "heterobenzenes" have been carried out, comparatively little study has been carried out on metallabenzenes in which a transition-metal fragment replaces a benzene CH group. There has been particularly interest in the question of whether (or to what extent) "metallabenzenes" would exhibit aromatic physical and chemical properties.

Transition metals can stabilize some unstable reactive species through coordination. There are many examples of complexes with metal-carbon multiple bonds. These compounds can be derived by formal replacement of a carbon atom or group in organic compounds with an isolobal transition-metal fragment. For example, the carbene complexes (**1**) or carbyne complexes (**2**) shown in Scheme 1 can be thought as being formed by replacing the carbon groups in olefins and alkynes, respectively. Metallabenzenes (**3**) are particularly interesting example of cyclic carbene complexes derived from replacement of one of the CH groups in benzene by a metal center and associated ligands.



Scheme 1. Some known classes of compound with metal-carbon multiple bonds.

Metallacyclohexatrienes or metallabenzenes were first studied theoretically. On the basis of extended Hückel molecular orbital calculations, Thorn et al.[5] in 1979 predicted that the hypothetical metallacycles **4**, **5** and **6** shown in Scheme 2 should exhibit delocalized bonding and some aromatic character (L = $2e^-$ neutral donor ligand, X=halide). In each of these structures, the metal-fragment is isolobal with CH.



Scheme 2. Three classes of hypothetical metallacycles with some aromatic character.

The first comprehensive review of the previous studies of metallabenzenes (especially on their synthesis, structure, and spectroscopy) was written by Bleeke[6] and appeared in 2001. This paper mainly concerns the recent progress in the synthesis, aromaticity, and reactivity of metallabenzenes, metallaheterobenzenes, dimetallabenzenes, and metallabenzynes. The earlier work will also be briefly discussed.

1 Osmabenzenes

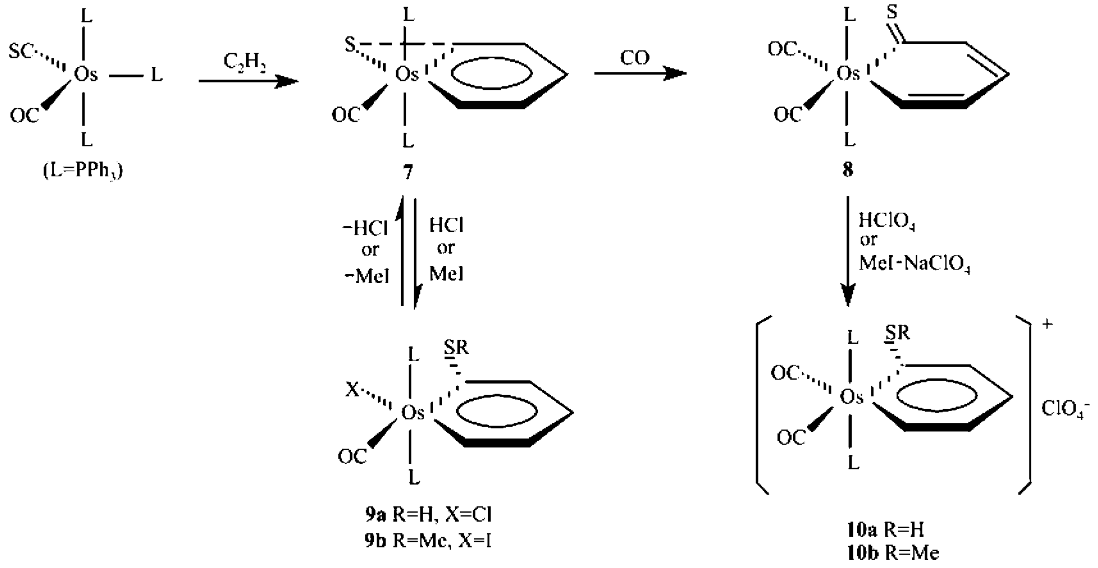
(i) Synthesis of the first example of stable metallabenzenes. In 1982, Elliott et al.[7] reported the first example of stable metallabenzenes, (see **7** in Scheme 3), which was synthesized by a cyclization reaction of an osmium-thiocarbonyl with acetylene. Since metallacyclopentadiene complexes can be commonly assembled by direct reactions between acetylenes and a metal carbyne complex, they have tried to prepare metallabenzene through a similar cyclization reaction involving acetylenes and a transition metal carbyne complex (LnM≡CR).

However, saturated 18-electron carbyne complexes such as $Os(CR)Cl(CO)(PPh_3)_2$ are unreactive towards acetylenes. The unavailability of co-ordinatively unsaturated carbyne complexes turned their attention to the thiocarbonyl complex $Os(CO)(CS)(PPh_3)_3$. The complex has an easily dissociating phosphine ligand and a thiocarbonyl ligand which has the potential to be converted into a thiocarbyne through alkylation on sulphur (see eq. (1)). As expected, the reaction of $Os(CO)(CS)(PPh_3)_3$ with acetylene in benzene affords "osmabenzene", 7. The X-ray crystal structure of 7 has a planar six-membered ring with no significant alternation in C-C bond lengths, supporting the idea of electron delocalization within the ring. Furthermore, low-field chemical shifts for the ring protons are observed in the ^1H NMR spectrum, providing additional supporting evidence for aromaticity[8].

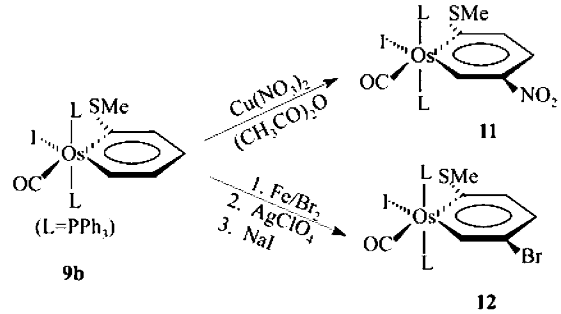
$$L_nM-CS \xrightarrow{R^+} [L_nM\equiv CSR]^+ \qquad (1)$$

(ii) Chemical reactivity of osmabenzenes. Reaction of complex 7[7] with CO opened the C-S bond and gave the bronze complex **8**. Treatment of complexes **7** and **8** with HCl, MeI, $HClO_4$, or MeI-$NaClO_4$ leads to complexes **9a**, **9b**, **10a** and **10b**, respectively. All these osmabenzene derivatives retain their planar metallabenzene structure, and represent a new class of heterocycles.

In 2000, Rickard et al.[9] reported the first examples of electrophilic aromatic substitution of a metallabenzene, specifically the mononitration and monohalogenation of osmabenzene **9b** (Scheme 4). The X-ray diffraction studies on the nitrated and brominated products **11** and **12** reveal that both the nitro and bromo groups lie in the plane of the osmabenzene ring, and the sites of nitration and bromination are para to the SMe group. Chlorination of **9b**, in the same ring position, has also been achieved through treatment of **9b** with $PhICl_2$. These results indicate that osmabenzene **9b** shows chemical characteristics of aromaticity in undergoing the classical electrophilic aromatic substitution reactions. Furthermore, normal directing substituent effects are apparently operative.



Scheme 3. Synthesis and reactivity of osmabenzenes.



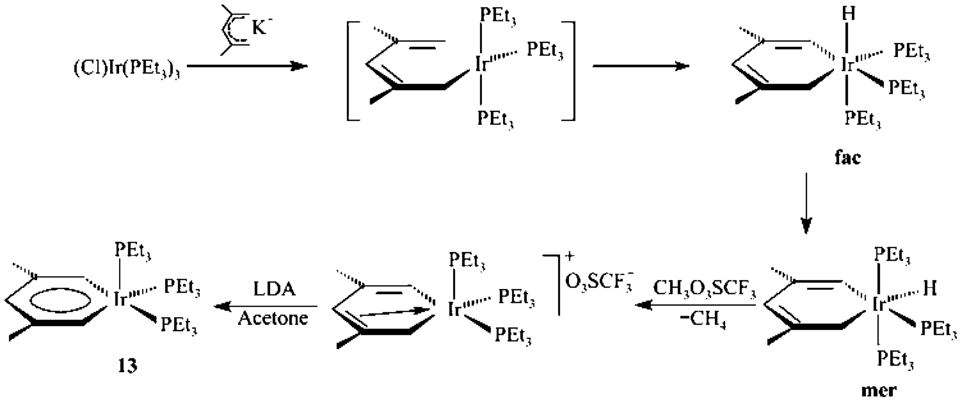
Scheme 4. Electrophilic aromatic substitution reactions of osmabenzene.

2 Iridabenzenes

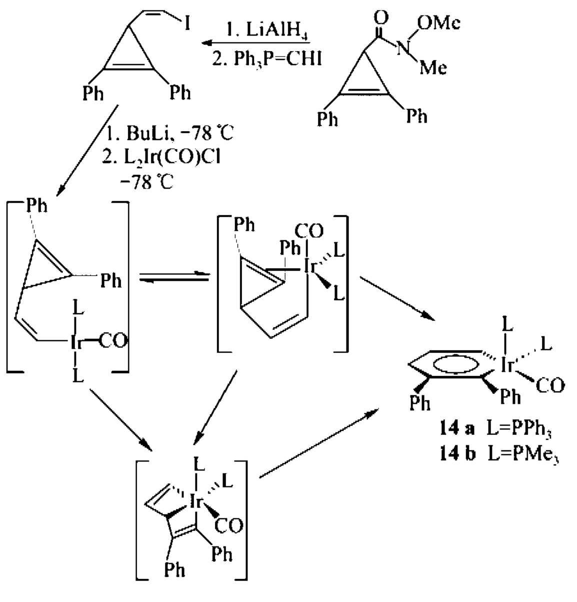
(i) The first synthetic example of metallabenzenes with a structure similar to those predicted by Thorn and Hoffmann——an iridabenzene. Activation of a pentadienyl C-H bond by a transition metal center can provide a convenient synthetic route to unsaturated six-membered metallacycles. Bleeke et al.[10,11] in 1991 developed a new route for the preparation of metallabenzenes. The metallacyclohexadiene complex, produced from metallapentadienide, can be readily converted to the stable iridabenzene, **13**, via a two-step "dehydrogenation" reaction (Scheme 5). **13** is the first synthetic example of metallabenzenes predicted by Hoffmann et al. (Scheme 2).

(ii) Direct synthesis of iridabenzenes. Reactions of cyclopropenes with transition-metal complexes often easily generate interesting organometallic products, due to the large strain energy associated with the three-membered ring. Gilbertson et al.[12,13] reported the synthesis of iridabenzenes, **14a** and **14b** (Scheme 6), which have a structure similar to that of **13**, from cyclopropene derivatives. Unlike Bleeke's work, they prepared the iridabenzenes **14a** and **14b** directly from the reactions of a nucleophilic 3-vinyl-1-cyclopropene with Vaska's complexes, Ir(CO) ClL$_2$ (L = PPh$_3$, PMe$_3$). The reaction involves an Ir-mediated intramolecular rearrangement of a cyclopropene. Recently, Gilbertson et al.[14] extended this method for the synthesis of a series of iridabenzenes by using other Vaska's complexes, Ir(CO)ClL$_2$ (L=PMe$_2$Ph, PEt$_3$, PMePh$_2$, P(i-Bu)$_3$, P(p-MeOPh)$_3$). As the reactions involved in the preparation of this series of iridabenzenes (i.e. addition of carbon nucleophiles to low-valent metals and metal-promoted cyclopropene rearrangements) commonly encounter numerous transition metals[15—18], it might be possible to extend the methodology to prepare metallabenzenes incorporating other transition metals.

(iii) Chemical reactivity of iridabenzenes. Although many metallabenzenes have only been implicated as intermediates in the formation of (cyclopentadienyl)metal complexes[19—23], complex **13** is quite robust. It is stable indefinitely in the solid state or in solutionat room temperature under a N$_2$ atmosphere. Decomposition does occur slowly in refluxing benzene. The decomposition process is significantly retarded by the addition of excess PEt$_3$, indicating that phosphine dissociation precedes decomposition.



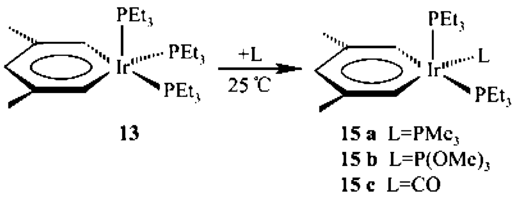
Scheme 5. Synthesis of the first example of iridabenzene.



Scheme 6. Direct synthesis of iridabenzenes.

While **13** shows good thermal stability, it is reactive toward a range of substrates[24,25].

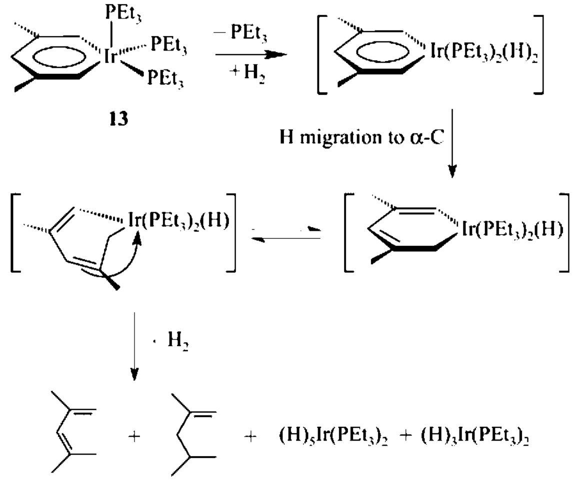
(1) Ligand substitution. Iridabenzene **13** undergoes ligand replacement reactions with various small 2e$^-$ ligands L, including PMe$_3$, P(OMe)$_3$, and CO, to produce complexes **15a**—**15c** (see eq. (2)), in which L resides preferentially in the basal plane.



(2)

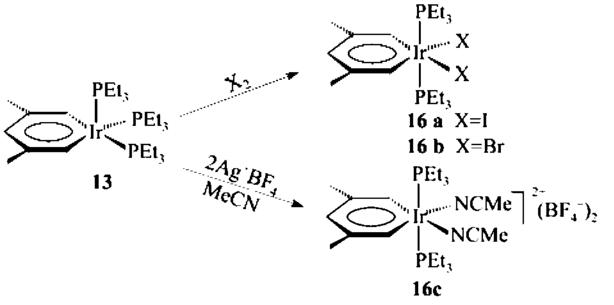
(2) Oxidative addition/oxidation. Iridabenzene **13** slowly reacts with H$_2$ gas at room temperature and 101325 Pa of pressure to give 2,4-dimethyl-1,3-pentadiene, 2,4-dimethyl-1-pentene, and iridium polyhydrides (Scheme 7). In contrast, complexes **15a**—**15c** do not react with H$_2$ at

25℃, probably because the 16e$^-$ intermediates cannot be accessed in these cases. Treatment of **13** with iodine and bromine rapidly leads to the oxidative addition products, **16a** and **16b**; that with 2 equiv. of $AgBF_4$ in acetonitrile leads to the clean production of complex **16c** (Scheme 8).



Scheme 7. Oxidative addition of iridabenzene.

(3) Cycloadditions. Iridabenzene **13** readily undergoes cycloaddition reactions. Treatment of compound **13** with molecular oxygen, nitrosobenzene, maleic anhydride, or carbon disulfide leads to clean [4+2] cycloaddition reactions in which the substrates add across iridium and C3 of the iridabenzene ring, producing compounds **17**—**20**, respectively. Similarly, **13** undergoes a cheleotropic [4+2] cycloaddition with sulfur dioxide to produce **21**. Unlike the reactions discussed above, **13** reacts with CO_2 to produce the [2+2] cycloaddition product **22** (Scheme 9).



Scheme 8. Oxidation of iridabenzene.

Treatment of **13** with nitrous oxide leads to ring-contraction and formation of iridacyclopentadiene complex **23** (Scheme 10). The same product is obtained when **13** is treated with amine N-oxides, such as 4-methylmorpholine N-oxide and trimethylamine N-oxide.

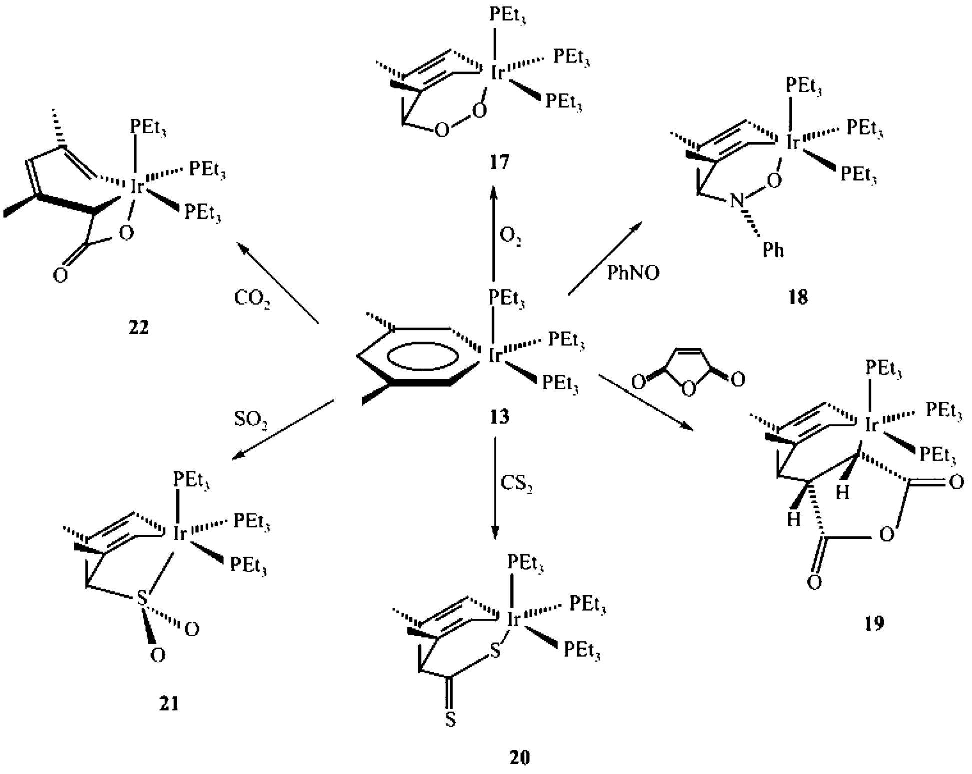
The ligand exchange and oxidative addition reactions lead to products in which the aromatic ring system is retained. In contrast, the cycloaddition reactions disrupt the aromaticity of **13**, generating octahedral Ir(Ⅲ) products in which the iridabenzene ring is converted to a boat-shaped 1-iridacyclohexa-2,5-diene ring ([4+2] cycloaddition) or a half-boat 1-iridacyclohexa-2,4-diene ring ([2+2] cycloaddition).

(4) Electrophilic addition. Unlike osmabenzene **9b** (Scheme 4), iridabenzene **13** does not undergo classical electrophilic substitution reactions. Instead, electrophiles tend to react at the very electron-rich iridium center, C1/C5, leading to a variety of interesting products (Scheme 11). Treatment of **13** with 1 equiv. of $H^+O_3SCF_3^-$ results in clean protonation at the α-C to give **24**. Similarly, protonation of **13** with acetylacetone ($pK_a \approx 9$) or diethyl malonate ($pK_a \approx 13$) also occurs at the α-C. However, in these cases, the cationic pentadienediyl product is rapidly attacked by the counter anion to give neutral complexes **25** and **26**, respectively. Iridabenzene **13** does not react with acids having pK_a values above ~15 (for example, water). When **13** is treated with 2 equiv. of strong acids such as $H^+O_3SCF_3^-$, protonation occurs at both C1 and C5 to give complex **27**. Treatment of **13** with excess boron trifluoride leads to the formation of the novel (η^6-borabenzene)metal complex **28**.

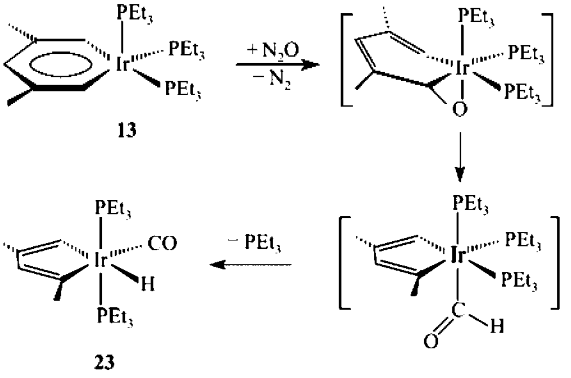
(5) Coordination of $Mo(CO)_3$. Complex **13** can displace *p*-xylene from (*p*-xylene) $Mo(CO)_3$ in tetrahydrofuran to produce the metal-coordinated metallabenzene complex **29a** (Scheme 12)[26, 27].

13 and **29a** represent the first pair of metallabenzene and coordinated-metallabenzene and provide a unique opportunity for comparing the physical and chemical properties of these two classes of compounds. While **13** undergoes facile intramolecular phosphine exchange, this process does not occur for **29a**. Like **13**, **29a** reacts with a variety of 2e$^-$ ligands L, including PMe_3, and CO, to produce the ligand-substituted complexes **29b**, and **29c** (Scheme 12) in which the ligands L reside in a basal coordination site. While protonation of **13** occurs at α-C, protonation of **29a**—**29c** with $HBF_4 \cdot OEt_2$ occurs at the metal centers, producing the novel heterobimetallic μ-hydride complexes, **30a**—**30c**. In solution, both complexes **29** and **30** undergo arene rotation with respect to the $Mo(CO)_3$ moiety. The barriers ($\Delta G^{\neq}$) for the rotation for the neutral complexes **29a**—**29c** are less than 33.5 kJ/mol, while those for the protonated complexes **30a**—**30c** are ~56.5 — 62.8 kJ/mol (calculated from variable-temperature ^{13}C NMR[27]).

Iron and his coworkers[28] have made detailed theoretical studies on the reactivity of iridabenzenes. Much research work on the synthesis and reactivity of iridabenzenes discussed above was carried out by Bleeke's group.



Scheme 9. Cycloaddition reactions of iridabenzene.



Scheme 10. Ring contraction reaction of iridabenzene.

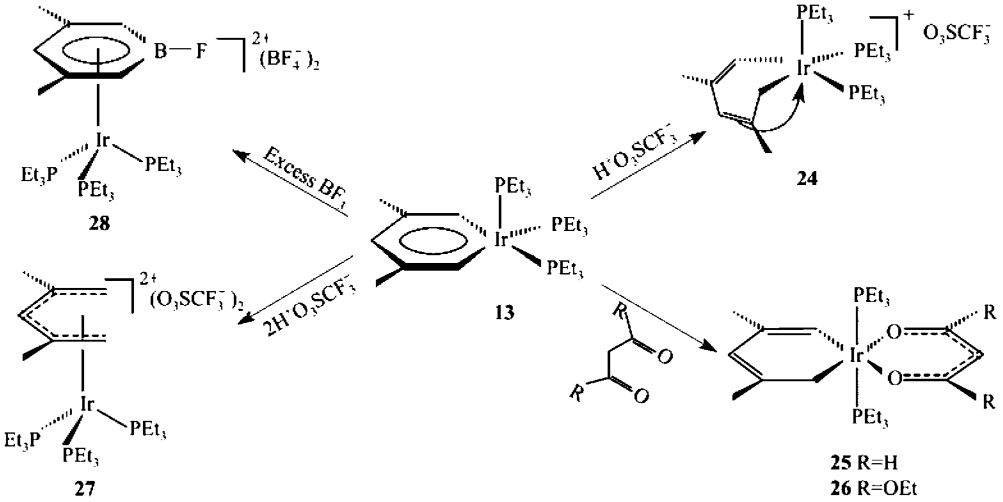
3 Ruthenabenzenes

(i) The first unsubstituted metallabenzene. In 1993, Lin et al.[29] succeeded in synthesizing the first example of metallabenzene complexes with no substituents on the ring carbon framework. Treatment of a methylene-bridged ruthenium dimer with acetylene gives complex **31** in which the ruthenabenzene is η^6-coordinated to another ruthenium center (Scheme 13). This complex bears a strong structural similarity to Bosch's[30] η^6-ruthenabenzene complex **32** (Scheme 18), except that complex **31** has no substituents on the carbons of the aromatic ring. The comparison of the chemical and physical properties of these two sandwich compounds will be an interesting subject in the future.

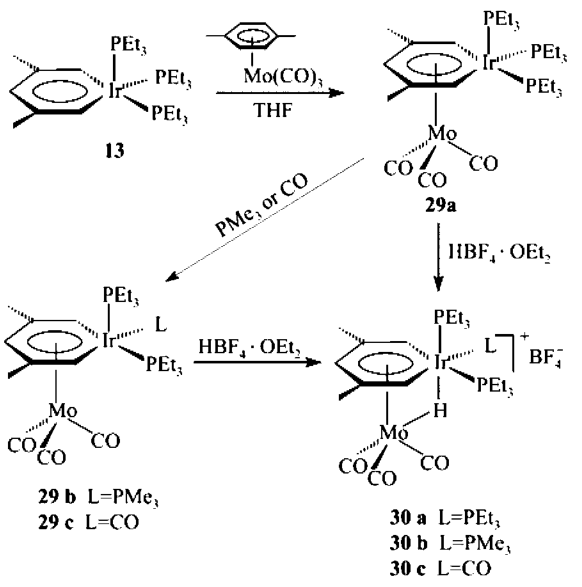
(ii) A ruthenabenzene detected at low temperature. In 1995, Yand et al.[31] reported the low-temperature NMR detection of ruthenabenzene **33** (Scheme 14), which was produced by intramolecular attack of a butadienyllithium ligand on a bound carbonyl. The ruthenabenzene **33** is reasonably stable at –50℃, however, this complex rearranges, resulting in the (η^3-cyclopentadienyl)ruthenium complex **34** through carbene migratory insertion at –30℃.

(iii) The first bis(ruthenabenzene) sandwich complex. In 1998, Englert et al.[32] reported a stable sandwich complex **35**, the first sandwich metallabenzene complex, by insertion of unsaturated metal fragments into the "half-open" metallocenes. Complex **35** comprises two metallacyclic ligands (Scheme 15).

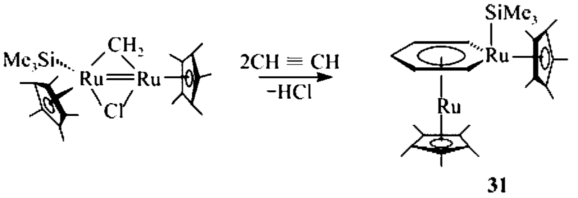
(iv) A triple-decker complex with a central ruthenabenzene. In 2002, Liu et al.[33] reported the first triple-decker complex **36** (Scheme 16), with a central metallabenzene. This interesting complex, which contains three ruthenium atoms in one molecule and has a central ruthenabenzene, was prepared by C-C bond activation of norbornadiene under mild conditions.



Scheme 11. Electrophilic addition reactions of iridabenzene.



Scheme 12. Coordination reaction of iridabenzene and reactions of metal-coordinated metallabenzene.

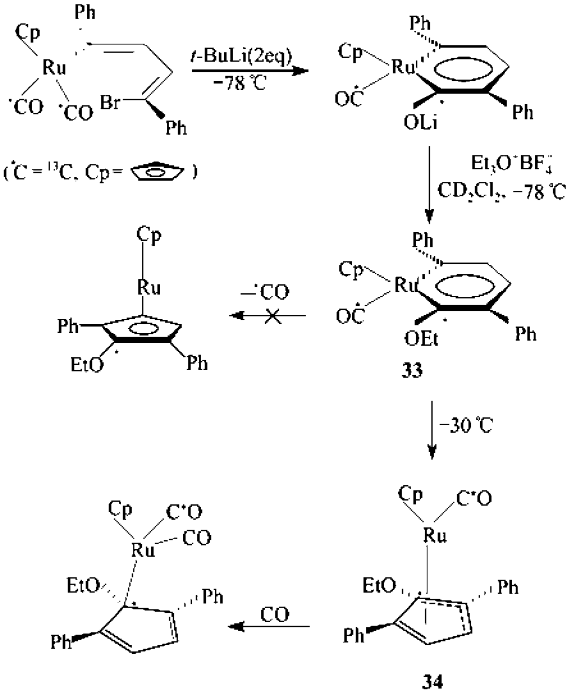


Scheme 13. Synthesis of the first unsubstituted ruthenabenzene.

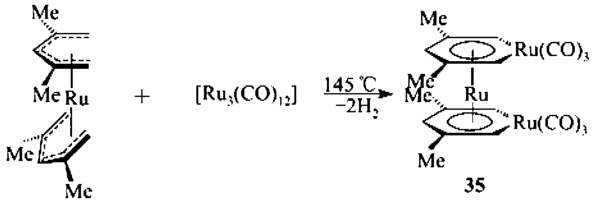
4 Other metal-coordinated metallabenzenes and metallaheterobenzenes

Most of the reported transition-metal-containing metallabenzenes have Os, Ir, and Ru. However, several other species, including those with Fe, Ni, Pt, Mo, Ta, Nb, and W, have also been synthesized. In addition, several metallaheterobenzenes which contain both a transition metal and a heteroatom (N, S, etc.) reside in the six-membered ring, and dimetallabenzenes which contain two metals are also known. These complexes will be briefly described in this section.

(i) Ferrabenzene. Hein et al.[34] reported the first ferrabenzene **37** (Scheme 17), which was produced from



Scheme 14. Synthesis and stability of a ruthenabenzene detected at low temperature.

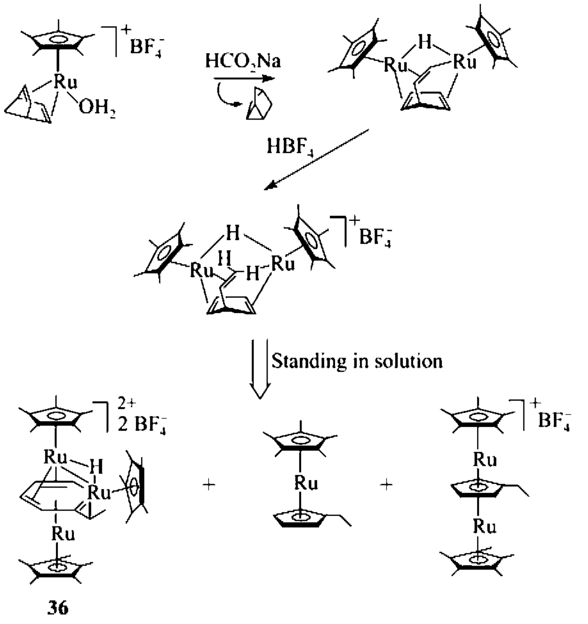


Scheme 15. Synthesis of bis(ruthenabenzene) sandwich complex.

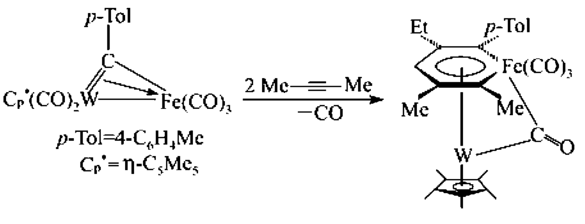
the reaction of a bismetallic μ-carbyne complex with 2 equiv. of 2-butyne in low yield (ca. 5%—10%).

(ii) Nickelabenzene. Salzer et al.[30,35] prepared η^6-coordinated cationic ruthenabenzene **32** and nickelabenzene **39** by treating the "half-open" metallocene **38** with $[\mathrm{CpRu(MeCN)_3}]^+$ and $[\mathrm{Cp_3Ni_2}]^+$, respectively (Scheme 18). The intermediates in these reactions appear to be triple-decker complexes with a central pentadienyl ligand.

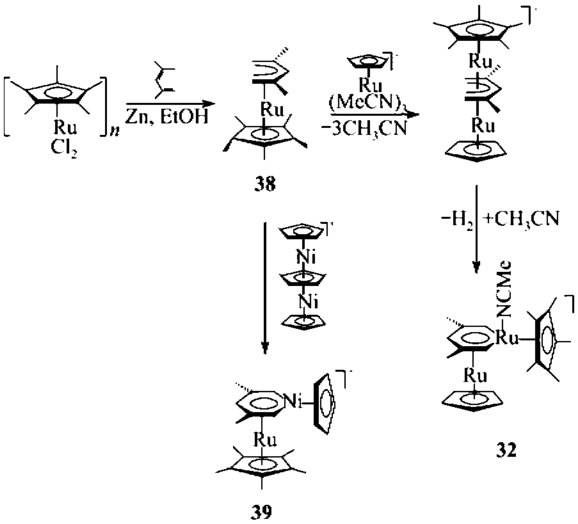
(iii) Platinabenzene. The convenient method[12] for the preparation of iridabenzenes mentioned in sec. 2 (ii) of this paper has been extended to prepare metallabenzenes incorporating platinum other than iridium. For example, the platinabenzene **40**[36] was reported in 2002 and was prepared through the reactions shown in Scheme 19. The formation of complex **40** as a stable product from the reaction can be related to mutual stabilization of the η^5-bonded cyclopentadienyl ligand and the platinabenzene moiety.



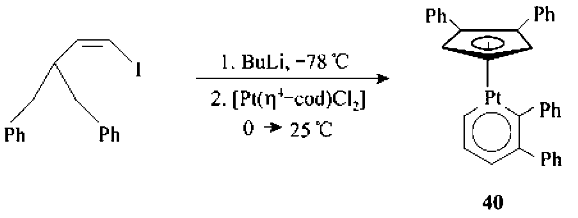
Scheme 16. Synthesis of triple-decker complex with a central ruthenabenzene.



Scheme 17. Synthesis of ferrabenzene.

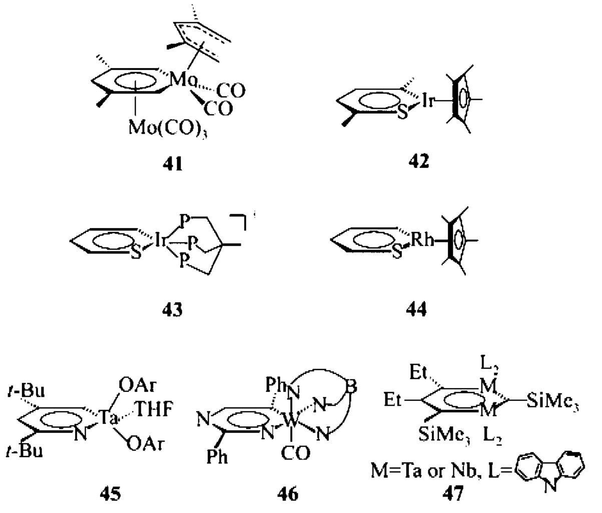


Scheme 18. Synthesis of ruthenabenzene and nickelabenzene.



Scheme 19. Synthesis of platinabenzene.

(iv) Other related compounds. Several other related molecules are worthy of mention besides the metallabenzenes described above. For instance, Kralik et al.[37] have prepared the (η^6-molybdabenzene)metal complex **41** (Scheme 20) from the reaction of 2 equiv. of (2,4-dimethylpentadienyl)molybdenum tricarbonyl anion with ICH_2CH_2I. Bonding parameters indicate that the molybdabenzene fragment is η^6 coordinated to the other molybdenum atom. Chen et al.[38] and Bianchini et al.[39,40] have independently synthesized iridathiabenzenes **42** and **43** via insertion of iridium into C-S bonds of thiophene. The rhodium analogue **44**[41] has been similarly generated in a thiophene ring-opening reaction. A tantalapyridine complex **45** has been reported by Wigley et al.[24], while tungstapyrimidine complex **46** has been reported by Feng et al.[42]. A family of 1,3-dimetallabenzenes **47**, generated by alkyne insertion into dimetallacyclobutadienes, have been reported by Profilet et al.[43,44].



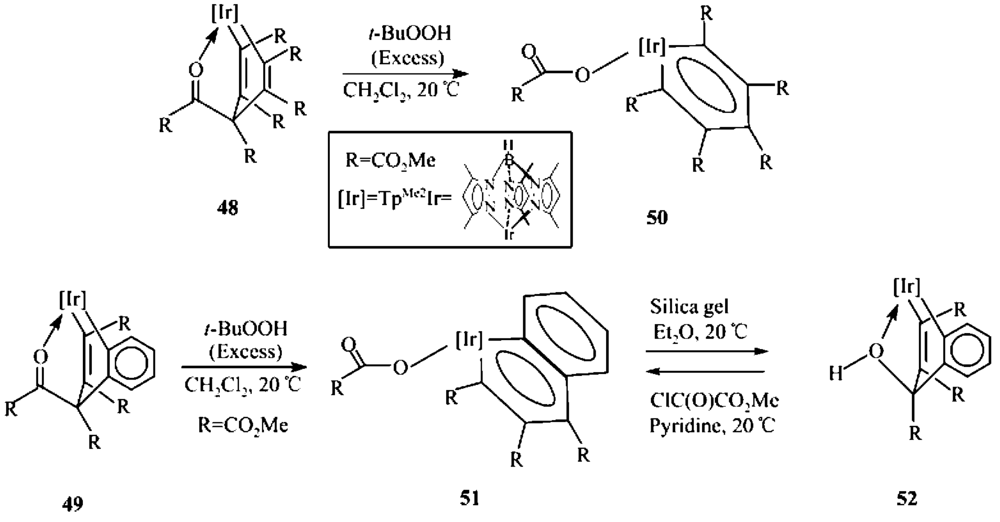
Scheme 20. Some other metal-coordinated metallabenzenes and metallaheterobenzenes.

5 Metallanaphthalenes and metallabenzynes

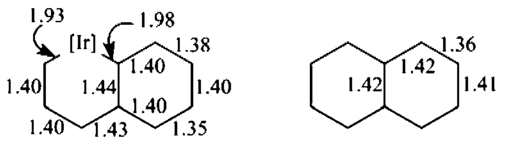
(i) Unusual metallanaphthalene. Recently, Paneque et al.[45] reported complexes **50** and **51**, which contain a methyloxalate ligand (Scheme 21) and were prepared by treatment of the bicyclic iridium derivatives **48** and **49**[46] with *t*-BuOOH, respectively. Compound **50** is a new example of iridabenzene, and compound **51** is a unique example of metallanaphthalene known. It is worth noting that compounds **50** and **51** are the only metalla-aromatic species known that contain electron-withdrawing CO_2Me groups. In the X-ray crystal structure of **51**, all the C—C distances in iridanaphthalene ring compare well with those found in naphthalene (Scheme 22), providing the evidence for electron delocalization within the metallanaphthalene ring.

Both **50** and **51** are thermally stable in solution and exhibit interesting reactivity. For instance, column chromatography of **51** through silica gel produces the benzannelated iridacyclohexadiene **52** (Scheme 21). Formation of **52** may involve hydrolysis of **51** to give rise to a hydroxo complex intermediate which undergoes nucleophilic attack at the γ-C atom of the electron-poor iridanaphthalene. This transformation can be reversed. Thus when **52** is treated with $ClC(O)CO_2Me$, in the presence of pyridine, **52** is cleanly converted to **51** (Scheme 21).

(ii) Stable and novel metallabenzynes. Benzynes are important organic molecules which have been widely used in organic synthesis. However, it is difficult to isolate free benzynes because of their low stability. Replacement of C or CH groups in benzene with isolable metal fragments would give metallabenzynes **53**, **54**, and **55** (Scheme 23). At first sight, one might expect that metallabenzynes may be also unstable. Isomer **53** is related to a metal carbyne complex just as metallabenzene **3** (Scheme 1) is related to a metal carbene complex. Many metal carbyne complexes[47] have an angle at the carbyne carbon atom near to 180° (the mean is 173°). Only a few exceptional cases have such angles as low as 160°. Similar angles are also found for acetylenes. Therefore, considerable ring-strain would be expected in **53**, **54** and **55**, resulting in low thermal stability.

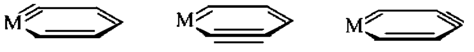


Scheme 21. Synthesis and reactivity of iridabenzene and iridanaphthalene.



51 Naphthalene

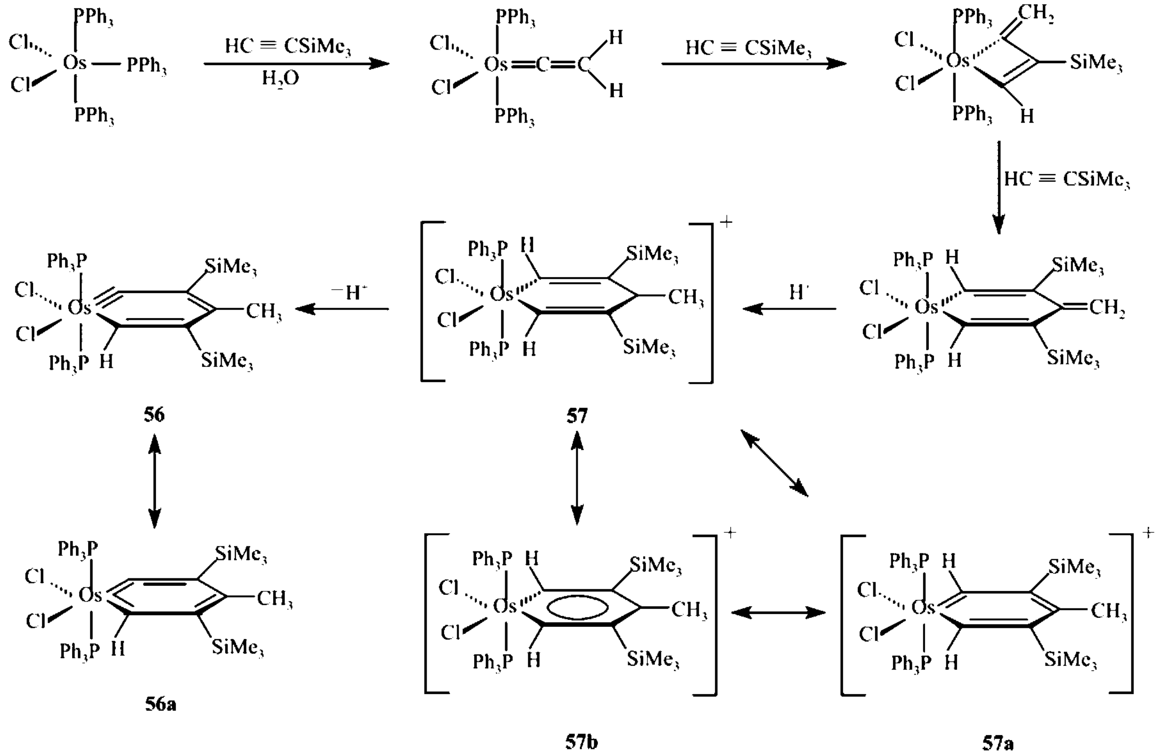
Scheme 22. Comparison of the C-C distances in iridanaphthalene and naphthalene.



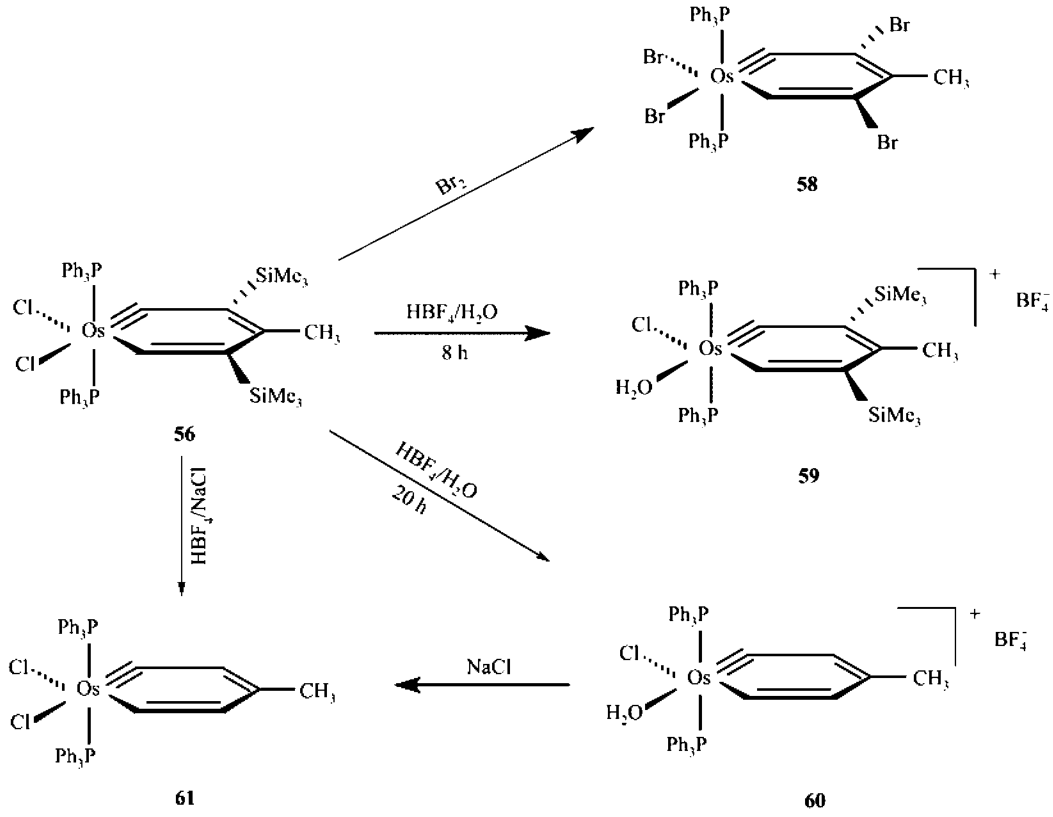
53 **54** **55**

Scheme 23. Some known and unknown metallabenzynes.

However, the expectation that a complex of type **53** is unstable is proven to be incorrect by the recent success in the isolation of **56**[48,49]. As described above, many metallabenzenes are previously known, complex **56** is the first well-characterized example of metallabenzynes. Treatment of $OsCl_2(PPh_3)_3$ with an excess of HC≡C-$SiMe_3$ produces four products, the major one of which is metallabenzyne **56** with the structure of type **53**. Scheme 24 shows a proposed mechanism for the formation of **56**. Reaction between $OsCl_2(PPh_3)_3$ and HC≡C-$SiMe_3$, in the presence of H_2O, can initially produce the coordinatively unsaturated vinylidene complex, $Os(=C=CH_2)Cl_2(PPh_3)_2$, which undergoes cycloaddition reactions with additional HC≡C-$SiMe_3$ to give first an osmacyclobutene and then an osmacyclohexadiene intermediate. The regiochemistry of the addition reactions is probably controlled by electronic/steric factors. Protonation of the osmacyclohexadiene complex then gives **57** which can be represented as **57a** or **57b** and can be regarded as a cationic osmabenzene complex. Deprotonation from a metal- bound carbon atom can then give the metallabenzyne **56**. The ^{13}C NMR spectrum of **56** shows two Os-C signals at δ 306.6 and 227.8 corresponding to two metal-bound carbon atoms. The former chemical shift is carbene-like and the other one is carbyne-like. Complex **56** shows one Os-C bond of 0.1815(4) nm (at the high end of typical Os≡C[50-54] bonds), and one Os-C bond of 0.1939(5) nm (slightly shorter than observed in osmabenzenes[9]). The ring C-C distances are normal compared with those of regular aromatic systems. The angle at the carbyne carbon atom is 148.7(3)°, which is considerably larger than the angle at the other osmium bound carbon (138.6(5)°). The angle at osmium is at 78.1(2)°, which may help to reduce the ring strain. One may ask why metallabenzyne **56** is a stable isolable complex. Possibly, the reactivity of **56** is reduced by the steric protection of the strained Os≡C bond by the ligands at the osmium and the trimethylsilyl group of the ring; protonation of **56** to give **57**, **57a**, or **57b** is not expected because



Scheme 24. A plausible mechanism for the formation of osmabenzyne.



Scheme 25. Synthesis of osmabenzynes.

the cationic osmabenzene is 16e and is expected to be highly acidic and unstable; it may also be that the ring strain is not as great as expected. In fact, a recent study shows that the ring strain of osmabenzynes is much smaller than that of benzyne[55].

Bromination and protonation of metallabenzyne **56** lead to the formation of novel neutral or cationic products, metallabenzynes **58**—**61**[49,55](Scheme 25), respectively. Thus metallabenzynes can also undergo typical aromatic substitution reactions.

6 Prospects

So far, the research in metallabenzenes, metallabenzynes and metallanaphthalenes is still at an early stage and the chemistry is much less developed compared to arenes. There are still needs to further study on their synthesis, and chemical and physical properties. The diversity of transition metals complexes (including different metals, ligands, oxidation states, and geometry) definitely will make it much more difficult to fully define their physical and chemical properties than the traditional aromatic compounds. However, such diversity also provides more challenges and opportunities for molecule design. It is expected that the chemistry of metallabenzenes, metallabenzynes, and metallanaphthalenes will be a fruitful research topic and will greatly advance in the near future.

References

1. Kekulé, F. A., Sur la constitution des substances aromatiques, Bull. Soc. Chim., 1865, 3(2): 98—111.
2. Kekulé, F. A., Note sur quelques produits de substitution de la benzine, Bull. Acad. R. Belg., 1865, 19: 551—563.
3. Ashe, A. J., The group 5 heterobenzenes, III. Acc. Chem. Res., 1978, 11(4): 153—157.
4. Jutzi, P., New element-carbon (p-p)π bonds, Angew. Chem. Int. Ed. Engl., 1975, 14(4): 232—245.
5. Thorn, D. L., Hoffmann, R., Delocalization in metallocycles, Nouv. J. Chim., 1979, 3(1): 39—45.
6. Bleeke, J. R., Metallabenzenes, Chem. Rev., 2001, 101(5): 1205—1227.
7. Elliott, G. P., Roper, W. R., Waters, J. M., Metallacyclohexatrienes or "metallabenzenes", J. Chem. Soc. Chem. Commun., 1982, (14): 811—813.
8. Elliott, G. P., Mcauley, N. M., Roper, W. R., An osmium containing benzene analog and its precursors, Inorg. Synth., 1989, 26: 184—189.
9. Rickard, C. E. F., Roper, W. R., Woodgate, S. D. et al., Electrophilic aromatic substitution reactions of a metallabenzene, Angew. Chem. Int. Ed., 2000, 39(4): 750—752.
10. Bleeke, J. R., Peng, W. -J., Synthesis, structure, and spectroscopy of iridacyclohexadiene complexes, Organometallics, 1987, 6(7): 1576—1578.
11. Bleeke, J. R., Metallabenzene chemistry, Acc. Chem. Res., 1991, 24(9): 271—277.
12. Gilbertson, R. D., Weakley, T. J. R., Haley, M. M., Direct synthesis of an iridabenzene from a nucleophilic 3-vinyl-1-cyclopropene, J. Am. Chem. Soc., 1999, 121(11): 2597—2598.
13. Gilbertson, R. D., Weakley, T. J. R., Haley, M. M., Synthesis, characterization, and isomerization of an iridabenzvalene, Chem. Eur. J., 2000, 6(3): 437—441.

14. Gilbertson, R. D., Lau, T. L. S., Lanza, S. et al., Synthesis, spectroscopy, and structure of a family of iridabenzenes generated by the reaction of Vaska-type complexes with a nucleophilic 3-vinyl-1-cyclopropene, Organometallics, 2003, 22(16): 3279—3289.
15. Hemond, R. C., Hughes, R. P., Robinson, D. J. et al., Activation of a fluorinated carbon-carbon bond by oxidative addition of tetrafluorocyclopropene to platinum(0), Organometallics, 1988, 7(10): 2239—2241.
16. Hughes, R. P., King, M. E., Robinson, D. J. et al., Stereoselective oxidative additions of a carbon-carbon σ-bond in tetrafluorocyclopropene to iridium (Ⅰ) complexes, J. Am. Chem. Soc., 1989, 111(24): 8919—8920.
17. Binger, P., Müller, P., Hermann, A. T. et al., Metallacyclobutene aus η2-Cyclopropen-Komplexen des titanocens und zirkonocens, Chem. Ber., 1991, 124(10): 2165—2170.
18. Hughes, R. P., Trujillo, H. A., Gauri, A. J., Stereoselective ring expansion of 3-Vinyl-1-cyclopropenes to give (5-Cyclopentadienyl) ruthenium and (4-Cyclohexadienone)iron complexes, Organometallics, 1995, 14(9): 4319—4324.
19. Ferede, R., Allison, N. T., Possible formation of ferrabenzene and its novel conversion to 1,3-diphenyl-2-methoxyferrocene, Organometallics, 1983, 2(3): 463—465.
20. Ferede, R., Hinton, J. F., Korfmacher, W. A. et al., Possible formation of rhenabenzene, Organometallics, 1985, 4(3): 614— 616.
21. Mike, C. A., Ferede, R., Allison, N. T., Evidence for rhenaphenanthrene formation and its conversion to fluorenone, Organometallics, 1988, 7(7): 1457—1459.
22. Schrock, R. R., Pedersen, S. F., Churchill, M. R. et al., Formation of cyclopentadienyl complexes from tungstenacyclobutadiene complexes and the X-ray crystal structure of an 3-Cyclopropenyl complex, Organometallics, 1984, 3(10): 1574—1583.
23. Hughes, R. P., Trujillo, H. A., Egan, J. W. et al., Iridium-promoted reactions of carbon-carbon bonds: skeletal rearrangement of a vinylcyclopropene during iridacyclohexadiene formation and subsequent isomerization of iridacyclohexadienes via α,α'-substituent migrations, J. Am. Chem. Soc., 2000, 122(10): 2261—2271.
24. Bleeke, J. R., Behm, R., Xie, Y. -F. et al., Synthesis, structure, spectroscopy, and reactivity of a metallabenzene, Organometallics, 1997, 16(4): 606—623.
25. Bleeke, J. R., Behm, R., Synthesis, structure, and reactivity of iridacyclohexadienone and iridaphenol complexes, J. Am. Chem. Soc., 1997, 119(36): 8503—8511.
26. Bleeke, J. R., Xie, Y. -F., Bass, L. et al., Chemical reactivity of a metallabenzene, J. Am. Chem. Soc., 1991, 113(12): 4703—4704.
27. Bleeke, J. R., Bass, L., Xie, Y. -F. et al., Chemistry of an (6-Metallabenzene) metal complex, J. Am. Chem. Soc., 1992, 114(11): 4213—4219.
28. Iron, M. A., Martin, J. M. L., Boom, M. E., Cycloaddition reactions of metalloaromatic complexes of iridium and rhodium: a mechanistic DFT investigation, J. Am. Chem. Soc., 2003, 125(38): 11702—11709.
29. Lin, W., Wilson, S. R., Girolami, G. S., The first unsubstituted metallabenzene complex, J. Chem. Soc. Chem. Commun., 1993, (3): 284—285.
30. Bosch, H. W., Hund, H. -U., Nietlispach, D. et al., General route to the "half-open" metallocenes C5Me5Ru(pentadienyl) and C5Me-5Ru (diene)Cl, Organometallics, 1992, 11(6): 2087—2098.
31. Yand, J., Jones, W. M., Detection of a ruthenabenzene, ruthenaphenoxide, and ruthenaphenanthrene oxide: the first metalla aromatics of a second-row transition metal, J. Am. Chem. Soc., 1995, 117(38): 9776—9777.
32. Englert, U., Podewils, F., Schiffers, I. et al., The first homoleptic metallabenzene sandwich complex, Angew. Chem. Int. Ed., 1998, 37(15): 2134—2136.
33. Liu, S. H., Ng, W. S., Chu, H. S. et al., A triple-decker complex with a central metallabenzene, Angew. Chem. Int. Ed., 2002, 41(9): 1589—1591.
34. Hein, J., Jeffery, J. C., Sherwood, P. et al., Chemistry of polynuclear metal complexes with bridging carbene or carbyne ligands, J. Chem. Soc. Dalton. Trans., 1987, (9): 2211—2218.
35. Bertling, U., Englert, U., Salzer, A., From triple-decker to metallabenzene: a new generation of sandwich complexes, Angew. Chem. Int. Ed. Engl., 1994, 33(9): 1003—1004.
36. Jacob, V., Weakley, T. J. R., Haley, M. M., Metallabenzenes and valence isomers: synthesis and characterization of a platinabenzene, Angew. Chem. Int. Ed., 2002, 41(18): 3470—3473.
37. Kralik, M. S., Rheingold, A. L., Ernst, R. D., (Pentadienyl)molybdenum carbonyl chemistry: conversion of a pentadienyl ligand to a coordinated metallabenzene complex, Organometallics, 1987, 6(12): 2612—2614.
38. Chen, J., Daniels, L. M., Angelici, R. J., New modes of thiophene coordination and reactivity: structures of Cp*Ir(2-thiophene), an iridathiabenzene, and Cp*Ir(4-thiophene.BH3), J. Am. Chem. Soc., 1990, 112(1): 199—204.
39. Bianchini, C., Meli, A., Peruzzini, M. et al., Opening, desulfurization, and hydrogenation of thiphene at iridium, J. Am. Chem. Soc., 1993, 115(7): 2731—2742.
40. Bianchini, C., Meli, A., Peruzzini, M. et al., HDS model systems, coordination, opening, and hydrogenation of Benzo[b]thiophene at iridium, J. Am. Chem. Soc., 1994, 116(10): 4370—4381.
41. Chin, R. M., Jones, W. D., Dimerization of thiophene to give a linear S(CH)8S fragment with [(C5Me5)Rh(C2H4)2], Angew. Chem. Int. Ed. Engl., 1992, 31(3): 357—358.
42. Feng, S. G., White, P. S., Templeton, J. L., Amine addition to coordinated nitriles in tungsten (Ⅱ) alkyne complexes, Organometallics, 1993, 12(5): 1765—1774.
43. Profilet, R. D., Fanwick, P. E., Rothwell, I. P., 1,3-Dimetallabenzene derivatives of niobium or tantalum, Angew. Chem. Int. Ed. Engl., 1992, 31(9): 1261—1263.
44. Riley, P. N., Profilet, R. D., Salberg, M. M. et al., 1,3-Dimetallabenzene' derivatives of niobium or tantalum, polyhedron, 1998, 17(5-6): 773—779.
45. Paneque, M., Posadas, C. M., Poveda, M. L. et al., Formation of unusual iridabenzene and metallanaphthalene containing electron-withdrawing substituents, J. Am. Chem. Soc., 2003, 125(33): 9898—9899.
46. Álvarez, E., Gómez, M., Paneque, M. et al., Coupling of internal alkynes in TpMe2Ir derivatives: selective oxidation of a noncoordinated double bond of the resulting iridacycloheptatrienes, J. Am. Chem. Soc., 2003, 125(6): 1478—1479.
47. Roper, W. R., First metallabenzenes and now a stable metallabenzyne, Angew. Chem. Int. Ed., 2001, 40(13): 2440—2441.
48. Wen, T. B., Zhou, Z. Y., Jia, G., Synthesis and characterization of a metallabenzyne, Angew. Chem. Int. Ed., 2001, 40(10): 1951—1954.
49. Wen, T. B., Ng, S. M., Hung, W. Y. et al., Protonation and bromination of an osmabenzyne: reactions leading to the formation of new metallabenzynes, J. Am. Chem. Soc., 2003, 125(4): 884—885.
50. Clark, G. R., Edmonds, N. R., Pauptit, R. A. et al., Octahedral carbyneosmium (Ⅱ) complexes, J. Organomet. Chem., 1983, 244(4): C57—C60.
51. Clark, G. R., Cochrane, C. M., Marsden, K. et al., Synthesis and some reactions of a terminal carbyne complex of osmium, J. Organomet. Chem., 1986, 315(2): 211—230.
52. Hodges, L. M., Sabat, M., Harman, W. D., Carbynes and carbenes in coordination chemistry: a new class of pentaammine and tetraammine complexes of osmium(Ⅱ), Inorg. Chem., 1993, 32(4): 371—372.
53. Baker, L-J., Clark, G. R., Rickard, C. E. F. et al., Syntheses and reactions of the carbyne complexes, J. Organomet. Chem., 1998, 551(1-2): 247—259.
54. Werner, H., Jung, S., Weberndörfer, B. et al., Vinylidene transition-metal complexes, 50 carbynehydrido-and vinylidenehydridoosmium complexes with Os(PCy3)2 as a molecular unit, Eur. J. Inorg. Chem., 1999, (6): 951—957.
55. Ng, S. M., Huang, X., Wen, T. B. et al., Theoretical studies on the stabilities of metallabenzynes, Organometallics, 2003, 22(19): 3898—3904.

(Received January 7, 2004; accepted April 13, 2004)