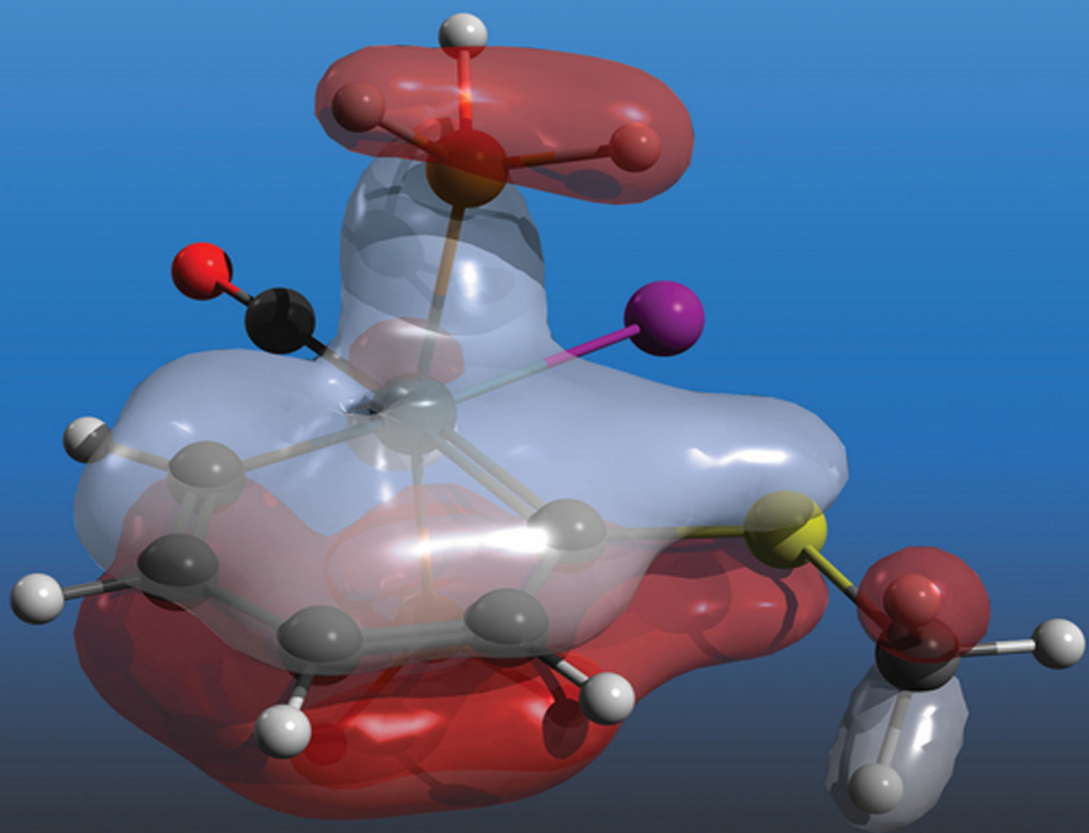


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Edited by L. James Wright

Metallabenzenes

An Expert View



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An Expert View

Edited by
L. James Wright
University of Auckland
New Zealand

WILEY

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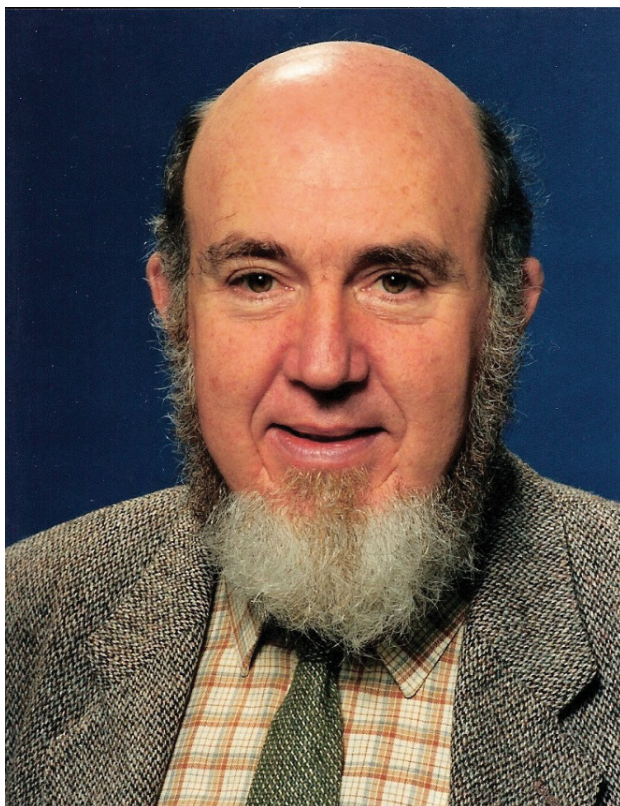
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Preface



Professor Warren R. Roper FRS

(Photo taken in 1989, seven years after his group isolated the first metallabenzene). Source: Image provided courtesy of Professor Warren R. Roper FRS.

Metallabenzenes are a fascinating class of compounds which can be viewed as analogues of benzene in which one of the CH groups has formally been replaced by an isolobal transition metal fragment. Although benzene itself was discovered by Michael Faraday in 1825, it was not until 1982 that the first metallabenzene, an osmabenzene, was isolated by Warren R. Roper and his group at the University of Auckland, New Zealand. Since that time, interest in these compounds has steadily grown, and today it has become a flourishing area of chemistry with new developments and discoveries regularly appearing in the literature. A diverse range of synthetic approaches to these compounds have been developed. The more common of these involve the direct addition to the metal of groups that contain the five

carbon atoms that eventually become the metallabenzene ring atoms, the insertion of a carbon atom from an adjacent ligand into the M–C bond of a metallacyclopentadiene, and the ring contraction of metallacycloheptatrienes.

As might be expected, the presence of the transition metal in the metallabenzene ring has a profound effect on the properties of these compounds. Theoretical studies confirm that metallabenzenes are indeed aromatic compounds with aromatic stabilization energies between *ca.* 20 and 80% that of benzene. However, the delocalized π -system is more complex than that of benzene. Instead of the six π -electrons present in benzene, reported metallabenzenes have either eight or ten π -electrons, depending on whether the *p*-orbitals of ligands such as chloride participate in the π -bonding scheme of the metallacyclic ring. Some of the occupied metallabenzene π -orbitals have Möbius character and so the standard Hückel ($4n + 2$) π -electron rule cannot be used as a criterion for aromaticity.

The presence of the metal adds an important dimension to the reaction chemistry of metallabenzenes. Reactions that are not observed (e.g. cycloadditions) or are not even possible for benzene (e.g. coupling of the two C α atoms to form a cyclopentadienyl ligand) have been reported. At the same time other reactions that are characteristic for benzene such as electrophilic aromatic substitution and π -coordination to metal fragments such as Mo(CO)₃ have also been observed. The metal significantly influences the spectral and structural properties of metallabenzenes. For example, in the ¹H and ¹³C NMR spectra the resonances of the C α (metal-bound) atoms and attached protons appear at very low field values. These resonances are almost invariably observed in between the values observed for related carbene and σ -vinyl complexes and are consistent with partial multiple bond character between the metal and the C α atoms. The shifts of the remaining three carbon atoms and accompanying protons are in the normal ranges found for benzene derivatives. Structurally, metallabenzenes also display some distinctive features. Although the five-ring carbon atoms are always approximately coplanar, the metal is sometimes found significantly displaced from this plane, while in other cases it sits within this plane. Theoretical studies have shown that both electronic and steric effects are responsible for the location of the metal relative to the five-carbon plane. Unlike the situation for benzene, the energy profile associated with moving the metal out of the five-carbon plane is very shallow since this movement considerably decreases the π -antibonding interactions associated with the ring.

Although major advances have been made, the study of metallabenzenes is still very much in the early stages of development and it can be expected that many important new developments await discovery. The compounds and the reactions they undergo not only are of intrinsic interest but also do much to broaden our understanding of aromaticity. Furthermore, it can be anticipated that, owing to the special properties some of these species exhibit, future applications may be found in areas such as photoelectronics, molecular magnets, conducting polymers, fluorescent molecular probes, and new materials.

The field of metallabenzene chemistry is in the unusual situation that almost all the major synthetic, reaction chemistry, spectroscopic and structural studies have thus far come from just six research groups around the world. Accordingly, this book is arranged so that the work of each of these groups is covered in the form of personal perspectives in the first six chapters. Our own work (Warren R. Roper, L. James Wright and co-workers) from New Zealand, which includes the syntheses of osma-, ruthena- and iridabenzenes (including the first metallabenzene), the electrophilic aromatic substitution and nucleophilic aromatic substitution of hydrogen reactions they undergo, and the synthesis and reactions of fused-ring metallabenzenes, is covered in

the first chapter. The research of John R. Bleeker's group (USA) is presented in Chapter 2, and includes, amongst other things, the synthesis and chemistry of the first iridabenzenes as well as heteroatom-substituted analogues such as iridathiabenzenes and iridapyrylium. The chapter ends with a short summary of metal-coordinated metallabenzenes. Michael M. Haley and co-workers (USA) in Chapter 3 describe the development of new synthetic routes to iridabenzenes and the first platinabenzenes, as well as studies of the mechanisms of synthesis and decomposition. Margarita Paneque and Nuria Rendón (Spain) summarize in Chapter 4 their group's contributions that include the development of a diverse range of metallaaromatics (including the first metallanaphthalene) which display unique chemistry and utilize supporting tris(pyrazolyl)borate ligands. The work of Guochen Jia and his group (Hong Kong), which has led to many new metallabenzenes incorporating osmium and rhenium as well as the related metallabenzynes species, is covered in Chapter 5. Haiping Xia and Hong Zhang (China) describe, in Chapter 6, the many significant contributions they and their co-workers have made to the field, largely through investigations into osma- and ruthenabenzenes containing one or more triphenylphosphonium ring substituents. These include new synthetic routes, reaction chemistry, bonding interactions, and the formation of fused-ring derivatives. Important computational investigations into the nature of metallabenzenes and the reactions of these compounds have been made by a number of different groups. In the final chapter (Chapter 7), this work is summarized by Israel Fernández and Gernot Frenking (Spain and Germany), who also highlight their own major contributions to this field.

L. James Wright
Auckland
May 2017

Metallabenzenes and Fused-Ring Metallabenzenes of Osmium, Ruthenium and Iridium: Syntheses, Properties and Reactions

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1.1 Introduction

The origin of metallabenzenes can be traced back almost two centuries to the discovery of benzene by Michael Faraday in 1825 [1]. He managed to separate benzene from the oily liquid obtained as a by-product during the manufacture of an “illuminating gas” by the destructive distillation of fish or whale oil. He correctly described a wide range of its properties and identified the formula as two proportions of carbon to one proportion of dihydrogen gas – thus describing it by the name “bicarburet of hydrogen”. A few years later, in 1833, it was also isolated by the German chemist Eilhard Mitscherlich by the distillation of benzoic acid from gum benzoin. Mitscherlich correctly noted that it was identical to Faraday’s bicarburet of hydrogen and gave it the name “benzin”, from which the common name benzene is derived [2].

The molecular structure eluded chemists for many years. It was not until 1865 that German scientist Friedrich August Kekulé proposed the six-membered cyclohexatriene ring structure with alternating single and double bonds which subsequently led to the development of the concept of aromaticity [3, 4]. These advances revolutionised organic chemistry and began a flood of research into this exciting new area of so-called aromatic chemistry. Benzene is now considered the archetypical aromatic compound, and it is often used as the yardstick against which other species are compared with regard to aromatic character. While a precise definition of “aromaticity” remains somewhat nebulous, properties associated with benzene that have been classically used to characterise aromaticity include planarity, bond length equalisation, π -electron delocalisation, aromatic stabilisation energy, diamagnetic ring currents and electrophilic substitution, rather than addition, reactions. In more recent times, determinations of aromatic stabilisation energies by computational methods have been used to obtain more tangible measures of aromaticity.

Heteroaromatic species could be considered the next generation of aromatic compounds to be discovered. Amongst this large class of compounds, there are many

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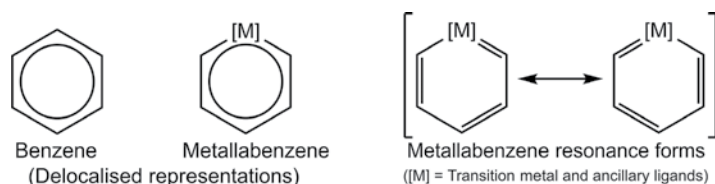


Chart 1.1 Metallabenzene delocalised representation and contributing resonance forms.

six-membered heterocycles that can be thought of as benzene analogues in which one CH unit of benzene has been formally replaced by an appropriate heteroatom. Pyridine, with the heteroatom nitrogen, was one of the earliest examples, and Scottish scientist Thomas Anderson is credited with the first report of this compound in 1849 [5]. Since then, related benzene analogues incorporating a wide array of main group heteroatoms have been isolated and these include, but are not limited to, phosphorus [6, 7], arsenic [7, 8], silicon [9], antimony [10], bismuth [10], germanium [11] and tin [12].

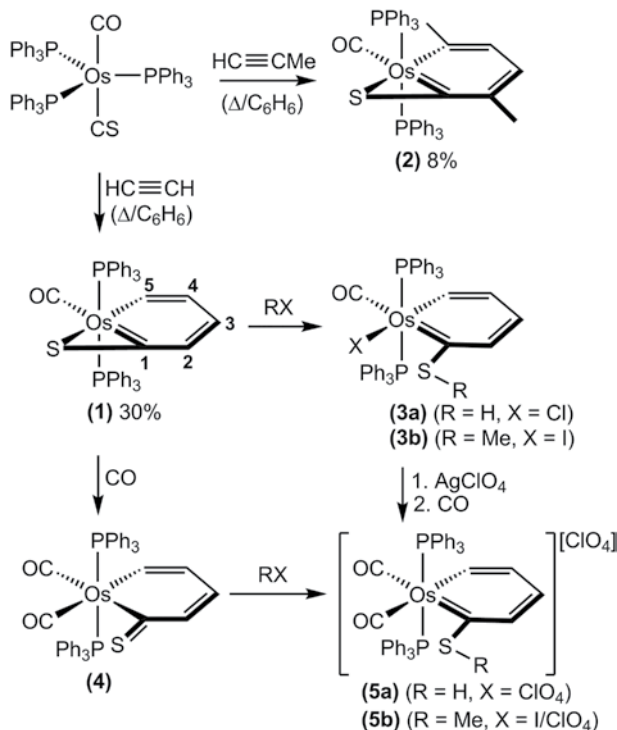
Metallabenzenes, which are perhaps the third generation of related aromatic compounds, have arrived comparatively recently in this timeline. The notion of formally replacing one CH unit of benzene with an appropriate transition metal (and its ancillary ligands) was proposed theoretically in 1979 by Thorn and Hoffmann [13] and it was only a short three years later before the first metallabenzene, an osmabenzene, was synthesised and characterised by Warren Roper and co-workers in New Zealand [14]. The aromatic character of this and other metallabenzenes (Chart 1.1) has now been thoroughly established through a range of different computational methods, and these are discussed in detail in Chapter 7 of this book. From these beginnings a new class of aromatic compounds, the metallabenzenes, was born.

In this chapter we provide a personal perspective on the contributions our group has made to this field, including studies of the syntheses, properties and reaction chemistry of osma-, ruthena- and iridabenzenes as well as related fused-ring derivatives.

1.2 Syntheses and Properties of Metallabenzenes with Methylthiolate Substituents

1.2.1 Osmabenzenes

In the 1970s and early 1980s, there was an acceleration of research efforts focused on the organometallic chemistry of transition metals, particularly on species where a transition metal is multiply bonded to a carbon donor ligand. We had been working in this area for some time and had developed a number of new carbene [15, 16], carbyne [17, 18] and thiocarbonyl [19–21] complexes of second- and third-row transition metals. We were aware of the 1979 theoretical paper by Thorn and Hoffmann that briefly describes the possibility of metallabenzenes as stable species [13]. Therefore, a few years later, when we were exploring the coordination of ethyne at the osmium centre of the zero-valent complex $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$, it did not take long for us to realise the CS ligand and two ethyne molecules had cyclised at the metal centre to produce the first metallabenzene, the osmabenzene, $\text{Os}(\text{C}_5\text{H}_4\{\text{S}-1\})(\text{CO})(\text{PPh}_3)_2$ (**1**) (Scheme 1.1). In this

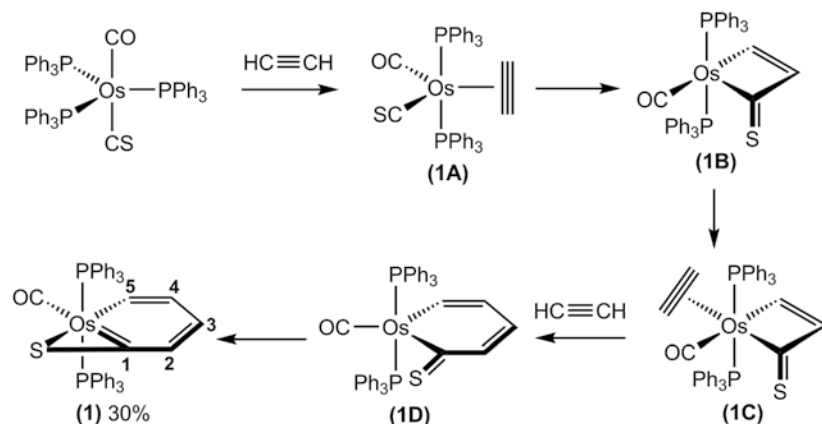


Scheme 1.1 Preparation of osmium complexes **1–5**.

compound the six-membered metallacyclic ring comprises the thiocarbonyl carbon atom, the four carbons of the two ethyne molecules and the osmium atom. The sulfur atom is also coordinated to the osmium metal centre, generating a secondary three-membered Os–C–S osmathiirene ring [14]. Therefore, the osmabenzene **1** could also formally be considered an osmabenzothiirene [22].

To synthesise the osmabenzene **1**, a solution of $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ in benzene or toluene was treated with a slow stream of ethyne at 70°C for 20 min. Dark-brown crystals of pure **1** were formed in around 30% yield following purification by recrystallisation from *n*-hexane and column chromatography of the solid obtained [23].

This reaction can be considered a formal [1+2+2] cyclisation at the osmium centre of two molecules of ethyne and the carbon of the CS ligand. The most likely mechanism has been determined computationally using the model complex $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ [24]. The adduct **1A** (Scheme 1.2) is formed by coordination of the first molecule of ethyne after phosphine dissociation. The thiocarbonyl and ethyne ligands then combine to give the osmacyclobutenethione **1B**. The propensity of ligands such as CS to engage in cyclisation and migratory insertion reactions has proven to be invaluable in the synthesis of a number of metallaaromatic compounds. Coordination of the second molecule of ethyne, to give **1C**, and subsequent insertion of both carbon atoms into the four-membered ring gives the osmacyclohexadienethione **1D**. Finally, coordination of the sulfur atom to osmium results in aromatisation of the six-membered ring and formation of the osmabenzene **1**.



Scheme 1.2 Proposed mechanism for the synthesis of the osmabenzene **1** based on computational studies using PH_3 model compounds.

This cyclisation reaction is not limited to ethyne, and later we found the related dimethyl-substituted osmabenzene $\text{Os}(\text{C}_5\text{H}_2\{\text{S}-1\}\{\text{Me}-2\}\{\text{Me}-4\})(\text{CO})(\text{PPh}_3)_2$ (**2**) (Scheme 1.1) is formed as dark-brown crystals when $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ is treated with propyne, albeit in the low yield of 8%. The major product from this reaction is the complex $\text{OsH}(\text{C}\equiv\text{CMe})(\text{CS})(\text{CO})(\text{PPh}_3)_2$ which arises from the simple C–H oxidative addition of propyne. Fortunately, this can be easily separated from the metallabenzene **2** by column chromatography and isolated in 23% yield [25].

Our original report of the first metallabenzenes also included several derivatives of **1** which could be prepared through reactions in which the osmium–sulfur bond was cleaved. The sulfur atom in **1** is nucleophilic and readily undergoes protonation with hydrochloric acid or alkylation with methyl iodide to give the neutral osmabenzenethiol **3a** or the methylthiolate-substituted osmabenzene **3b**, respectively (Scheme 1.1). The sulfur atom in **1** is also displaced from osmium on treatment with carbon monoxide. The resulting osmacyclohexadienethione, **4**, does not have the same π -bond delocalisation about the six-membered ring that is present in **1**, but this can be returned by protonation or alkylation of the thione sulfur. Thus, treatment of **4** with perchloric acid or methyl iodide followed by crystallisation in the presence of sodium perchlorate gives the corresponding osmabenzenes **5a** or **5b**, respectively, which are the cationic analogues of **3a** and **3b** (Scheme 1.1) [14]. **5a** or **5b** can be prepared by an alternative route starting from **3a** or **3b**, respectively, as indicated in Scheme 1.1.

A key question that had to be addressed in the original paper describing the osmabenzene **1** was whether it was best described as a metallabenzene with delocalised π -bonding or, alternatively, as an osmacyclohexatriene with localised double bonds. Key information that strongly supported a delocalised π -system was provided by the single crystal X-ray structure determination (see Figure 1.1). The structure of **1**, and later **2** (Figure 1.2), showed a planar six-membered metallacyclic ring with similar carbon–carbon bond lengths that were midway between standard sp^2 carbon–carbon single (1.46 Å) and double (1.34 Å) bonds. Importantly, the two osmium–carbon bonds were essentially equal in length and midway between those of typical single and double osmium–carbon bonds [26]. Since ring planarity and bond length equalisation are both

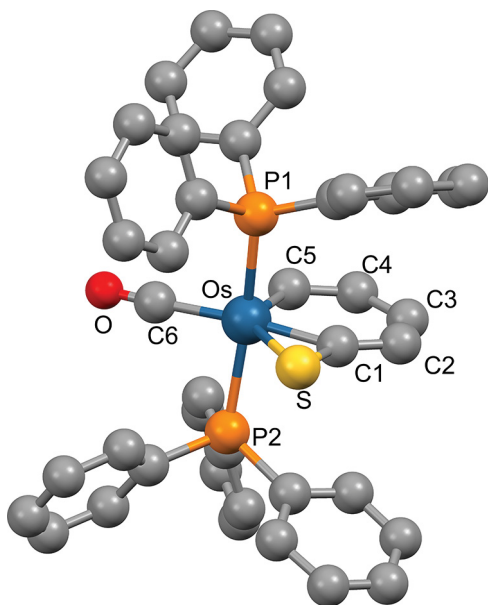


Figure 1.1 Molecular structure of osmabenzene **1**. Hydrogen atoms have been omitted for clarity. Selected distances [Å]: Os–C1 2.00(1), Os–C5 2.00(1), Os–S 2.474(3), Os–C6 1.92(1), C1–C2 1.36(2), C2–C3 1.38(2), C3–C4 1.42(2), C4–C5 1.39(2).)

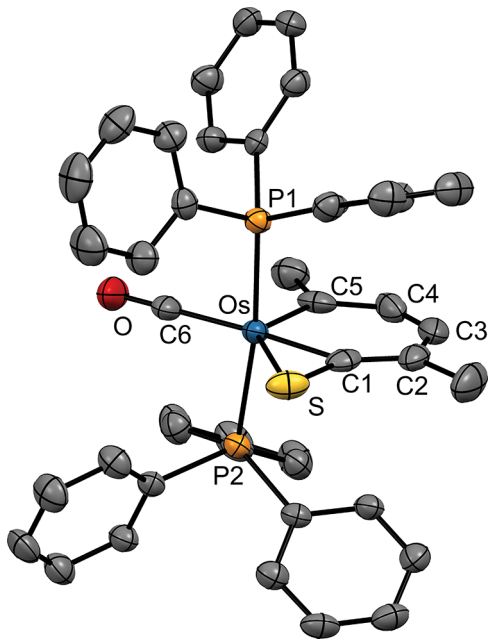


Figure 1.2 Molecular structure of osmabenzene **2** showing 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected distances [Å]: Os–C1 2.027(4), Os–C5 2.022(5), Os–S 2.4990(12), Os–C6 1.908(4), C1–C2 1.365(6), C2–C3 1.400(7), C3–C4 1.385(7), C4–C5 1.415(6). (See color plate section for the color representation of this figure.)

classic indicators of aromatic character, the structural data (together with the low field chemical shifts of the ring protons and carbon atoms in the ^1H and ^{13}C NMR spectra) [23] strongly supported a metallabenzene formulation for **1**.

Regarding the $\eta^2\text{-C(S)}$ moiety in both **1** and **2**, the Os–S bond lengths (2.474(3) and 2.4990(12) Å, respectively) are slightly longer than normal Os–S single bonds, while the C–S bond lengths, (1.66(1) and 1.689(6) Å, respectively) are slightly shorter than standard C–S single bonds. These observations suggest that in both complexes the sulfur atom is not strongly bound to the metal centre [14, 25].

An X-ray crystal structure determination has also been obtained for the osmabenzene $\text{Os}(\text{C}_5\text{H}_4\{\text{SMe-1}\})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, an analogue of **3b** which has a chloride rather than iodide ligand. The structural parameters associated with the osmabenzene ring in this complex display the same key features found for **1** and **2**, i.e. near bond length equalisation and ring planarity (Os–C1 2.109(3), Os–C5 2.027(3), C1–C2 1.412(4), C2–C3 1.371(4), C3–C4 1.393(5), C4–C5 1.368(4) Å) [27].

The NMR spectroscopic data obtained for the osmabenzenes **1** and **2** provide important indications that a delocalised representation of the π -bonding within the metallacyclic ring is appropriate. In the ^1H NMR spectrum of **1**, H5, which is attached to a metal-bound carbon atom (see Scheme 1.1 for numbering system), is found at 13.95 ppm [23]. This notable down-field chemical shift is consistent with transition metal–carbon multiple bonding character and approaches, but does not quite meet the down-field shifts typically observed for related osmium carbene protons (*ca.* 18 ppm) [27]. H3 and H4 in **2** are found in the ^1H NMR spectrum at the “benzene-like” chemical shifts of 7.59 and 6.65 ppm, respectively.

The metal-bound carbon atoms of **2**, C1 and C5, are found at 257.43 and 220.07 ppm, respectively in the ^{13}C NMR spectrum. These considerable down-field chemical shifts are also consistent with osmium–carbon multiple bonding character. The remaining ring carbon atoms that are remote from the metal centre are observed at positions similar to those found in benzene and benzene derivatives (119.89 (C2), 147.98 (C3) and 129.22 (C4) ppm) [25]. These distinctive chemical shifts for the ring protons and carbon atoms are not limited to the osmabenzenes with the $\eta^2\text{-CS}$ moiety, as is evidenced by the very similar spectra found for the methylthiolate-substituted osmabenzene $\text{Os}(\text{C}_5\text{H}_4\{\text{SMe-1}\})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (^1H NMR: 6.65 (H2), 7.07 (H3), 6.57 (H4), 13.27 (H5) ppm, ^{13}C NMR: 237.4 (C1), 121.6 (C2), 145.8 (C3), 123.8 (C4), 211.0 (C5) ppm) [27].

Further general features are apparent in the NMR spectra of these and related osmabenzenes. Many of the resonances in the ^1H and ^{13}C NMR spectra are split into fine triplets due to coupling to the two phosphorus atoms of the mutually *trans* triphenylphosphine ligands. In most cases, coupling to the two phosphorus atoms is observed for carbons C1 and C5 in the ^{13}C NMR spectra, and $^2J_{\text{CP}}$ is usually in the order of 5–10 Hz. When present, the H1 and/or H5 protons will often also display coupling to phosphorus in the ^1H NMR spectra and this is usually in the order of 1–3 Hz. This phenomenon can sometimes also be noted in the atoms more remote from the metal, although this is much less common. In addition, the ring protons on the majority of related metallabenzenes and metallabenzenoids usually display long-range proton–proton coupling across three or more bonds in a manner similar to the *meta*-coupling often observed in aromatic organic compounds.

1.2.2 Iridabenzenes

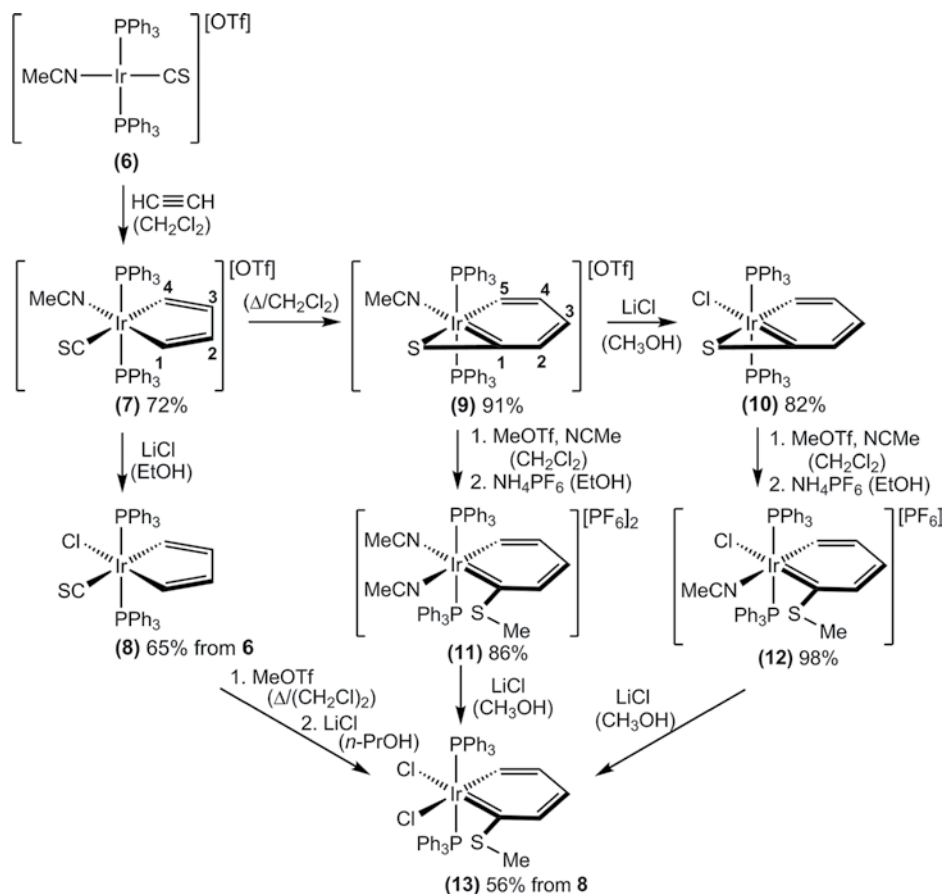
The success encountered in synthesising these osmabenzenes was in large part due to the remarkable propensity of the thiocarbonyl ligand to undergo cyclisation and migratory insertion reactions. A natural progression was to then extend this work and prepare iridabenzenes using the same strategy. At the time this work was carried out, a number of iridabenzenes had already been reported using alternative routes, and these are discussed in Chapters 2, 3 and 4 of this book. However, it was reasoned that if the thiocarbonyl route was successfully applied to iridium it would give iridabenzenes with very different ancillary ligands and ring substituents to those that had been prepared previously.

It had already been shown that the iridacyclopentadiene complex $[\text{Ir}(\text{C}_4\text{H}_4)(\text{NCMe})(\text{CO})(\text{PPh}_3)_2][\text{OTf}]$ (^-OTf or triflate = $^-\text{O}_3\text{SCF}_3$) could be prepared by a cyclisation reaction involving two ethyne molecules at the iridium centre of the cation $[\text{Ir}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2][\text{OTf}]$ [28]. This iridium cation is in turn obtained from Vaska's complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ [29], through treatment with silver triflate in acetonitrile solvent [30]. Although the CO ligand in this complex does not insert into the iridacyclopentadiene ring, we reasoned that the thiocarbonyl analogue might undergo this rearrangement to give an iridabenzene that is closely related to **1**.

We had already developed a route to the thiocarbonyl analogue of Vaska's compound, $\text{IrCl}(\text{CS})(\text{PPh}_3)_2$ [20, 31], and so the cation, $[\text{Ir}(\text{CS})(\text{NCMe})(\text{PPh}_3)_2][\text{OTf}]$ (**6**), was readily accessible through treatment of this complex with AgOTf/NCMe . When a dichloromethane solution of this orange species was treated with ethyne under ambient conditions, the cationic iridacyclopentadiene complex, $[\text{Ir}(\text{C}_4\text{H}_4)(\text{CS})(\text{NCMe})(\text{PPh}_3)_2][\text{OTf}]$ (**7**), formed spontaneously (Scheme 1.3). This complex could be isolated as a yellow solid if the temperature was kept low (*ca.* 0°C) and precipitation carried out rapidly by addition of *n*-hexane [32]. The barrier to rearrangement of this cationic iridacyclopentadiene to the corresponding iridabenzene, through migratory insertion of the CS ligand, is relatively low. Even at 20°C, after 1 h in solution some rearrangement of **7** to the cationic iridabenzene $[\text{Ir}(\text{C}_5\text{H}_4\{\text{S-1}\})(\text{NCMe})(\text{PPh}_3)_2][\text{OTf}]$ (**9**) can easily be detected by ^1H NMR spectroscopy. Complete conversion of **7** to the iridabenzene **9** occurs on heating **7** under reflux in dichloromethane (*ca.* 40°C) for 16 h (Scheme 1.3). In practice, if the iridabenzene is the target product, all these transformations can be carried out in one pot starting from **6** to give **9** in yields of over 90%. It is noteworthy that if chloride is added to **7** the neutral iridacyclopentadiene complex $\text{Ir}(\text{C}_4\text{H}_4)\text{Cl}(\text{CS})(\text{PPh}_3)_2$ (**8**) is obtained, and this complex is significantly more resistant to migratory insertion of the CS ligand (Scheme 1.3). However, **8** can be converted into the iridabenzene, $\text{Ir}(\text{C}_5\text{H}_4\{\text{SMe-1}\})\text{Cl}_2(\text{PPh}_3)_2$ (**13**), by treatment with methyl triflate in a refluxing 1, 2-dichloroethane solution followed by the addition of lithium chloride (Scheme 1.3) [32–34].

The acetonitrile ligand in **9** is fairly labile and the neutral iridabenzene $\text{Ir}(\text{C}_5\text{H}_4\{\text{S-1}\})\text{Cl}(\text{PPh}_3)_2$ (**10**) can easily be prepared by the addition of chloride (Scheme 1.3) [33]. The iridabenzenes **9** and **10** can both be considered analogues of the original osmabenzene **1**.

Isolation of the intermediate **7** indicates that the reaction mechanism for the formation of iridabenzene **9** is different from that determined by computational studies for the formation of the closely related osmabenzene **1**. Formation of **9** involves cyclisation of two ethyne molecules at iridium to give the isolated intermediate iridacyclopentadiene



Scheme 1.3 Synthesis of the iridacyclopentadienes **7–8** and the iridabenzene **9–13**.

7, followed by insertion of CS into an Ir–C bond to give the iridabenzene **9** [32]. In contrast, calculations predict that formation of the osmabenzene **1** occurs via cyclisation of one ethyne and CS to form an osmacyclobutenethione intermediate (**1B**; Scheme 1.2) which subsequently inserts both carbon atoms of a second ethyne to form the six-membered metallacyclic ring in **1** [24].

A number of simple derivatives of the iridabenzene **9** and **10** are readily accessible through alkylation of the sulfur atoms with methyl triflate (MeOTf). When the methylation reaction of **9** is conducted in the presence of a small amount of acetonitrile, the maroon dicationic iridabenzene $[\text{Ir}(\text{C}_5\text{H}_4\{\text{SMe-1}\})(\text{NCMe})_2(\text{PPh}_3)_2][\text{PF}_6]_2$ (**11**) can be isolated after addition of NH_4PF_6 . Methylation of **10** under the same conditions gives the red monocationic iridabenzene $[\text{Ir}(\text{C}_5\text{H}_4\{\text{SMe-1}\})\text{Cl}(\text{NCMe})(\text{PPh}_3)_2][\text{PF}_6]$ (**12**) (Scheme 1.3). The acetonitrile ligands in both complexes are labile, and treatment of either **11** or **12** with lithium chloride yields the neutral dichloride iridabenzene, **13**, as a purple crystalline solid (Scheme 1.3) [34].

The crystal structures of iridabenzene **9** and **13** (Figure 1.3) have been determined and provide interesting comparisons with the structures of the osmabenzene **1** and **2**

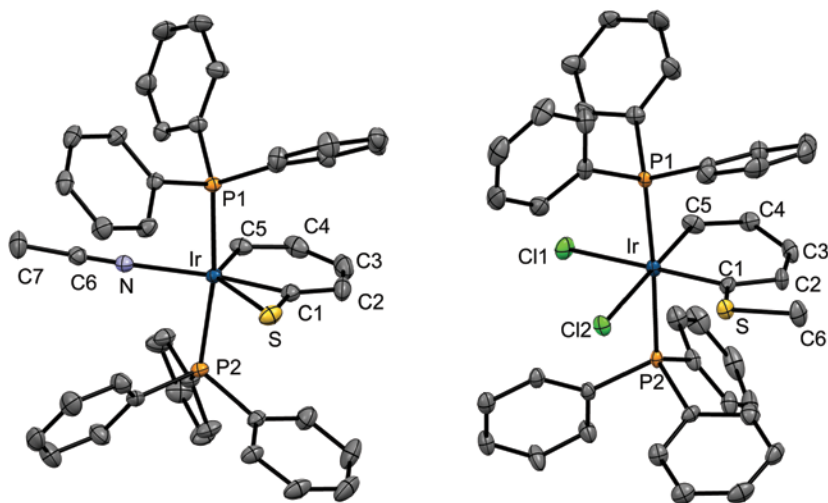


Figure 1.3 Molecular structures of iridabenzene **9** (left) and **13** (right) showing 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected distances [Å] for **9**: Ir–C1 1.933(2), Ir–C5 1.989(2), Ir–S 2.6326(6), Ir–N 2.1340(16), C1–C2 1.398(3), C2–C3 1.366(4), C3–C4 1.421(4), C4–C5 1.365(3). Selected distances [Å] for **13**: Ir–C1 1.993(4), Ir–C5 1.992(4), Ir–Cl1 2.4846(10), Ir–Cl2 2.4606(11), C1–C2 1.427(6), C2–C3 1.363(6), C3–C4 1.413(6), C4–C5 1.352(6), S–C6 1.820(5).

(Scheme 1.1) and the iridacyclopentadiene **8**. The bonds within the almost perfectly planar five-membered metallacyclic ring of **8** serve as benchmarks for the lengths of (presumably) essentially localised C–C double bonds and Ir–C(sp²) single bonds within an iridacyclic ring. The relevant distances in **8** are: iridium–carbon single bonds (Ir–C1 2.051(3), Ir–C4 2.093(3) Å), carbon–carbon double bonds (C1–C2 1.327(4), C3–C4 1.350(5) Å), and carbon–carbon single bonds (C2–C3 1.446(5) Å) [33]. The iridabenzene **9** is also very planar, with the greatest deviation from the Ir, C1–C5, S1 least-squares plane occurring for the iridium metal (0.038 Å). The iridium–carbon bonds (Ir–C1 1.933(2), Ir–C5 1.989(2) Å) are significantly shorter than they are in **8**, as would be expected if there is some multiple bond character in these bonds arising from a delocalised π -bonding system. The remaining carbon–carbon bonds in the IrC₅ ring of **9** display some alternation in their distances but all fall well between the single and double carbon–carbon bond lengths observed in **8** [32, 33]. The structural evidence for the classification of **9** as having a delocalised, aromatic π -bonding system is therefore quite compelling. The bond lengths in the neutral methylthiolate-substituted iridabenzene, **13**, follow the same trends, although in this case the iridium metal lies quite significantly (0.307 Å) out of the least squares plane formed by the iridium metal and carbons C1–C5, although the plane formed by these five carbon atoms is itself very planar[33]. While non-planarity is often associated with a loss of aromaticity in simple carbocyclic compounds, it has been shown computationally that distortions of this type do not adversely affect the aromaticity in metallabenzenes [35].

Interestingly, the sulfur atom of the η^2 -C(S) moiety in **9** does not appear to interact with the iridium metal as strongly as it does with the osmium metal in the osmabenzenes **1** and **2**. The Ir–S bond length of 2.6326(6) Å is considerably longer than the Os–S

bond lengths in **1** and **2** (2.474(3) and 2.4990(12) Å, respectively), and the Ir–C1–S angle of 93.80(9)° is larger (*cf.* 84.58° and 84.00° in osmabenzenes **1** and **2**, respectively) [14, 25, 33].

In addition to the structural data, the spectroscopic data also support the notion that the iridabenzenes **9**–**13** are indeed aromatic. In the ¹H NMR spectrum of cationic **9**, H5, which is attached to the iridium-bound C5 atom, resonates at 12.47 ppm. This is significantly down-field compared to the resonances of the corresponding protons (H1 and H4, which are attached to the metal-bound carbon atoms) in the iridacyclopentadiene complex **7** (7.20 and 6.53 ppm, respectively). Likewise in the ¹³C NMR spectrum of iridabenzene **9**, the iridium-bound carbons C1 and C5 are found at the low-field positions of 243.9 and 176.9 ppm, respectively, while the iridium-bound carbons C1 and C4 in **7** are found at 152.6 and 136.0 ppm, respectively [32]. The characteristically large down-field chemical shifts that are found for the metal-bound carbon atoms in these iridabenzenes are consistent with there being multiple-bond character in each of the iridium–carbon bonds, further supporting a delocalised π -bonding system [27]. The remaining hydrogen and carbon atoms of **9** that are remote from the iridium metal centre exhibit NMR resonances in regions typical of traditional organic aromatics (¹H NMR: 6.24 (H2), 7.50 (H3), 6.81 (H4) ppm, ¹³C NMR: 117.6 (C2), 153.9 (C3), 127.4 (C4) ppm) [32]. The chemical shifts found in the neutral iridabenzene **10** are very similar (¹H NMR: 12.45 (H1), 5.65 (H2), 6.80 (H3) and 6.54 (H4) ppm, ¹³C NMR: 249.47 (C1), 118.71 (C2), 149.40 (C3), 125.99 (C4), 171.43 (C5) ppm).

The complexes **11**–**13**, which arise from methylation of the sulfur function in **9** or **10**, display very similar chemical shifts for the metallabenzene ring atoms in the NMR spectra. For example, for the dicationic **11**, H5 is found at 11.59 ppm in the ¹H NMR spectrum, while in the ¹³C NMR spectrum C1 and C5 are found at 224.4 and 180.9 ppm, respectively [32]. In the neutral **13**, H5 is observed at 12.31 ppm (¹H NMR spectrum), and C1 and C5 at 229.12 and 198.19 ppm, respectively (¹³C NMR spectrum). The remaining ring signals are found in the expected aromatic positions [33].

1.3 Syntheses and Properties of Fused-Ring Metallabenzenes

By the start of the 21st century the study of metallabenzenes had expanded into a diverse field featuring a variety of different metal centres and differently substituted carbon skeletons prepared via a wide range of synthetic routes. In spite of this, the sister field of fused-ring metallabenzenes, where the primary six-membered ring is fused with a secondary ring structure, was still very much in its infancy and examples with fused heterocyclic rings were very rare. We therefore directed our attention to compounds of this type.

Metallabenzofurans are now the largest class of the otherwise relatively unexplored fused-ring metallabenzenes. In all the reported examples of metallabenzofurans, the metal occupies a ring junction position and bonds to the oxygen of the fused five-membered furan ring (see Chart 1.2). In principle many other metallabenzofuran isomers are possible, but these have yet to be reported. The three important valence bond structures, as well as a delocalised representation with the general numbering scheme for the known isomer, are given in Chart 1.2.

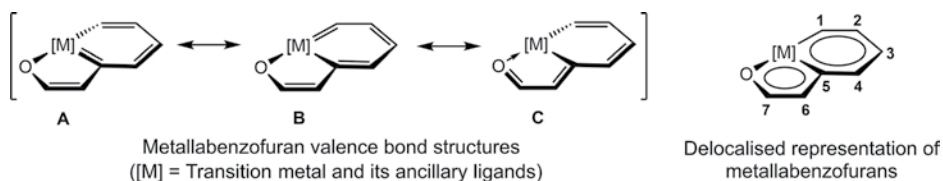
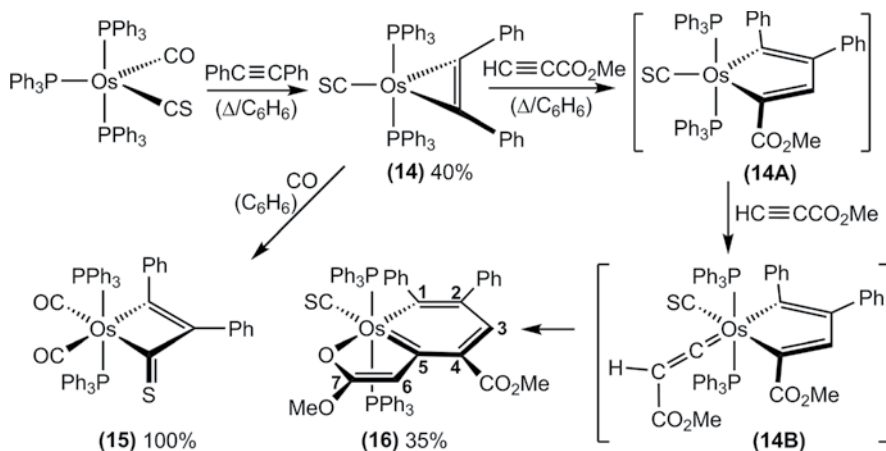


Chart 1.2 General representation and valence bond structures for the single metallabenzofuran isomer that has been reported.

1.3.1 Osmabenzofurans

The synthesis of the first osmabenzene by the reaction between two ethyne molecules and the osmium complex $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$ naturally led us to consider further investigations involving substituted acetylenes. The reaction with propyne to give the osmabenzene **2** has already been noted above. Interestingly, it was found that, with diphenylacetylene, only one molecule adds to $\text{Os}(\text{CS})(\text{CO})(\text{PPh}_3)_3$, with accompanying loss of both PPh_3 and (surprisingly) CO , to yield the osmacyclopropene complex $\text{Os}(\text{CS})(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ (**14**) (Scheme 1.4) [36, 37]. This complex did not undergo further reaction with diphenylacetylene even in the presence of a large excess of this reagent. However, on treatment of **14** with CO , the coordinated diphenylacetylene could be induced to combine with the thiocarbonyl carbon to give the osmabutenethione, **15**. This very unreactive species bears some similarity to **1B** in Scheme 1.1, which has been proposed as an intermediate in the synthesis of osmabenzene **1**.

Compound **14** is remarkably stable towards further reaction with most alkynes. However, the facile reaction between **14** and CO suggested that **14** might undergo reaction with a suitably activated alkyne and this could lead to a new osmabenzene through formal $[1 + 2 + 2]$ cyclisation of the two alkyne molecules and the thiocarbonyl ligand. One of the activated alkynes chosen for study was methyl propiolate ($\text{HC}\equiv\text{CCO}_2\text{CH}_3$). When **14** was heated under reflux in benzene with this alkyne, a reaction ensued but not in the way initially anticipated. The product obtained was the osmabenzofuran **16**.



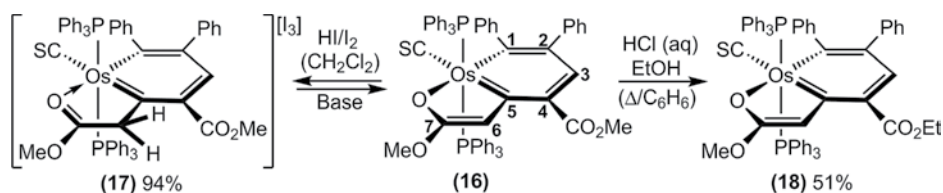
Scheme 1.4 Synthesis of the osmabenzofuran **16**.

$\text{Os}(\text{C}_7\text{H}_2\text{O}\{\text{Ph}-1\}\{\text{Ph}-2\}\{\text{CO}_2\text{Me}-4\}\{\text{OMe}-7\})(\text{CS})(\text{PPh}_3)_2$ (**16**) in 35% isolated yield after chromatography (Scheme 1.4) [38]. Surprisingly, the CS ligand remained intact and was not incorporated into either of the two fused rings. It was proposed that the reaction proceeds via cyclisation of the diphenyl acetylene with a coordinated methyl propiolate to give the intermediate osmacyclopentadiene **14A**. This does not then undergo a migratory insertion reaction with the adjacent CS. Instead an additional methyl propiolate coordinates and rearranges into a vinylidene ligand to give intermediate **14B** (Scheme 1.4). It is well known that coordinated methyl propiolate can rearrange to a vinylidene ligand ($\text{M}=\text{C}=\text{CR}_2$) [39–41]. After insertion of the vinylidene carbon, coordination of the carbonyl oxygen of the ester substituent forms the fused metallafuran ring in **16** [38].

The osmabenzofuran **16** was found to be relatively unreactive and the extensive ring substitution may be, at least in part, responsible for this. It does, however, undergo protonation and on treatment with aqueous hydrochloric acid the colour changes from blue-green to green. The protonation occurs at C6 and this was confirmed by ^1H NMR spectroscopy (Scheme 1.5). The protonation is readily reversed, and if dilute acid is used only unreacted **16** is collected when attempts are made to isolate the protonated species. However, if gaseous HI (contaminated with a small amount of iodine impurity) is added to a dichloromethane solution of **16**, the green cationic tethered osmabenzene $[\text{Os}(\text{C}_5\text{H}\{\text{Ph}-1\}\{\text{Ph}-2\}\{\text{CO}_2\text{Me}-4\}\{\text{CH}_2\text{C}(\text{O})\text{OMe}-5\})(\text{CS})(\text{PPh}_3)_2][\text{I}_3]$ (**17**) (Scheme 1.5) can be isolated and structurally characterised. Protonation at C6 saturates this carbon atom and this disrupts the π -delocalisation in the five-membered ring. The five-membered ring can then be viewed as a simple “tethering arm” to the osmabenzene. We have used the term “tethering arm” to distinguish this type of fused ring from those that can support delocalised π -systems [38, 42]. As might be expected, treatment of these protonated osmabenzofurans with base instantly returns the original osmabenzofuran **16**.

An illustration of the chemically robust nature of this osmabenzofuran skeleton is provided by the observation that heating **16** under reflux in a benzene/ethanol mixture containing a small amount of concentrated HCl for 1 h results in the formation of the blue-green *trans*-esterified osmabenzofuran, $\text{Os}(\text{C}_7\text{H}_2\text{O}\{\text{Ph}-1\}\{\text{Ph}-2\}\{\text{CO}_2\text{Et}-4\}\{\text{OMe}-7\})(\text{CS})(\text{PPh}_3)_2$ (**18**), which can be isolated in 51% yield (Scheme 1.5). It is noteworthy that the methyl ester function on the six-membered metallacyclic ring undergoes *trans*-esterification under these conditions, but the methoxy substituent on the five-membered ring remains intact. This suggests that even under these harsh conditions the osmafuran ring is not opened by cleavage of the Os–O bond to give a pendant methyl ester function [38].

The structures of the osmabenzenoids **16**–**18** have been determined unambiguously by single crystal X-ray crystallographic studies (Figure 1.4). In all cases the osmium



Scheme 1.5 Preparation of derivatives of **16**.

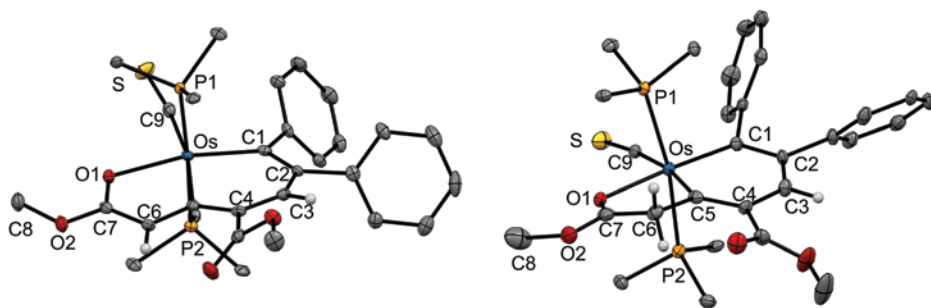


Figure 1.4 Molecular structures of the osmabenzofuran **16** (left) and the cation of the tethered osmabenzene **17** (right) showing 50% probability thermal ellipsoids. Some hydrogen atoms and the phenyl rings of the triphenylphosphine ligands are not shown for clarity. Selected distances [Å] for **16**: Os–C1 2.068(3), Os–C5 2.142(3), Os–O1 2.2178(17), Os–C9 1.846(3), C1–C2 1.376(4), C2–C3 1.442(3), C3–C4 1.359(4), C4–C5 1.436(4), C5–C6 1.371(3), C6–C7 1.416(4), C7–O1 1.250(3). Selected distances [Å] for **17**: Os–C1 1.996(5), Os–C5 2.103(6), Os–O1 2.221(4), Os–C9 1.901(6), C1–C2 1.450(8), C2–C3 1.374(8), C3–C4 1.438(8), C4–C5 1.375(8), C5–C6 1.507(8), C6–C7 1.495(9), C7–O1 1.226(8). (See color plate section for the color representation of this figure.)

metal lies at a ring junction position of the two fused rings with the oxygen atom coordinated to osmium. The two fused rings are essentially planar in the osmabenzofurans **15** and **16**. The tethered osmabenzene **17**, on the other hand, displays moderate non-planarity with the mean deviation from the Os, C1–C7, O1 least-squares plane being 0.14 Å. It is perhaps not surprising that the largest deviation from the mean plane was observed for the saturated atom, C6 (0.25 Å) [38].

In the osmabenzofuran **16**, the osmium–carbon bond lengths (Os–C1 2.068(3), Os–C5 2.142(3) Å) are similar to those observed in osmabenzenes [14, 25, 43–45], and the longer Os–C5 distance is most likely due to the *trans* influence of the thiocarbonyl ligand. The carbon–carbon bonds in the two rings display some bond length alternation but all fall midway between the expected distances for single and double bonds and are similar to the C–C distances reported for other metallabenzenes. The structure of **18** is essentially the same as **16** except for the presence of the ethyl rather than methyl group [38].

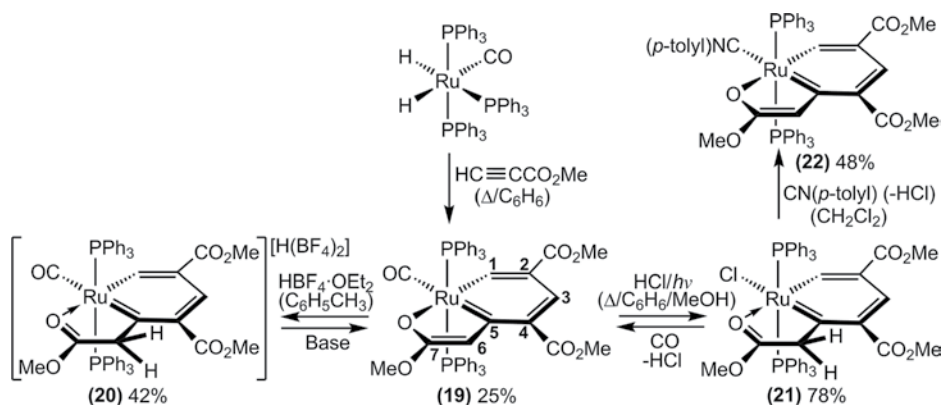
Protonation of C6 in **16** to give the cationic tethered osmabenzene **17** causes a number of significant changes in the structural parameters. The osmium–carbon bond lengths in **17** are notably shorter (Os–C1 1.996(5), Os–C5 2.103(6) Å), and the bonds to C6 are significantly longer (C5–C6 1.507(8), C6–C7 1.495(9) Å) and are consistent with single bonds. The carbon–carbon bond lengths in the six-membered osmabenzene ring are similar to those found in **16** and **18**. The long C5–C6 and C6–C7 distances in particular provide compelling evidence for the “tethered osmabenzene” formulation of **17** [38].

In the infrared spectrum of **16**, a strong absorbance at 1229 cm^{−1} is assigned to the thiocarbonyl ligand and the two bands at 1695 and 1569 cm^{−1} are assigned to the ester function on C4. Absorbance bands in similar positions are also found in **17** and **18**. The extensive substitution on the osmabenzofuran rings means that there are few signals in the aromatic region of the ¹H NMR spectra of these compounds. The H3 protons are found at 6.99, 8.39 and 6.98 ppm in **16**, **17** and **18**, respectively. It is possible that the

lower-field H3 shift for **17** results from the π -system that is now delocalised over only the six atoms of the osmabenzene ring. The single protons on C6 in **16** and **18** are found at 6.51 and 6.49 ppm, respectively, while in the spectrum of the tethered osmabenzene **17**, the two protons on C6 are observed at 2.94 ppm. The large up-field shift is consistent with saturation of C6 and the loss of π -delocalisation in the furan ring. There are significant differences between the ^{13}C NMR spectra of **16** and **17**. For **16**, C1 and C5 are observed at 196.4 and 218.9 ppm, respectively, suggesting multiple bond character in each of the Os–C1 and Os–C5 bonds. The remaining carbon atoms of the two fused rings are found in typical aromatic positions (137.6 (C2), 158.1 (C3), 124.4 (C4), 123.6 (C6), 184.7 (C7) ppm) and are consistent with significant delocalised bonding in the two fused rings. In the ^{13}C NMR spectra of **17**, C1 and C5 are observed at considerably lower field positions (279.2 and 243.5 ppm, respectively), which may suggest increased multiple bonding to osmium with π -delocalisation now only over the six-membered ring. The remaining osmabenzene ring carbon atoms appear in the normal aromatic range (148.3 (C2), 153.8 (C3), 135.7 (C4) ppm). Carbon C6 in **17** is saturated, and accordingly is found in the up-field position of 52.7 ppm. In summary, the combination of the spectral and structural data corroborates the osmabenzene description for this complex [38].

1.3.2 Ruthenabenzofurans

Preparation of the osmabenzofuran complexes focused our attention on the possibility that metallabenzofurans involving other metals can also be prepared. On searching the literature we found that a ruthenium compound which fulfilled the criterion to be considered a ruthenabenzofuran had already been reported (complex **19**; Scheme 1.6), although at the time it was not recognised as such [46, 47]. With the benefit of the knowledge we had obtained from our studies of the osmabenzofurans **16** and **18**, it became clear to us that this alternative formulation was appropriate [42]. The ruthenabenzofuran $\text{Ru}(\text{C}_7\text{H}_3\text{O}\{\text{CO}_2\text{Me}-2\}\{\text{CO}_2\text{Me}-4\}\{\text{OMe}-7\})(\text{CO})(\text{PPh}_3)_2$ (**19**) had been prepared by treatment of the ruthenium complex $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2$ with methyl propiolate in refluxing benzene (Scheme 1.6) [46]. Three molecules of methyl propiolate cyclised at the ruthenium metal centre to form the red-violet product. It was proposed that the



Scheme 1.6 Syntheses of the ruthenabenzene **19** and its derivatives.

mechanism of this reaction first involved the cyclisation of two molecules of methyl propiolate at the ruthenium centre to form a ruthenacyclopentadiene intermediate. A third methyl propiolate then rearranged at the metal centre to form a coordinated vinylidene ligand, the α -carbon atom of which then inserted into an Ru–C bond of the ruthenacyclopentadiene. Coordination of the carbonyl oxygen of the ester function from the vinylidene ligand then formed the fused ruthenafuran ring and at the same time aromatised the six-membered ring, thereby forming the ruthenabenzofuran.

Since we had shown that the furan carbon atom C6 of the osmabenzofuran **16** was susceptible to protonation, the reactivity of ruthenabenzofuran **19** towards acids was investigated. Indeed, it was found that on addition of the anhydrous acid $\text{HBF}_4 \cdot \text{OEt}_2$ to a solution of **19** in toluene, protonation at C6 occurred immediately and the dark blue $[\text{Ru}(\text{C}_5\text{H}_2\{\text{CO}_2\text{Me}-2\}\{\text{CO}_2\text{Me}-4\}\{\text{CH}_2\text{C}(\text{O})\text{OMe}-5\})(\text{CO})(\text{PPh}_3)_2][\text{H}(\text{BF}_4)_2]$ (**20**) precipitated from solution in 42% isolated yield (Scheme 1.6). The two protons on the saturated carbon atom C6 are observed in the ^1H NMR spectrum at 2.73 ppm. This tethered ruthenabenzene complex, which has been structurally characterised, is stable for several days in solution at ambient temperature. However, on the addition of bases such as triethylamine, the protonation reaction is easily reversed and **19** is returned in excellent yield [42].

A related neutral tethered ruthenabenzene can be obtained if very different reaction conditions are employed. Treatment of a refluxing benzene/methanol solution of the ruthenabenzofuran **19** with trimethylsilyl chloride (which acts as a source of anhydrous hydrochloric acid) while simultaneously irradiating with visible light (to accelerate CO dissociation) over a period of 3–4 h gives the green, tethered ruthenabenzene, $\text{Ru}(\text{C}_5\text{H}_2\{\text{CO}_2\text{Me}-2\}\{\text{CO}_2\text{Me}-4\}\{\text{CH}_2\text{C}(\text{O})\text{OMe}-5\})\text{Cl}(\text{PPh}_3)_2$ (**21**), in 78% yield after purification by column chromatography. Under these conditions C6 is protonated and the carbonyl ligand is replaced by chloride. The two protons on the saturated carbon atom C6 are observed in the ^1H NMR spectrum at 3.19 ppm. The stability of **19** in the presence of HCl, while being irradiated and heated under reflux for hours in a benzene/methanol solution, is remarkable. Although only a few ruthenabenzenes have been reported, it is interesting to note that in some cases they are thermally unstable [48], while other examples show unexpectedly high thermal stability [49–51]. The tethered ruthenabenzene **21** is very stable in solutions containing traces of HCl, but on the addition of bases intractable mixtures of products are formed. Treatment of a dichloromethane solution of **21** with carbon monoxide, on the other hand, results in the replacement of chloride by CO, proton loss from C6 and reformation of the ruthenabenzofuran **19** in good yield. Treatment of **21** with the isoelectronic *p*-tolylisocyanide ($\text{CN}\{p\text{-tolyl}\}$) proceeds in a similar manner to give the new ruthenabenzofuran, $\text{Ru}(\text{C}_7\text{H}_3\{\text{CO}_2\text{Me}-2\}\{\text{CO}_2\text{Me}-4\}\{\text{OMe}-7\})(\text{CN}(p\text{-tolyl}))(\text{PPh}_3)_2$ (**22**) (Scheme 1.6), which is the *p*-tolylisocyanide analogue of **19** [42].

The NMR spectral data have been reported for the ruthenabenzofurans **19** and **22**, as well as the related tethered ruthenabenzenes **20** and **21**. In addition, the molecular structures of **19**, **20** and **21** have been obtained. This enables useful comparisons to be made between the properties of these ruthenabenzofurans and the closely related tethered ruthenabenzenes.

In the ^1H NMR spectra of the ruthenabenzofurans **19** and **22**, the fused ring protons unsurprisingly appear in similar positions (**19** 11.67 (H1), 7.2–7.5 (H3 obscured by PPh_3 multiplet), 6.06 (H6) ppm [47]; **22** 12.40 (H1), 7.3–7.4 (H3 obscured by PPh_3),

6.17 (H6) ppm). However, the corresponding signals for the metallabenzene ring protons of the related tethered ruthenabenzenes **20** and **21** are both observed at considerably lower-field positions (**20** 14.97 (H1), 8.83 (H3) ppm; **21** 16.45 (H1), 8.76 (H3) ppm) [42]. A similar trend is observed for the chemical shifts of the ring carbon atoms in the ^{13}C NMR spectra. Thus, the signals for the metal-bound carbon atoms C1 and C5 in the tethered ruthenabenzenes **20** and **21** are observed at significantly lower field positions (**20** 290.8 (C1) and 283.6 (C5) ppm, **21** 289.3 (C1) and 287.8 (C5) ppm) than the resonances for the corresponding carbon atoms in the related ruthenabenzofurans **19** and **22** (**19** 232.9 (C1) and 227.0 (C5) ppm, **22** 245.0 (C1) and 232.8 (C5) ppm) [42]. Shifts of the $\text{C}\alpha$ and $\text{H}\alpha$ resonances to lower field values is consistent with increasing π -bonding between the metal and $\text{C}\alpha$ in these closely related compounds and hence may signal increased π -delocalisation over the six-membered metallacyclic rings in the tethered ruthenabenzenes in comparison to the ruthenabenzofurans [22].

There are also some interesting differences in the structural parameters associated with the six-membered metallacyclic rings of the ruthenabenzofurans **19** and **22** compared to those of the tethered ruthenabenzene **20** (Figure 1.5) [42, 46, 47]. While these rings are essentially planar in all three compounds, the Ru–C distances in the tethered ruthenabenzene **20** (Ru–C1 1.933(4), Ru–C5 2.045(5) Å) are significantly shorter than those in the ruthenabenzofurans **19** (Ru–C1 2.004(6), Ru–C5 2.093(5) Å) and **22** (Ru–C1 1.986(3), Ru–C5 2.092(4) Å). In addition, the range of metallabenzene ring C–C distances in **20** show a smaller spread (1.374(7)–1.413(7) Å) compared to the ranges in **19** (1.338(9)–1.450(10) Å) and **22** (1.368(5)–1.475(5) Å). These structural features are also consistent with greater aromatic character for the six-membered metallacyclic ring of the tethered ruthenabenzene **20** compared to the ruthenabenzofurans **19** and **22**.

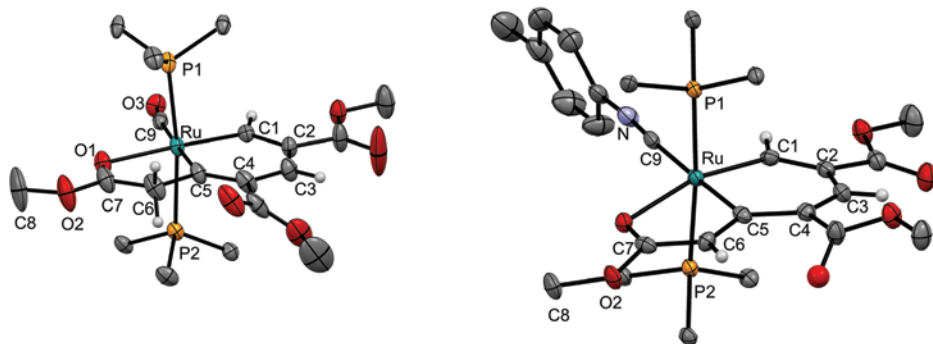


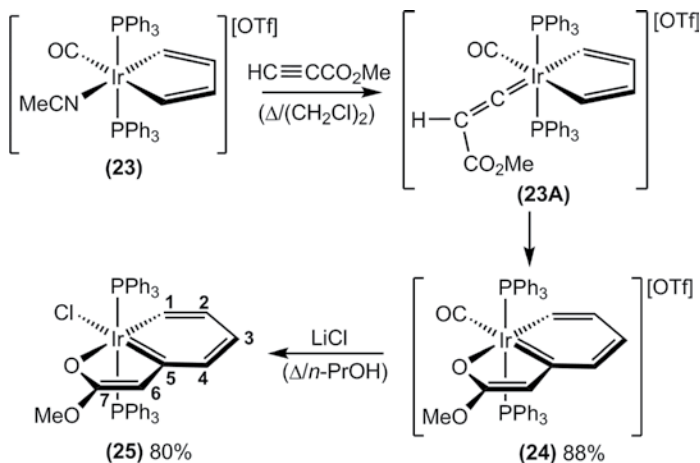
Figure 1.5 Molecular structures of the cation of the tethered ruthenabenzene **20** (left) and the ruthenabenzofuran **22** (right) showing 50% probability thermal ellipsoids. The phenyl rings of the triphenylphosphine ligands and most hydrogen atoms are not shown for clarity. Selected distances [Å] for **20**: Ru–C1 1.933(4), Ru–C5 2.045(5), Ru–O1 2.216(3), Ru–C9 1.941(5), C1–C2 1.404(6), C2–C3 1.383(7), C3–C4 1.413(7), C4–C5 1.374(7), C5–C6 1.518(7), C6–C7 1.504(8), C7–O1 1.231(7). Selected distances [Å] for **22**: Ru–C1 1.986(3), Ru–C5 2.092(4), Ru–O1 2.266(2), Ru–C9 1.954(4), C1–C2 1.368(5), C2–C3 1.437(5), C3–C4 1.376(5), C4–C5 1.475(5), C5–C6 1.376(5), C6–C7 1.437(5), C7–O1 1.242(4).

1.3.3 Iridabenzofurans

The successful isolation of osmabenzofuran and ruthenabenzofuran derivatives led us to consider the synthesis of the related iridabenzofurans. The mechanisms proposed for the formation of the group 8 metallabenzofurans involved, in the last steps, the insertion of a vinylidene ligand (formed by the rearrangement of a coordinated methyl propiolate) into preformed (but not isolated or detected) metallacyclopentadiene intermediates. Since the stable, isolated iridacyclopentadiene $[\text{Ir}(\text{C}_4\text{H}_4)(\text{CO})(\text{NCMe})(\text{PPh}_3)_2][\text{O}_3\text{SCF}_3]$ (**23**) (see Scheme 1.7) was known, it seemed logical that we should investigate the reaction of this compound with methyl propiolate [28]. Attractive features of **23** were that it could be synthesised easily and in high yield through reaction between the iridium(I) cation, $[\text{Ir}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2][\text{OTf}]$, and ethyne, and that the relatively labile acetonitrile ligand should facilitate coordination of the alkyne.

Naturally we were delighted to find that when a mixture of iridacyclopentadiene **23** and an excess of methyl propiolate was heated under reflux in 1, 2-dichloroethane, the bright orange cationic iridabenzofuran $[\text{Ir}(\text{C}_7\text{H}_5\text{O}\{\text{OMe-7}\})(\text{CO})(\text{PPh}_3)_2][\text{OTf}]$ (**24**) (Scheme 1.7) was formed in 88% isolated yield. It seems likely that the mechanism does indeed proceed via the intermediate vinylidene complex **23A**, which undergoes migratory insertion of C_α into the iridacyclopentadiene ring. Coordination of the ester carbonyl oxygen atom to iridium then forms the iridafuran ring. The neutral iridabenzofuran derivative $\text{Ir}(\text{C}_7\text{H}_5\text{O}\{\text{OMe-7}\})\text{Cl}(\text{PPh}_3)_2$ (**25**) may be formed by treating **24** with lithium chloride in refluxing *n*-propanol for several hours. Isolation of the bright red crystalline **25** in very good yield following these reaction conditions is a testament to the stability of the iridabenzofurans **24** and **25** [52].

One of the remarkable features of the iridabenzofurans **24** and **25** is the near absence of substituents on the fused rings. In each case there is only a methoxy substituent at C7 on the iridafuran ring. In all previously reported metallabenzofurans the metallacyclic rings had been quite heavily substituted. This minimal ring substitution, coupled with the high-yielding syntheses of **24** and **25**, paved the way for extended studies of the



Scheme 1.7 Synthesis of the iridabenzofurans **24** and **25**.