

Nucleophilic Aromatic Addition Reactions of the Metallabenzenes and Metallapyridinium: Attacking Aromatic Metallacycles with Bis(diphenylphosphino)methane to Form Metallacyclohexadienes and Cyclic η^2 -Allene-Coordinated Complexes

Hong Zhang,* Ran Lin, Guangning Hong, Tongdao Wang, Ting Bin Wen, and Haiping Xia*^[a]

Abstract: The reactions of phosphonium-substituted metallabenzenes and metallapyridinium with bis(diphenylphosphino)methane (DPPM) were investigated. Treatment of $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{PPh}_3)\text{CH}\}\text{Cl}_2(\text{PPh}_3)_2]\text{Cl}$ with DPPM produced osmabenzene $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{PPh}_3)\text{CH}\}\text{Cl}_2\text{-}\{(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}_2]\text{Cl}$ (**2**), $[\text{Os}\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{PPh}_3)\text{CH}\}\text{Cl}\{(\text{PPh}_2)\text{CH}_2\text{-}(\text{PPh}_2)\}_2]\text{Cl}_2$ (**3**), and cyclic osmium η^2 -allene complex $[\text{Os}\{\text{CH}=\text{C}(\text{PPh}_3)\text{CH}=(\eta^2\text{-C}=\text{CH})\}\text{Cl}_2\{(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}_2]\text{Cl}$ (**4**). When the analogue complex of osmabenzene **1**, ruthenabenzene $[\text{Ru}$ -

$\{\text{CHC}(\text{PPh}_3)\text{CHC}(\text{PPh}_3)\text{CH}\}\text{Cl}_2\text{-}(\text{PPh}_3)_2]\text{Cl}$, was used, the reaction produced ruthenacyclohexadiene $[\text{Ru}\{\text{CH}=\text{C}(\text{PPh}_3)\text{CH}=\text{C}(\text{PPh}_3)\text{CH}\}\text{Cl}\text{-}\{(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}_2]\text{Cl}_2$ (**6**), which could be viewed as a Jackson–Meisenheimer complex. Complex **6** is unstable in solution and can easily be converted to the cyclic ruthenium η^2 -allene com-

Keywords: metallabenzenes • metallacycles • metallapyridinium • nucleophilic addition • transition metals

plexes $[\text{Ru}\{\text{CH}=\text{C}(\text{PPh}_3)\text{CH}=(\eta^2\text{-C}=\text{CH})\}\text{Cl}\{(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}_2]\text{Cl}_2$ (**7**) and $[\text{Ru}\{\text{CH}=\text{C}(\text{PPh}_3)\text{CH}=(\eta^2\text{-C}=\text{CH})\}\text{Cl}_2\text{-}\{(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}_2]\text{Cl}$ (**8**). The key intermediates of the reactions have been isolated and fully characterized, further supporting the proposed mechanism for the reactions. Similar reactions also occurred in phosphonium-substituted metallapyridinium $[\text{OsCl}_2\{\text{NHC}(\text{CH}_3)\text{C}(\text{Ph})\text{C}(\text{PPh}_3)\text{CH}\}(\text{PPh}_3)_2]\text{BF}_4$ to give the cyclic osmium η^2 -allene-imine complex $[\text{OsCl}_2\{\text{NH}=\text{C}(\text{CH}_3)\text{C}(\text{Ph})=(\eta^2\text{-C}=\text{CH})\}\{(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\}\text{-}(\text{PPh}_3)]\text{BF}_4$ (**11**).

Introduction

Transition-metal-containing metallaaromatics have recently attracted considerable attention because they can display aromatic properties and mediate organometallic reactions.^[1–4] Particularly, significant progress of the chemistry of metallabenzene has been made.^[2,4] Previous studies have led to the isolation and characterization of a remarkable number of stable metallabenzene.^[2] Very rich chemical properties of metallabenzene have also been demonstrated. Unique char-

acteristic chemical reactions, for example, electrophilic aromatic substitution ($\text{S}_{\text{E}}\text{Ar}$) and nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$), provide strong chemical support for the aromaticity of the metallabenzene ring. However, $\text{S}_{\text{E}}\text{Ar}$ and $\text{S}_{\text{N}}\text{Ar}$ reactions of metallabenzene are only seen in a few reports,^[5,6] partly due to the relatively more reactive metal center.

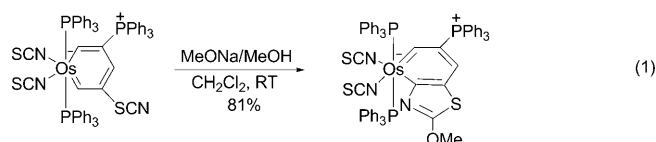
In agreement with the theoretical prediction about the stability of metallabenzene by Thorn and Hoffmann,^[7] most of the stable metallabenzene are those with π donors *ortho* or *para* to the metal. In contrast, well-characterized metallabenzene bearing electron-withdrawing groups have rarely been isolated.^[6,8–10] The iridabenzene and related iridanaphthalene reported by Paneque et al. represent the first examples of metallabenzene with electron-withdrawing groups, namely CO_2Me .^[8] We prepared a series of phosphonium-substituted metallabenzene, including osmabenzene and ruthenabenzene.^[6,9] The bicyclic species, which were described as tethered metallabenzene by Roper, Wright, and co-workers, constitute an addition to the special class of

[a] Dr. H. Zhang, R. Lin, G. Hong, T. Wang, Prof. Dr. T. B. Wen, Prof. Dr. H. Xia
State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University
Xiamen 361005 (P.R. China)
Fax: (+86) 592-2186628
E-mail: hpxia@xmu.edu.cn

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201000324>.

metallaaromatics containing electron-withdrawing groups.^[10] It has been demonstrated that Paneque's iridabenzene could undergo nucleophilic attack at the *para* carbon atom of a metallacycle due to the electronic effects introduced by the electron-withdrawing groups.^[8a,d] In this regard, it is reasonable to assume that nucleophilic attack would also occur in our phosphonium-substituted metallaaromatics.

Recently, we reported the first S_NAr reaction of metallabenzene [Eq. (1)].^[6] In light of the success that the osmaben-



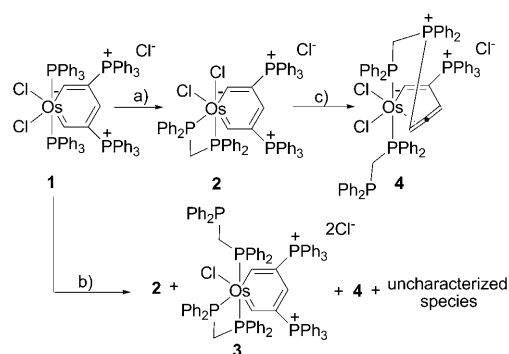
zene [Os{CHC(PPh₃)CHC(SCN)CH}(NCS)₂(PPh₃)₂] bearing a phosphonium substituent and a reactive thiocyanate group on the metallacycle could undergo intramolecular S_NAr reaction, we studied the reactions of phosphonium-substituted metallabenzene and metallapyridinium with external nucleophile bis(diphenylphosphino)methane (DPPM), which may provide various binding modes besides being a nucleophilic reagent. However, the nucleophilic aromatic addition reactions of aromatic metallacycles were observed, rather than the expected S_NAr reactions. During this study, we isolated interesting metallacyclohexadiene and η^2 -allene-coordinated metallacycles. Thus, it gives new hope for the future development of our metallaaromatics in the synthesis of new metallacycles. The details of our findings are reported in this paper.

Results and Discussion

Reactions of osmabenzene with DPPM: We presented that osmabenzene [Os{CHC(PPh₃)CHC(SCN)CH}(NCS)₂(PPh₃)₂] could undergo an intramolecular S_NAr reaction at ambient temperature and pressure to form a new fused metallaaromatic compound [Eq. (1)], which demonstrated that the nucleophilic reactivity of the metallacycle can be promoted when the electron density of the aromatic ring is significantly decreased in the presence of the transition-metal center and the electron-withdrawing phosphonium group.^[6] Since the phosphonium group can decrease the electron density of the metallacycle, we expect that osmabenzene **1**, which has two phosphonium groups positioned *meta* to the metal center on the metallacycle, is more likely to facilitate the approach of a nucleophile.

To test this hypothesis, we initially studied the reactivity of **1** with DPPM. However, **1** is not reactive enough and does not undergo a S_NAr reaction. Instead, it was consumed very slowly, as indicated by in situ NMR spectroscopy, when a solution of complex **1** and DPPM (in 1:1 molar ratio) in CHCl₃ was stirred at room temperature. When the mixture

was heated at 60°C for about 20 min, the reaction produced a green solution and the product could be isolated in high yield and identified as osmabenzene **2** (Scheme 1).



Scheme 1. Reaction of osmabenzene **1** with DPPM: a) DPPM (1:1 molar ratio), CHCl₃, 60°C, 20 min; b) excess DPPM (1:3 molar ratio), CHCl₃, 60°C, 5 h; c) excess DPPM (1:2 molar ratio), CHCl₃, 60°C, 24 h.

The structure of **2** has been confirmed by an X-ray diffraction study. In agreement with the structure, the ¹H NMR spectrum displays the two characteristic OsCH signals at $\delta = 17.3$ and 17.0 ppm. The ¹³C{¹H} NMR spectrum shows five signals at $\delta = 253.8$ (OsCH), 245.6 (OsCH), 150.4 (OsCHC(PPh₃)CH), 120.0 (C(PPh₃)), and 114.0 ppm (C(PPh₃)) for the carbon atoms of the metallacyclic ring. It clearly reveals that the two P atoms chelate to the metal center to result in a four-membered osmacycle and the complex is only a simple diphosphane substitution product with displacement of two PPh₃ ligands of the metal center in complex **1** (see Figure S1 in the Supporting Information).^[12]

To achieve the nucleophilic attack on a carbon atom of the metallacycle, we increased the proportion of DPPM in the reaction. When a mixture of **1** and excess DPPM (in a 1:3 molar ratio) in CHCl₃ was heated at 60°C for 5 h, a yellow/brown solution containing predominantly **2** along with small amounts of **4** and some unidentified species was produced (Scheme 1). When the solution was left heating for 24 h, the reaction was cleaner. In this case, complex **4** can be isolated as a yellow solid in 82% yield. The reaction of isolated **2** with excess DPPM gave the same result.

As the unidentified species are in small amounts, it is difficult to characterize them. Fortunately, after recrystallization of the crude product from dichloromethane/*n*-hexane, a single crystal of **3** was obtained, making it possible to determine its solid-state structure. As suggested by the structure (see Figure S2 in the Supporting Information),^[12] complex **3** may be regarded as an intermediate of the transformation of **2** to **4**.

Complex **4** can be stored in the solid form in an inert atmosphere for at least one month without appreciable decomposition. The structure of **4** can be readily deduced on the basis of NMR spectroscopy. The ¹H NMR spectrum shows the signal of OsCH at $\delta = 11.7$ ppm, the signal of η^2 -C=CH(PPh₂) at $\delta = 3.4$ ppm, and the signal of C(PPh₃)CH

at $\delta=7.2$ ppm. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the signal of CPh_3 appears at $\delta=9.3$ ppm. And those signals of two DPPM chains are observed at $\delta=43.8$ ($(\text{PPh}_2)\text{CH}_2-(\text{PPh}_2)\text{CH}$), -13.1 ($(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\text{CH}$), -5.8 ($\text{OsPPh}_2\text{CH}_2\text{PPh}_2$), and -28.2 ppm ($\text{OsPPh}_2\text{CH}_2\text{PPh}_2$), respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the signals of OsCH and CPh_3 appear at $\delta=207.2$ and 116.5 ppm, whereas the three carbon signals of the coordinated allene backbone appear at $\delta=184.6$ ($\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 120.8 ($\text{OsCHC}(\text{PPh}_3)\text{CH}$), and 18.6 ppm ($\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), respectively.

The structure of **4** has also been determined by X-ray crystallography. A view of the complex cation is shown in Figure 1. The X-ray diffraction study confirmed that the

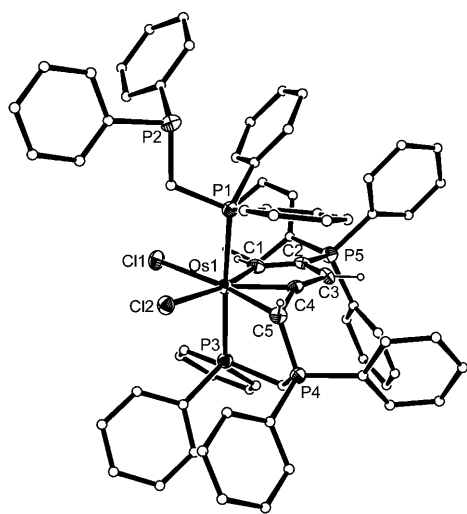


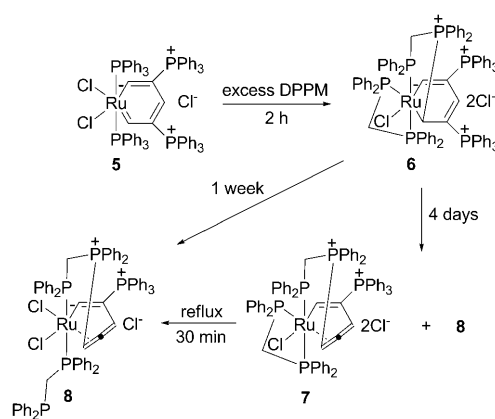
Figure 1. Molecular structure for the cation of complex **4** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Os1–P1: 2.4057(15), Os1–P3: 2.3540(14), Os1–Cl1: 2.4319(15), Os1–Cl2: 2.5098(14), Os1–C1: 2.028(6), Os1–C4: 2.003(5), Os1–C5: 2.158(6), C1–C2: 1.364(7), C2–C3: 1.459(8), C3–C4: 1.348(7), C4–C5: 1.387(8), P4–C5: 1.779(6), P5–C2: 1.757(6); P1–Os1–P3: 176.11(6), Cl1–Os1–Cl2: 84.12(5), C1–Os1–C4: 72.5(2), C1–Os1–C5: 109.5(2), Os1–C1–C2: 122.2(4), C1–C2–C3: 111.1(5), C2–C3–C4: 108.8(5), C3–C4–C5: 152.2(6), C3–C4–Os1: 125.3(5), C4–C5–Os1: 64.6(3), C5–C4–Os1: 76.7(3).

complex contains a conjugated osmacycle with a terminal double bond of an allene coordinated to the metal atom. The metallacycle of **4** deviates significantly from planarity, as reflected by the sum of angles in the six-membered ring of 668.4° , which is significantly smaller than the ideal value of 720° . C5 lies 0.4135 \AA out of the plane of the five-membered ring (Os1/C1/C2/C3/C4). The dihedral angle between the Os1/C1/C2/C3/C4 plane and the Os/C4/C5 plane is 18.1° . As a consequence of its coordination to the metal center, the allene unit is strongly bent with a C3–C4–C5 angle of 152.2° .

Complex **4** is structurally related to our previously reported cyclic osmium η^2 -allene complexes, which belong to the rare examples of metallacycles bearing an intramolecularly coordinated allene group.^[9c,d] We have also demonstrated that a similar cyclic η^2 -allene complex can isomerize to met-

allabenzene.^[9c] Although the related metallabenzene product of the $\text{S}_{\text{N}}\text{Ar}$ reaction was not detected, we suppose that the nucleophilic attack of DPPM to osmabenzene **1** may occur and it may also be possible that the η^2 -allene-coordinated osmacycle **4** is the isomer of the product of an $\text{S}_{\text{N}}\text{Ar}$ reaction.

Reactions of ruthenabenzene with DPPM: To further study the nucleophilic attack of DPPM to a metallacycle, we also investigated the reactions of DPPM with the ruthenabenzene **5**, that is, the analogue complex of osmabenzene **1**, which is much more reactive as shown by our previous study.^[9b,f] As indicated by an in situ NMR spectroscopic experiment, the reaction of ruthenabenzene **5** with DPPM (in 1:3 molar ratio) in CHCl_3 cleanly produced the ruthenacyclohexadiene complex **6** (Scheme 2). The reaction was essentially completed in approximately 2 h at room temperature.



Scheme 2. Reaction of ruthenabenzene **5** with DPPM.

Complex **6** was isolated as a reddish-brown solid. Its structure has been established by X-ray diffraction. As shown in Figure 2, Ru1, C1, C2, C3, and C4 are almost coplanar, which is reflected by the deviation (0.0363 \AA) from the RMS planes of the best fit, whereas C5 lies 0.5209 \AA out of the ring. The dihedral angle between the Ru1/C1/C2/C3/C4 plane and the Ru1/C4/C5 plane is 31.4° . The nonplanarity of the metallacycle is presumably due to the steric effects of the substituent DPPM. The nonplanar structure of **6** is similar to the six-membered ring of the iridacyclohexadiene $[\text{Ir}\{\text{CH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}\}\{\text{O}-\text{C}(-5)=\text{O}\}](\text{PEt}_3)_3$, which has been described as a half-boat conformation by Bleeke.^[13] The bond length of Ru1–C1 ($1.977(8)$ \AA) is within the range of those observed for typical Ru–C(vinyl) single bonds (1.932 – 2.141 \AA).^[14] The Ru1–C5 length ($2.261(8)$ \AA), which is appreciably longer than the bond length of Ru1–C1 ($1.977(8)$ \AA), is expected for Ru–C(sp^3) single bonds (1.954 – 2.418 \AA).^[14] The original delocalization in the metallacycle has been destroyed, as reflected by the marked short-long C–C distance alternations. The C1–C2 ($1.382(11)$ \AA) and C3–C4 ($1.345(11)$ \AA) bonds are apprecia-

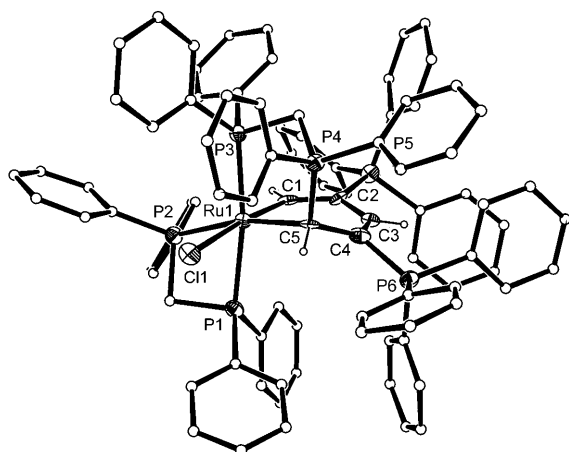
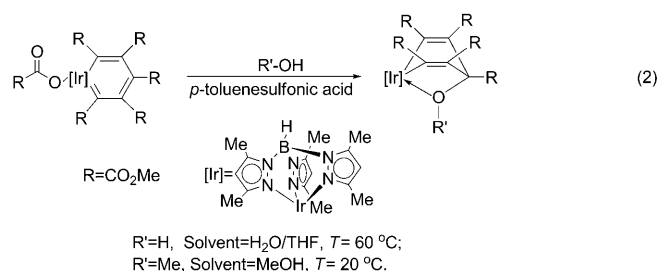


Figure 2. Molecular structure for the cation of **6** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–P3: 2.333(2), Ru1–P1: 2.429(2), Ru1–P2: 2.374(2), Ru1–Cl1: 2.538(2), Ru1–C1: 1.977(8), Ru1–C5: 2.261(8), C1–C2: 1.382(11), C2–C3: 1.436(10), C3–C4: 1.345(11), C4–C5: 1.501(12), P4–C5: 1.803(7), P5–C2: 1.791(9), P6–C4: 1.826(9); P1–Ru1–P3: 171.13(8), P2–Ru1–Cl1: 87.97(8), C1–Ru1–C5: 89.8(3), Ru1–C1–C2: 129.3(6), C1–C2–C3: 123.5(8), C2–C3–C4: 128.7(8), C3–C4–C5: 124.1(8), C4–C5–Ru1: 115.0(5).

bly shorter than the C2–C3 (1.436(10) Å) and C4–C5 (1.501(12) Å) bonds.

The solution NMR spectroscopic data and elemental analysis of **6** are consistent with its solid-state structure. Six sets of resonances and reciprocal coupling lead to the quite complicated $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6**. The signals of CPh_3 appear at $\delta = 22.0$ and 17.7 ppm and those of $\text{RuPPh}_2\text{CH}_2\text{PPh}_2$ appear at $\delta = -14.5$ and -17.9 ppm, whereas the other two phosphorus signals of the $\text{RuPPh}_2\text{CH}_2\text{PPh}_2\text{CH}$ chain are observed at $\delta = 48.5$ and 25.5 ppm, respectively. The ^1H NMR spectrum has three characteristic CH signals at $\delta = 13.4$ ($\text{RuCH}(\text{sp}^2)$), 6.4 ($\text{RuCHC}(\text{PPh}_3)\text{CH}$), and 4.8 ppm ($\text{RuCH}(\text{sp}^3)$). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays the carbon signals of the metallacycle at $\delta = 251.8$ ($\text{RuC}(\text{sp}^2)$), 112.3 ($\text{C}(\text{PPh}_3)$), 151.7 ($\text{RuCHC}(\text{PPh}_3)\text{CH}$), 107.7 ($\text{C}(\text{PPh}_3)$), and 13.2 ppm ($\text{RuC}(\text{sp}^3)$), respectively.

Metallacyclohexadienes and their reaction chemistry are currently of considerable interest.^[15] The interconversions between metallacyclohexadienes and metallabenzenes have been explored during the last decade.^[2h,i,8,13] Paneque et al. demonstrated that the nucleophilic attack of OH^- or MeO^- to iridaaromatics allows the formation of Jackson–Meisenheimer complexes [Eq. (2)].^[8a,d,16] In our reaction, ruthenacyclohexadiene **6** could also be viewed as a Jackson–Meisenheimer complex and provides another piece of evidence for the aromatic nature of metallabenzenes, which could undergo the nucleophilic aromatic addition reaction. It is also worth noting that **6** could be described as the first example of isolated ruthenacyclohexadiene. The earlier reported complex $[\text{Ru}\{\text{C}_5\text{H}_2(\text{CO}_2\text{Me}-2)(\text{CO}_2\text{Me}-4)(\text{CHCO}_2\text{Me}-5)\}(\text{CO})(\text{PPh}_3)_2]$ is now generally recognized as a metallabenzofuran considering its delocalization within the ruthenabicyclic system.^[1d,10a,11a]



Solid samples of complex **6** can be stored in air at ambient temperature for at least two weeks without appreciable decomposition. However, **6** is unstable in solution and can easily convert to the cyclic ruthenium η^2 -allene complexes. As indicated by in situ NMR spectroscopy, when a solution of **6** in CHCl_3 was stirred at room temperature for four days, **6** was completely consumed to give a 1:1 mixture of **7** and **8** (Scheme 2). When the mixture of **7** and **8** was refluxed for a further 30 min, the mixture would entirely convert to **8** as the final product. A similar result was obtained when a stirred solution of **6** in CHCl_3 was left standing for one week.

The poor solubility of **7** in the solvent mixture helps the separation of **7** and **8**. Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution of **8** layered with *n*-hexane. Definite proof of the structure came from a single-crystal X-ray structure analysis. Obviously, **8** is the analogue complex of the cyclic osmium η^2 -allene complex **4**. As shown in Figure 3, Ru1, C1, C2, C3, and C4 are coplanar, which is reflected by the deviation (0.0039 Å) from the RMS planes of the best fit, whereas C5 deviates out of the

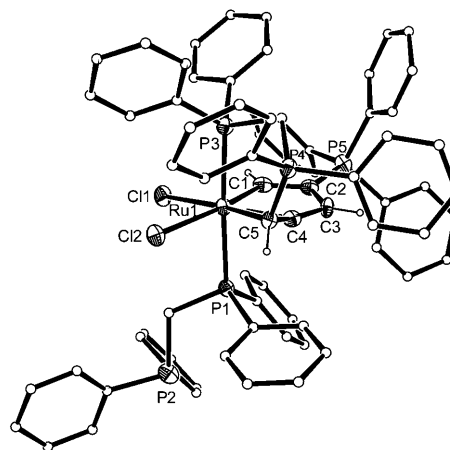


Figure 3. Molecular structure for the cation of complex **8** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–P3: 2.3517(13), Ru1–P1: 2.4094(13), Ru1–Cl1: 2.4272(11), Ru1–Cl2: 2.5285(12), Ru1–C1: 2.016(4), Ru1–C4: 2.020(4), Ru1–C5: 2.180(4), C1–C2: 1.364(6), C2–C3: 1.450(6), C3–C4: 1.311(6), C4–C5: 1.391(6), P4–C5: 1.774(5), P5–C2: 1.764(5); P1–Ru1–P3: 176.26(4), Cl1–Ru1–Cl2: 85.09(4), C1–Ru1–C4: 72.72(18), C1–Ru1–C5: 109.09(17), Ru1–C1–C2: 121.8(3), C1–C2–C3: 110.9(4), C2–C3–C4: 110.4(4), C3–C4–C5: 151.8(4), C3–C4–Ru1: 124.2(3), C4–C5–Ru1: 64.5(2), C5–C4–Ru1: 77.0(3).

ring. The dihedral angle between the five-membered ring (Ru1/C1/C2/C3/C4) and the three-membered ring made up of Ru1, C4, and C5 is 19.7°. Similar to complex **4**, the allene unit of **8** also deviates from linearity, as reflected by the C3-C4-C5 angle of 151.8°. The angle is close to the allenylcarbene complex $[\text{Ru}=\text{C}(\text{Rc})-\eta^2-\text{CH}=\text{C}=\text{CH}(\text{Rc})](\text{Cp})-(\text{PPh}_3)]\text{PF}_6$ (138.6°),^[17] while much smaller than our previously reported osmium complex $[\text{Os}\{\text{CH}=\text{C}(\text{PPh}_3)\text{CH}=(\eta^2-\text{C}=\text{CH}_2)\}\text{Cl}_2(\text{PPh}_3)_2]$ (171.0°).^[9d]

Consistent with the solid-state structure, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays the five signals at $\delta=38.7$ ($(\text{PPh}_2)\text{CH}_2-(\text{PPh}_2)\text{CH}$), 24.4 ($\text{Ru}(\text{PPh}_2)$), 19.0 ($(\text{PPh}_2)\text{CH}_2(\text{PPh}_2)\text{CH}$), 5.6 ($\text{C}(\text{PPh}_3)$), and -27.5 ppm ($\text{Ru}(\text{PPh}_2)$), respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the signals of RuCH and $\text{C}(\text{PPh}_3)$ appear at $\delta=232.4$ and 116.0 ppm, whereas the three carbon signals of the coordinated allene backbone are observed at $\delta=121.4$ ($\text{RuCHC}(\text{PPh}_3)\text{CH}$), 199.3 ($\eta^2-\text{C}=\text{CH}(\text{PPh}_2)$), and 31.8 ppm ($\eta^2-\text{C}=\text{CH}(\text{PPh}_2)$), respectively. The ^1H NMR spectrum displays the RuCH signal at $\delta=11.5$ ppm and the signals of $\text{RuCHC}(\text{PPh}_3)\text{CH}$ and $\eta^2-\text{C}=\text{CH}(\text{PPh}_2)$ at $\delta=6.7$ and 3.3 ppm, respectively.

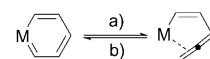
The structure of **7** can be deduced easily, as it has NMR spectroscopic data similar to those of **8**, which has been structurally characterized by X-ray diffraction. In terms of chemical composition, complex **7** is almost the same as **8** in that they all contain one Ru fragment, two DPPM substituents, and one η^2 -allene chain unit. The only difference is the coordinating mode of the diphosphanes towards the metal center: the two P atoms of one of the diphosphane ligands in **7** chelate to the Ru center. The accessible transformation of **7** to **8** can be attributed in part to the steric effect and the strained four-membered ring of **7** in which the diphosphane ligand has a great tendency to act as a monodentate ligand.

Proposed mechanism for the reaction of metallabenzene with DPPM: Scheme 3 shows a proposed mechanism for the formation of metallacyclohexadiene and η^2 -allene-coordinated metallacycles in the reaction of metallabenzene with DPPM. The PPh_3 ligand in metallabenzene **I** could initially be displaced by DPPM to give the intermediates **II**, in

which the bidentate ligand could undergo chelation with the metal center to give metallabenzene **III**. Coordination of another DPPM with only one P atom to **III** gives **IV**, leaving the other P atom free, providing the possibility to undergo nucleophilic attack. Then, the intramolecular nucleophilic addition of the DPPM to the aromatic metallacycle affords the metallacyclohexadienes **V**. Although not common, a few nucleophilic attacks between bidentate phosphines and unsaturated hydrocarbyl ligands are known. For example, the nucleophilic attack of DPPM at C_α of the phosphido-bridged diiron allenyl complex $[\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)\{\mu-\eta^1-\eta^2_{\alpha\beta}-(\text{H})\text{C}_\alpha=\text{C}_\beta=\text{C}_\gamma\text{H}_2\}]$ ^[18] and the nucleophilic attack of DPPM at the Rh end of the bridged alkyne of the complex $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\mu-\text{C}_2\text{H}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$.^[19] The Jackson–Meisenheimer complexes **V** convert to η^2 -allene-coordinated metallacycles **VI**, rather than the expected metallabenzene. Complexes **VI** could form by the cleavage of the C4–P bond of **V**, which may be driven by the ring strain of the DPPM-tethered metallacycle. Complexes **VI** can rearrange to give the more stable complexes **VII**.

A sequence of intermediates in the transformation of **I** to **VII**, except **II**, have been isolated from the reaction of DPPM with osmabenzene **1** or with ruthenabenzene **5**. Ready conversion of metallabenzene **I** to η^2 -allene-coordinated metallacycles **VII** is interesting, especially in view of the isolation and single-crystal X-ray structure determination of the Jackson–Meisenheimer complex **V**, which is derived from metallabenzene **IV** by the intramolecular nucleophilic addition reaction of DPPM to the aromatic metallacycle.

We have recently demonstrated the transformation of η^2 -allene-coordinated metallacycle to metallabenzene (Scheme 4, path b).^[9c] In connection with our study on the transformation of **I** into **VII**, which represents the first example of the conversion of metallabenzene to an allene-coordinated complex (Scheme 4, path a), our results show that the interconversion between metallabenzene and allene-coordinated complexes could now be viable.

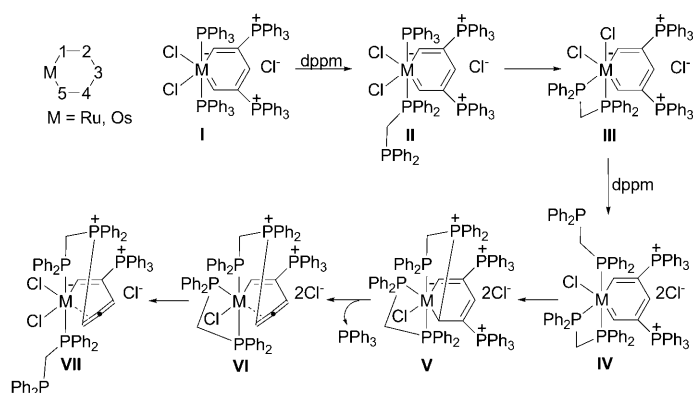


Scheme 4. Interconversion of metallabenzene and a η^2 -allene-coordinated metallacycle.

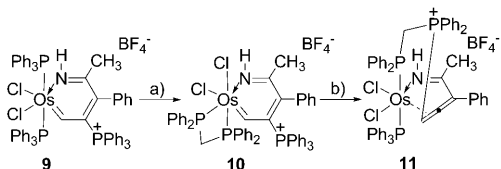
Reactions of osmapyridinium

with DPPM: The reaction of metallapyridinium **9**, a new member of metallaromatics,^[3a] with DPPM has also been investigated for comparison.

Due to the high stability of **9**, the reaction of osmapyridinium **9** with DPPM was performed in 1,2-dichloroethane at 80 °C (Scheme 5). Complex **10** could be isolated as a yellow solid in 81 % yield by heating the solution at 80 °C for 8 h. The structure of **10** is revealed by NMR spectroscopy. Complex **10** exhibits the signal of $\text{C}(\text{PPh}_3)$ at $\delta=21.1$ ppm and that of $\text{OsPPh}_2\text{CH}_2\text{PPh}_2$ at $\delta=-56.0$ and -70.3 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Consistent with the presence of the aromatic metallacycle, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows four signals at $\delta=231.2$ (OsCH), 177.9 ($\text{OsNHC}(\text{CH}_3)$),



Scheme 3. Plausible mechanism for the reaction of metallabenzene with DPPM.



Scheme 5. Reaction of osmapyridinium **9** with DPPM: a) DPPM (1:2 molar ratio), CH₂ClCH₂Cl, 80 °C, 8 h; b) PPh₃ (1:2 molar ratio), CH₂ClCH₂Cl, 80 °C, 4 days.

156.0 (*C*(Ph)), and 120.4 ppm (*C*(PPh₃)). In addition, the signals at δ = 18.6 (*OsCH*) and 14.0 ppm (*OsNH*) assigning to the protons of the metallacycle appear in the ¹H NMR spectrum. The structure of **10** has also been confirmed by X-ray diffraction and it can be described as a derivative of **9**, in which both P atoms of diphosphane chelate to the metal center (see Figure S3 in the Supporting Information).^[12]

When the mixture of **9** and DPPM in 1,2-dichloroethane was kept at 80 °C for several days, a mixture of **10** and **11** was identified by in situ NMR spectroscopy. Conversion of complex **10** to **11** seems to be promoted by PPh₃. It is found that the desired complex **11** cannot be obtained from the refluxing 1,2-dichloroethane solution of the pure sample **10**. When a solution of the isolated complex **10** in 1,2-dichloroethane was heated at 80 °C in the presence of purposely added PPh₃, the reaction was completed after four days to give **11** as the dominant product.

The structure of **11** has been clarified by an X-ray single-crystal diffraction experiment. As shown in Figure 4, the structure of **11** is similar to those of the cyclic η^2 -allene complexes **4** and **8**. The cyclic osmium η^2 -allene-imine complex **11** is also structurally similar to the Fischer carbene com-

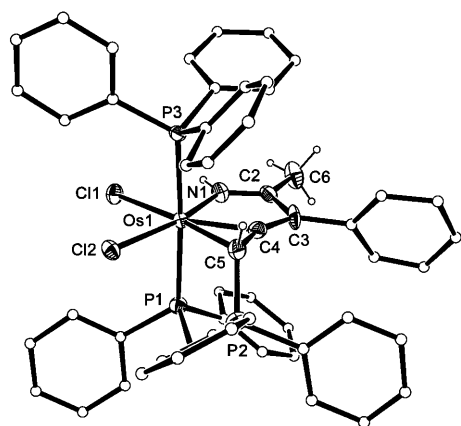


Figure 4. Molecular structure for the cation of complex **11** (ellipsoids at the 50% probability level). Counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–P3: 2.423(2), Os1–P1: 2.361(2), Os1–Cl1: 2.445(2), Os1–Cl2: 2.425(2), Os1–N1: 2.055(7), Os1–C4: 2.007(8), Os1–C5: 2.184(8), N1–C2: 1.299(11), C2–C3: 1.443(12), C3–C4: 1.350(12), C4–C5: 1.388(12), C6–C2: 1.488(12), P2–C5: 1.803(9); P1–Os1–P3: 172.46(8), Cl1–Os1–Cl2: 89.01(7), N1–Os1–C4: 70.9(3), N1–Os1–C5: 109.2(3), Os1–N1–C2: 123.4(6), N1–C2–C3: 112.1(8), C2–C3–C4: 108.2(8), C3–C4–C5: 156.8(9), C3–C4–Os1: 125.4(6), C4–C5–Os1: 63.9(5), C5–C4–Os1: 77.7(5).

plexes [M{=CH(Fc)N(C₅H₁₁)CH=(η^2 -C=CH₂)}(CO)₄] (M = W, Cr, Mo), which contain the bidentate allene-aminocarbene ligand.^[20] As discussed above, the metallacycles of **4** and **8** deviate significantly from planarity. However, the closely related intramolecularly coordinated η^2 -allene complex **11** adopts a nearly planar structure. The maximum deviation from the least-squares plane through Os1, N1, and C2–C5 is 0.0288 Å for C5. We suspected that the steric and electronic effects might play important roles in the planarity.

In contrast to the reaction of metallabenzene with DPPM, treatment of metallapyridinium **9** with one equivalent of DPPM yielded the cyclic η^2 -allene complex **11**. The difference in the amount of DPPM required is probably related to the electron-deficient metallacycle of metallapyridinium **9**, which facilitates the attack of the nucleophile. The reaction may also involve a Jackson–Meisenheimer intermediate relevant to the proposed mechanism in Scheme 3. Complex **11** may be formed through the conversion of the nondetectable Jackson–Meisenheimer intermediate, which is produced by the intramolecular nucleophilic addition reaction of DPPM with metallapyridinium **9**.

Conclusion

We have demonstrated the nucleophilic aromatic addition reactions of the phosphonium-substituted metallabenzene with bidentate DPPM. The process involves the nucleophilic attack of an aromatic metallacycle by the nucleophile DPPM, followed by the cleavage of the C–P bond. This was supported by the isolation and characterization of the intermediates, especially the Jackson–Meisenheimer complex. A similar reaction also occurred in our phosphonium-substituted metallapyridinium to give the cyclic osmium η^2 -allene-imine complex. The reactions are potentially useful as they provide a simple and efficient method for the synthesis of allene-coordinated metallacycles with different metals and substituents, through the intramolecular nucleophilic addition reaction, from the metallaromatics.

Experimental Section

General comments: Unless otherwise stated, all manipulations were carried out at room temperature under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium benzophenone (*n*-hexane, diethyl ether), or calcium hydride (CH₂Cl₂, CHCl₃, CH₂ClCH₂Cl). The starting materials [Os{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (**1**), [Ru{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (**5**), and [Os{NHC(CH₃)C(Ph)C(PPh₃)CH}Cl₂(PPh₃)₂]BF₄ (**9**) were synthesized by literature procedures.^[3a,9b,1] NMR spectroscopic experiments were performed on a Bruker AV-300 spectrometer (¹H: 300.1, ¹³C: 75.5, ³¹P: 121.5 MHz) or a Bruker AV-400 spectrometer (¹H: 400.1, ¹³C: 100.6, ³¹P: 162.0 MHz). ¹H and ¹³C NMR spectroscopic chemical shifts are relative to TMS, and ³¹P NMR spectroscopic chemical shifts are relative to 85% H₃PO₄. Elemental analyses data were obtained on a Thermo Quest Italia S.P.A. EA 1110 instrument.

[Os{CHC(PPh₃)CHC(PPh₃)CH}Cl₂{(PPh₂)CH₂(PPh₂)}]Cl (2**):** A mixture of [Os{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (**1**) (0.20 g, 0.14 mmol)

and DPPM (53.8 mg, 0.14 mmol) in CHCl_3 (10 mL) was heated at 60°C for about 20 min to give a green solution. The volume of the mixture was reduced to approximately 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a green solid, which was collected by filtration, washed with diethyl ether (3×2 mL), and dried under vacuum. Yield: 0.16 g, 90%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162.0 MHz): $\delta = 20.4$ (dd, $J(\text{PP}) = 31.3$, 7.3 Hz; $\text{C}(\text{PPh}_3)$, 19.8 (d, $J(\text{PP}) = 8.4$ Hz; $\text{C}(\text{PPh}_3)$), -31.9 (d, $J(\text{PP}) = 13.1$ Hz; $\text{Os}(\text{PPh}_2)$), -55.4 (dd, $J(\text{PP}) = 30.9$, 13.1 Hz; $\text{Os}(\text{PPh}_2)$); ^1H NMR plus HMQC (CD_2Cl_2 , 300.1 MHz): $\delta = 17.3$ (t, $J(\text{PH}) = 15.6$ Hz, 1H; $\text{Os}(\text{CH})$), 17.0 (d, $J(\text{PH}) = 19.2$ Hz, 1H; $\text{Os}(\text{CH})$), 8.0–6.3 (m, 52H; PPh_3 , PPh_2 , $\text{Os}(\text{CHC}(\text{PPh}_3)\text{CH})$), 7.9 (brs, 1H; $\text{Os}(\text{CHC}(\text{PPh}_3)\text{CH})$, obscured by the phenyl signals and confirmed by $^1\text{H}\text{-}^{13}\text{C}$ HMQC), 5.4 (dt, $J(\text{HH}) = 15.0$, $J(\text{PH}) = 8.7$ Hz, 1H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 4.7 ppm (dt, $J(\text{HH}) = 15.0$, $J(\text{PH}) = 13.2$ Hz, 1H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75.5 MHz): $\delta = 253.8$ (m; $\text{Os}(\text{CH})$), 245.6 (brs; $\text{Os}(\text{CH})$), 150.4 (t, $J(\text{PC}) = 22.7$ Hz; $\text{Os}(\text{CHC}(\text{PPh}_3)\text{CH})$), 136.7–119.9 (m; PPh_3 , PPh_2), 120.0 (dd, $J(\text{PC}) = 76.1$, 13.2 Hz; $\text{C}(\text{PPh}_3)$), 114.0 (dd, $J(\text{PC}) = 76.1$, 15.3 Hz; $\text{C}(\text{PPh}_3)$), 41.1 (dd, $J(\text{PC}) = 21.2$, 33.4 Hz; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); elemental analysis calcd (%) for $\text{C}_{66}\text{H}_{55}\text{P}_4\text{Cl}_3\text{Os}$: C 62.49, H 4.37; found: C 62.21, H 4.83.

[Os(CH=C(PPh₃)CH=CH₂)Cl₂(PPh₂)₂Cl]Cl (4): A mixture of [Os{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (1) (0.20 g, 0.14 mmol) and DPPM (161.4 mg, 0.42 mmol) in CHCl_3 (10 mL) was heated at 60°C for about 24 h to give a yellow/brown solution. The volume of the mixture was reduced to approximately 2 mL by evaporation of the solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (3×2 mL), and dried under vacuum. Yield: 0.16 g, 82%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121.5 MHz): $\delta = 43.8$ (dd, $J(\text{PP}) = 50.8$, 13.2 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 9.3 (d, $J(\text{PP}) = 4.3$ Hz; $\text{C}(\text{PPh}_3)$), -5.8 (ddd, $J(\text{PP}) = 330.2$, 35.1, 13.2 Hz; $\text{Os}(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), -13.1 (dddd, $J(\text{PP}) = 334.6$, 50.7, 12.7, 4.3 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), -28.2 (dd, $J(\text{PP}) = 35.1$, 12.6 Hz; $\text{Os}(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); ^1H NMR plus HSQC (CDCl_3 , 300.1 MHz): $\delta = 11.7$ (d, $J(\text{PH}) = 15.3$ Hz, 1H; $\text{Os}(\text{CH})$), 8.1–6.7 (m, 57H; PPh_3 , PPh_2 , $\text{Os}(\text{CHC}(\text{PPh}_3)\text{CH})$), 7.2 (brs, 1H; $\text{Os}(\text{CHC}(\text{PPh}_3)\text{CH})$, obscured by the phenyl signals and confirmed by $^1\text{H}\text{-}^{13}\text{C}$ HSQC), 5.6 (m, 1H; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 4.0 (m, 2H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 3.4 (dd, 1H, $J(\text{PH}) = 16.8$, 5.7 Hz; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 2.6 ppm (m, 1H; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$); $^{13}\text{C}\{^1\text{H}\}$ NMR plus HSQC (CDCl_3 , 100.6 MHz): $\delta = 207.2$ (brs; $\text{Os}(\text{CH})$), 184.6 (d, $J(\text{PP}) = 22.5$ Hz; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 140.0–119.9 (m; PPh_3 , PPh_2), 120.8 (d, $J(\text{PC}) = 28.0$ Hz; $\text{Os}(\text{CHC}(\text{PPh}_3)\text{CH})$), 116.5 (d, $J(\text{PC}) = 78.8$ Hz; $\text{C}(\text{PPh}_3)$), 18.6 (d, $J(\text{PC}) = 71.0$ Hz; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 20.0–18.8 (m; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$, $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); elemental analysis calcd (%) for $\text{C}_{73}\text{H}_{62}\text{P}_5\text{Cl}_3\text{Os}$: C 63.04, H 4.49; found: C 63.00, H 4.70.

[Ru(CH=C(PPh₃)CH=C(PPh₃)CH)Cl₂(PPh₂)₂Cl]Cl (6): A mixture of [Ru{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (5) (0.20 g, 0.15 mmol) and DPPM (173.0 mg, 0.45 mmol) in CHCl_3 (10 mL) was stirred at room temperature for about 2 h to give a reddish-brown solution. The volume of the mixture was reduced to approximately 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a reddish-brown solid, which was collected by filtration, washed with diethyl ether (5×2 mL), and dried under vacuum. Yield: 0.20 g, 85%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121.5 MHz): $\delta = 48.5$ (ddt, $J(\text{PP}) = 82.5$, 32.9, 9.1 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 25.5 (ddd, $J(\text{PP}) = 280.5$, 81.5, 34.2 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 22.0 (dd, $J(\text{PP}) = 22.7$, 6.9 Hz; $\text{C}(\text{PPh}_3)$), 17.7 (s; $\text{C}(\text{PPh}_3)$), -14.5 (m; $\text{Ru}(\text{PPh}_2)$), -17.9 ppm (dt, $J(\text{PP}) = 278.4$, 32.4 Hz; $\text{Ru}(\text{PPh}_2)$); ^1H NMR plus HMQC (CDCl_3 , 300.1 MHz): $\delta = 13.4$ (d, $J(\text{PH}) = 24.3$ Hz, 1H; $\text{Ru}(\text{CH}(\text{sp}^2))$), 7.9–6.4 (m, 71H; PPh_3 , PPh_2 , $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 6.4 (brs, 1H; $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$, obscured by the phenyl signals and confirmed by $^1\text{H}\text{-}^{13}\text{C}$ HMQC), 5.24–5.02, 4.03–3.90 (m, 4H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2) , $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 4.8 ppm (brs, 1H; $\text{Ru}(\text{CH}(\text{sp}^2))$); $^{13}\text{C}\{^1\text{H}\}$ NMR plus HMQC (CDCl_3 , 75.5 MHz): $\delta = 251.8$ (brs; $\text{Ru}(\text{CH}(\text{sp}^2))$), 151.7 (brs; $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 139.1–119.0 (m; PPh_3 , PPh_2), 112.3 (dd, $J(\text{PC}) = 72.7$, 12.5 Hz; $\text{C}(\text{PPh}_3)$), 107.7 (d, $J(\text{PC}) = 69.7$ Hz; $\text{C}(\text{PPh}_3)$), 49.0, 33.3 (m; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2) , $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 13.2 ppm (d, $J(\text{PC}) = 52.0$ Hz; $\text{Ru}(\text{CH}(\text{sp}^2))$); elemental analysis calcd (%) for $\text{C}_{91}\text{H}_{77}\text{P}_6\text{Cl}_3\text{Ru}$: C 69.89, H 4.96; found: C 69.94, H 4.57.

[Ru(CH=C(PPh₃)CH=CH₂)Cl₂(PPh₂)₂Cl]Cl (7): A mixture of [Ru{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (5) (0.20 g, 0.15 mmol) and DPPM (173.0 mg, 0.45 mmol) in CHCl_3 (10 mL) was stirred at room temperature for about 4 days to give a purplish-brown solution. The volume of the mixture was reduced to ca. 5 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a purplish-brown solid, which was collected by filtration, washed with diethyl ether/dichloromethane (3:1, 3×3 mL), and dried under vacuum. Yield: 58.0 mg, 30%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121.5 MHz): $\delta = 39.7$ (ddd, $J(\text{PP}) = 54.2$, 20.0, 6.8 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 35.1 (ddd, $J(\text{PP}) = 293.5$, 54.2, 22.5 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 6.8 (s; $\text{C}(\text{PPh}_3)$), -4.7 (dd, $J(\text{PP}) = 40.5$, 22.5 Hz; $\text{Ru}(\text{PPh}_2)$), -16.6 ppm (ddd, $J(\text{PP}) = 293.5$, 40.5, 20.0 Hz; $\text{Ru}(\text{PPh}_2)$); ^1H NMR plus HMQC (CDCl_3 , 400.1 MHz): $\delta = 10.7$ (t, $J(\text{PH}) = 18.4$ Hz, 1H; $\text{Ru}(\text{CH})$), 8.5–6.6 (m, 56H; PPh_3 , PPh_2 , $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 5.9, 5.3, 4.4, 3.6 (m, 4H; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$, $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 5.4 ppm (m; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$); $^{13}\text{C}\{^1\text{H}\}$ NMR plus DEPT-135 and HMQC (CDCl_3 , 100.6 MHz): $\delta = 219.0$ (brs; $\text{Ru}(\text{CH})$), 202.8 (m; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 135.1–119.3 (m; PPh_3 , PPh_2), 125.1 (d, $J(\text{PC}) = 24.1$ Hz; $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 124.3 (d, $J(\text{PC}) = 80.5$ Hz; $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 40.4 (dd, $J(\text{PC}) = 70.2$, 22.2 Hz; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 42.3, 24.8 ppm (m; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$, $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); elemental analysis calcd (%) for $\text{C}_{73}\text{H}_{62}\text{P}_5\text{Cl}_3\text{Ru}$: C 67.36, H 4.80; found: C 67.49, H 4.94.

[Ru(CH=C(PPh₃)CH=CH₂)Cl₂(PPh₂)₂Cl]Cl (8): A mixture of [Ru{CHC(PPh₃)CHC(PPh₃)CH}Cl₂(PPh₃)₂]Cl (5) (0.20 g, 0.15 mmol) and DPPM (173.0 mg, 0.45 mmol) in CHCl_3 (10 mL) was stirred at room temperature for about 1 week to give a yellow/brown solution. The volume of the mixture was reduced to ca. 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (3×2 mL), and dried under vacuum. Yield: 0.14 g, 77%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 121.5 MHz): $\delta = 38.7$ (dd, $J(\text{PP}) = 56.9$, 16.8 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 24.4 (ddd, $J(\text{PP}) = 355.3$, 29.8, 16.5 Hz; $\text{Ru}(\text{PPh}_2)$), 19.0 (ddd, $J(\text{PP}) = 355.4$, 56.7, 14.3 Hz; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 5.6 (s; $\text{C}(\text{PPh}_3)$), -27.5 ppm (dd, $J(\text{PP}) = 29.9$, 14.3 Hz; $\text{Ru}(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); ^1H NMR plus HSQC (CDCl_3 , 500.2 MHz): $\delta = 11.5$ (d, $J(\text{PH}) = 15.3$ Hz, 1H; $\text{Ru}(\text{CH})$), 6.7 (brs, 1H; $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$, obscured by the phenyl signals and confirmed by $^1\text{H}\text{-}^{13}\text{C}$ HSQC), 8.3–6.5 (m, 56H; PPh_3 , PPh_2 , $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 5.9 (m, 1H; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$), 4.0 (brs, 2H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 3.3 (dd, $J(\text{PH}) = 16.8$, 5.1 Hz, 1H; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 2.5 ppm (m, 1H; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$); $^{13}\text{C}\{^1\text{H}\}$ NMR plus HSQC (CDCl_3 , 100.6 MHz): $\delta = 232.4$ (brs; $\text{Ru}(\text{CH})$), 199.3 (d, $J(\text{PP}) = 22.8$ Hz; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 140.7–119.7 (m; PPh_3 , PPh_2), 121.4 (d, $J(\text{PC}) = 25.4$ Hz; $\text{Ru}(\text{CHC}(\text{PPh}_3)\text{CH})$), 116.0 (d, $J(\text{PC}) = 76.1$ Hz; $\text{C}(\text{PPh}_3)$), 31.8 (d, $J(\text{PC}) = 73.0$ Hz; $\eta^2\text{-C}=\text{CH}(\text{PPh}_2)$), 21.4–19.4 ppm (m; $(\text{PPh}_2)\text{CH}_2$ - $(\text{PPh}_2)\text{CH}$, $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); elemental analysis calcd (%) for $\text{C}_{73}\text{H}_{62}\text{P}_5\text{Cl}_3\text{Ru}$: C 66.44, H 4.89; found: C 66.67, H 4.96.

[Os(NHC(CH₃)C(Ph)C(PPh₃)CH)Cl₂(PPh₂)₂Cl]BF₄ (10): A mixture of [Os{NHC(CH₃)C(Ph)C(PPh₃)CH}Cl₂(PPh₃)₂]BF₄ (9) (0.20 g, 0.15 mmol) and DPPM (115.0 mg, 0.30 mmol) in CH_2Cl_2 (15 mL) was heated at 80°C for about 8 h to give a reddish-brown solution. The volume of the mixture was reduced to ca. 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (5×2 mL), and dried under vacuum. Yield: 0.14 g, 81%; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162.0 MHz): $\delta = 21.1$ (s, $\text{C}(\text{PPh}_3)$), -56.0 (d, $J(\text{PP}) = 48.9$ Hz; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), -70.3 ppm (d, $J(\text{PP}) = 48.9$ Hz; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)); ^1H NMR (CD_2Cl_2 , 400.1 MHz): $\delta = 18.6$ (m, 1H; $\text{Os}(\text{CH})$), 14.0 (s, 1H; $\text{Os}(\text{NH})$), 7.9–6.8 (m, 40H; PPh_3 , PPh_2 , Ph), 5.6 (m, 1H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 4.9 (m, 1H; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 3.2 ppm (s, 3H; CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR plus HSQC (CD_2Cl_2 , 100.6 MHz): $\delta = 231.2$ (brs; $\text{Os}(\text{CH})$), 177.9 (d, $J(\text{PC}) = 12.6$ Hz; $\text{Os}(\text{NHC}(\text{CH}_3))$), 156.0 (d, $J(\text{PC}) = 17.6$ Hz; $\text{C}(\text{Ph})$), 138.2–126.5 (m; PPh_3 , PPh_2 , Ph), 120.4 (d, $J(\text{PC}) = 86.4$ Hz; $\text{C}(\text{PPh}_3)$), 47.6 (dd, $J(\text{PC}) = 34.4$, 29.2 Hz; $(\text{PPh}_2)\text{CH}_2$ - (PPh_2)), 27.0 ppm (d, $J(\text{PC}) = 4.8$ Hz; CH_3); elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{47}\text{P}_3\text{BNCl}_2\text{F}_4\text{Os}$: C 56.36, H 4.12, N 1.22; found: C 56.52, H 4.31, N 1.16.

Table 1. Crystal data and structure refinement for **2**, **3**, **4**, **6**, **8**, **10**, and **11**.

	2 ·2CH ₂ Cl ₂ ·4.5H ₂ O	3 ·2.5H ₂ O	4 ·2CH ₂ Cl ₂ ·H ₂ O	6 ·2C ₂ H ₄ Cl ₂ ·3H ₂ O	8 ·2CH ₂ Cl ₂ ·H ₂ O	10 ·CH ₂ Cl ₂	11 ·0.5CH ₂ Cl ₂
formula	C ₁₃₄ H ₁₂₃ Cl ₁₀ O _{4.50} P ₈ Os ₂	C ₉₁ H ₈₂ Cl ₃ O _{2.5} P ₆ Os	C ₇₅ H ₆₈ Cl ₇ OP ₃ Os	C ₉₅ H ₉₁ Cl ₇ O ₃ P ₆ Ru	C ₇₅ H ₆₈ Cl ₇ OP ₃ Ru	C ₅₅ H ₄₉ BCl ₄ F ₄ NP ₃ Os	C _{54.50} H ₄₈ BCl ₃ F ₄ NP ₃ Os
<i>M_r</i>	2787.98	1697.94	1578.49	1815.72	1489.36	1235.67	1193.21
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>c</i>
<i>a</i> [Å]	14.760	14.0436(6)	12.8157(3)	13.7874(6)	12.8175(7)	17.7813(3)	16.2316(4)
<i>b</i> [Å]	16.574	16.2871(7)	12.9155(5)	14.3003(4)	12.9053(5)	25.6340(5)	14.2474(3)
<i>c</i> [Å]	26.142	18.7655(9)	23.0235(8)	23.3547(10)	22.9884(6)	11.2708(2)	22.2103(5)
α [°]	82.91	90.031(4)	97.802(3)	101.551(3)	97.775(3)	90.00	90.00
β [°]	89.37	98.024(4)	90.707(2)	97.563(4)	90.424(3)	92.294(2)	97.072(2)
γ [°]	77.00	99.948(4)	109.699(3)	94.731(3)	109.644(4)	90.00	90.00
<i>V</i> [Å ³]	6183.1	4185.0(3)	3547.7(2)	4444.0(3)	3542.7(3)	5133.18(16)	5097.2(2)
<i>Z</i>	2	2	2	2	2	4	4
ρ_{calcd} [g cm ⁻³]	1.497	1.347	1.478	1.357	1.396	1.599	1.555
μ [mm ⁻¹]	2.427	1.781	2.217	0.544	0.642	2.839	2.806
<i>F</i> (000)	2810	1730	1592	1876	1528	2464	2380
crystal size [mm ³]	0.20 × 0.20 × 0.20	0.35 × 0.30 × 0.25	0.18 × 0.15 × 0.15	0.35 × 0.20 × 0.20	0.30 × 0.25 × 0.10	0.40 × 0.30 × 0.30	0.40 × 0.40 × 0.40
θ range [°]	2.31–25.00	2.12–25.00	2.27–25.00	2.20–25.00	2.25–25.00	2.19–25.00	2.19–25.00
reflns collected	46436	30133	23929	29770	24981	25211	22234
independent reflns	21459	14427	12221	15229	12266	9042	8971
observed reflns	11077	7321	8882	7102	7684	6959	6230
[<i>I</i> ≥ 2 σ (<i>I</i>)]							
data/restraints/params	21459/114/1432	14427/30/940	12221/36/790	15229/80/1027	12266/30/802	9042/12/622	8971/148/622
GOF on <i>F</i> ²	1.000	1.001	0.999	1.000	1.000	1.000	1.000
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0531/0.1165	0.0595/0.1631	0.0415/0.0764	0.0806/0.1878	0.0531/0.1236	0.0433/0.1100	0.0465/0.1341
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.1068/0.1251	0.1105/0.1729	0.0631/0.0791	0.1665/0.2073	0.0911/0.1394	0.0617/0.1154	0.0754/0.1400
largest peak/hole [e Å ⁻³]	2.179/−1.383	2.149/−0.593	2.196/−1.392	1.768/−1.263	1.027/−0.826	2.018/−2.054	1.711/−1.319

[Os{NH=C(CH₃)C(Ph)=(η^2 -C=CH)Cl₂(PPh₂)CH₂(PPh₂)(PPh₂)}]BF₄ (11**):** A mixture of [Os{NHC(CH₃)C(Ph)C(PPh₂)CH}Cl₂(PPh₂)CH₂(PPh₂)]BF₄ (**10**) (0.20 g, 0.17 mmol) and PPh₃ (89.1 mg, 0.34 mmol) in CH₂ClCH₂Cl (15 mL) was heated at 80 °C for about 4 days to give a red-dish-brown solution. The volume of the mixture was reduced to ca. 2 mL by evaporation of solvent under vacuum. Addition of diethyl ether (15 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (5 × 2 mL), and dried under vacuum. Yield: 0.12 g, 61%; ³¹P{¹H} NMR (CD₂Cl₂, 162.0 MHz): δ = 45.6 (dd, *J*(PP) = 32.8, 15.2 Hz; (PPh₂)CH₂(PPh₂)CH), 1.7 (dd, *J*(PP) = 358.5, 15.2 Hz; OsPPh₃), −17.3 ppm (d, *J*(PP) = 358.9, 32.8 Hz; (PPh₂)CH₂(PPh₂)CH); ¹H NMR plus HMQC (CD₂Cl₂, 300.1 MHz): δ = 9.4 (s, 1H; NH), 8.2–6.6 (m, 40H; PPh₃, PPh₂, Ph), 5.0 (m, 1H; PPh₂CH₂PPh₂), 3.6 (m, 2H; PPh₂CH₂PPh₂, η^2 -C=CH(PPh₂)), 1.29 ppm (s, 3H; CH₃); ¹³C{¹H} NMR plus DEPT-135 and HMQC (CD₂Cl₂, 75.5 MHz): δ = 204.8 (s; C(CH₃)), 180.2 (s; η^2 -C=CH(PPh₂)), 135.0–127.0 (m; PPh₃, PPh₂, Ph), 134.2 (s; C(Ph)), 23.5–23.2 (m; (PPh₂)CH₂(PPh₂)), 22.5 (m; η^2 -C=CH(PPh₂)), 21.0 ppm (s; CH₃); elemental analysis calcd (%) for C₅₄H₄₇P₃BNCl₂F₄Os: C 56.36, H 4.12, N 1.22; found: C 56.26, H 4.22, N 1.42.

X-ray crystallography: Crystals suitable for X-ray diffraction were grown from CH₂Cl₂ or CH₂ClCH₂Cl solutions layered with *n*-hexane for **2–4**, **6**, **8**, **10**, and **11**. Data collections were performed on an Oxford Gemini S Ultra CCD area detector by using graphite-monochromated MoK α radiation (λ = 0.71073 Å). Multiscan absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on *F*² by using the Bruker SHELXTL-97 program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Further details on crystal data, data collection, and refinements are summarized in Table 1.

CCDC-710832 (**2**), 710833 (**3**), 710834 (**4**), 710830 (**6**), 710831 (**8**), 761767 (**10**), and 761768 (**11**) contain the supplementary crystallographic data for

this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (nos. 20872123, 20801046, and 20925208) and the Research Fund for the Doctoral Program of Higher Education of China (no. 200803841034).

- [1] For recent reviews, see: a) J. R. Blecke, *Acc. Chem. Res.* **2007**, *40*, 1035–1047; b) G. Jia, *Coord. Chem. Rev.* **2007**, *251*, 2167–2187; c) L. J. Wright, *Dalton Trans.* **2006**, 1821–1827; d) C. W. Landorf, M. M. Haley, *Angew. Chem.* **2006**, *118*, 4018–4040; *Angew. Chem. Int. Ed.* **2006**, *45*, 3914–3936; e) G. Jia, *Acc. Chem. Res.* **2004**, *37*, 479–486; f) J. R. Blecke, *Chem. Rev.* **2001**, *101*, 1205–1227.
- [2] Recent examples of metallabenzene: a) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536–5540; b) V. Jacob, C. W. Landorf, L. N. Zakharov, T. J. R. Weakley, M. M. Haley, *Organometallics* **2009**, *28*, 5183–5190; c) J. R. Blecke, P. Putprasernt, T. Thananathanachon, N. P. Rath, *Organometallics* **2008**, *27*, 5744–5747; d) G. He, J. Zhu, W. Y. Hung, T. B. Wen, H. H.-Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2007**, *119*, 9223–9226; *Angew. Chem. Int. Ed.* **2007**, *46*, 9065–9068; e) H.-P. Wu, D. H. Ess, S. Lanza, T. J. R. Weakley, K. N. Houk, K. K. Baldrige, M. M. Haley, *Organometallics* **2007**, *26*, 3957–3968; f) K. Ilg, M. Paneque, M. L. Poveda, N. Rendón, L. L. Santos, E. Carmona, K. Mereiter, *Organometallics* **2006**, *25*, 2230–2236; g) H.-P. Wu, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2005**, *11*, 1191–1200; h) C. S. Chin, H. Lee, M.-S. Eum, *Organometallics* **2005**, *24*, 4849–4852; i) C. S. Chin, H. Lee,

- Chem. Eur. J.* **2004**, *10*, 4518–4522; j) C. W. Landorf, V. Jacob, T. J. R. Weakley, M. M. Haley, *Organometallics* **2004**, *23*, 1174–1176; k) R. D. Gilbertson, T. L. S. Lau, S. Lanza, H.-P. Wu, T. J. R. Weakley, M. M. Haley, *Organometallics* **2003**, *22*, 3279–3289; l) U. Effertz, U. Englert, F. Podewils, A. Salzer, T. Wagner, M. Kaupp, *Organometallics* **2003**, *22*, 264–274; m) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem.* **2002**, *114*, 3620–3623; *Angew. Chem. Int. Ed.* **2002**, *41*, 3470–3473; n) S. H. Liu, W. S. Ng, H. S. Chu, T. B. Wen, H. Xia, Z. Y. Zhou, C. P. Lau, G. Jia, *Angew. Chem.* **2002**, *114*, 1659–1661; *Angew. Chem. Int. Ed.* **2002**, *41*, 1589–1591; o) H.-P. Wu, S. Lanza, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 2824–2826; p) C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *J. Organomet. Chem.* **2001**, *623*, 109–115; q) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2000**, *6*, 437–441.
- [3] Recent examples of other metallaaromatics except metallabenzene: a) B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem.* **2009**, *121*, 5538–5542; *Angew. Chem. Int. Ed.* **2009**, *48*, 5430–5434; b) M. A. Esteruelas, I. Fernández, S. Fuertes, A. M. López, E. Oñate, M. A. Sierra, *Organometallics* **2009**, *28*, 4876–4879; c) M. A. Esteruelas, A. B. Masamunt, M. Oliván, E. Oñate, M. Valencia, *J. Am. Chem. Soc.* **2008**, *130*, 11612–11613; d) W. Y. Hung, J. Zhu, T. B. Wen, K. P. Yu, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2006**, *128*, 13742–13752; e) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856–2857; f) P. Barrio, M. A. Esteruelas, E. Oñate, *J. Am. Chem. Soc.* **2004**, *126*, 1946–1947; g) J. R. Bleeker, P. V. Hinkle, M. Shokeen, N. P. Rath, *Organometallics* **2004**, *23*, 4139–4149; h) H.-P. Wu, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 4320–4322; i) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem.* **2001**, *113*, 2005–2008; *Angew. Chem. Int. Ed.* **2001**, *40*, 1951–1954; j) J. R. Bleeker, P. V. Hinkle, N. P. Rath, *Organometallics* **2001**, *20*, 1939–1951; k) J. R. Bleeker, J. M. B. Blanchard, E. Donnay, *Organometallics* **2001**, *20*, 324–336.
- [4] Recent examples of theoretical work: a) A. C. Tsipis, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8244–8261; b) W. R. W. Welch, S. Harris, *Inorg. Chim. Acta* **2008**, *361*, 3012–3016; c) G. Periyasamy, N. A. Burton, I. H. Hillier, J. M. H. Thomas, *J. Phys. Chem. A* **2008**, *112*, 5960–5972; d) E. M. Brzostowska, R. Hoffmann, C. A. Parish, *J. Am. Chem. Soc.* **2007**, *129*, 4401–4409; e) I. Fernández, G. Frenking, *Chem. Eur. J.* **2007**, *13*, 5873–5884; f) J. Zhu, G. Jia, Z. Lin, *Organometallics* **2007**, *26*, 1986–1995; g) A. Karton, M. A. Iron, M. E. van der Boom, J. M. L. Martin, *J. Phys. Chem. A* **2005**, *109*, 5454–5462; h) M. A. Iron, A. C. B. Lucassen, H. Cohen, M. E. van der Boom, J. M. L. Martin, *J. Am. Chem. Soc.* **2004**, *126*, 11699–11710; i) M. A. Iron, J. M. L. Martin, M. E. van der Boom, *J. Am. Chem. Soc.* **2003**, *125*, 13020–13021; j) M. A. Iron, J. M. L. Martin, M. E. van der Boom, *J. Am. Chem. Soc.* **2003**, *125*, 11702–11709; k) M. A. Iron, J. M. L. Martin, M. E. van der Boom, *Chem. Commun.* **2003**, 132–133; l) S. M. Ng, X. Huang, T. B. Wen, G. Jia, Z. Lin, *Organometallics* **2003**, *22*, 3898–3904; m) Y. Huang, S. Yang, X. Li, *Chin. J. Chem. Phys.* **2003**, *16*, 440–444.
- [5] S_EAr reactions of metallabenzene: a) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2008**, *27*, 451–454; b) T. B. Wen, S. M. Ng, W. Y. Hung, Z. Y. Zhou, M. F. Lo, L.-Y. Shek, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2003**, *125*, 884–885; c) C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *Angew. Chem.* **2000**, *112*, 766–768; *Angew. Chem. Int. Ed.* **2000**, *39*, 750–752.
- [6] S_NAr reactions of metallabenzene: T. Wang, S. Li, H. Zhang, R. Lin, F. Han, Y. Lin, T. B. Wen, H. Xia, *Angew. Chem.* **2009**, *121*, 6575–6578; *Angew. Chem. Int. Ed.* **2009**, *48*, 6453–6456.
- [7] D. L. Thorn, R. Hoffmann, *Nouv. J. Chim.* **1979**, *3*, 39–45.
- [8] CO_2Me -substituted iridaaromatics: a) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, L. L. Santos, E. Álvarez, V. Salazar, K. Mereiter, E. Oñate, *Organometallics* **2007**, *26*, 3403–3415; b) M. Paneque, M. L. Poveda, N. Rendón, E. Álvarez, E. Carmona, *Eur. J. Inorg. Chem.* **2007**, 2711–2720; c) E. Álvarez, M. Paneque, M. L. Poveda, N. Rendón, *Angew. Chem.* **2006**, *118*, 488–491; *Angew. Chem. Int. Ed.* **2006**, *45*, 474–477; d) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898–9899.
- [9] Phosphonium-substituted metallabenzene: a) B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem.* **2009**, *121*, 5569–5572; *Angew. Chem. Int. Ed.* **2009**, *48*, 5461–5464; b) H. Zhang, L. Wu, R. Lin, Q. Zhao, G. He, F. Yang, T. B. Wen, H. Xia, *Chem. Eur. J.* **2009**, *15*, 3546–3559; c) L. Gong, Z. Chen, Y. Lin, X. He, T. B. Wen, X. Xu, H. Xia, *Chem. Eur. J.* **2009**, *15*, 6258–6266; d) L. Gong, Y. Lin, T. B. Wen, H. Zhang, B. Zeng, H. Xia, *Organometallics* **2008**, *27*, 2584–2589; e) L. Gong, Y. Lin, G. He, H. Zhang, H. Wang, T. B. Wen, H. Xia, *Organometallics* **2008**, *27*, 309–311; f) H. Zhang, L. Feng, L. Gong, L. Wu, G. He, T. Wen, F. Yang, H. Xia, *Organometallics* **2007**, *26*, 2705–2713; g) H. Zhang, H. Xia, G. He, T. B. Wen, L. Gong, G. Jia, *Angew. Chem.* **2006**, *118*, 2986–2989; *Angew. Chem. Int. Ed.* **2006**, *45*, 2920–2923; h) H. Xia, G. He, H. Zhang, T. B. Wen, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 6862–6863.
- [10] CO_2Me -substituted tethered metallabenzene: a) G. R. Clark, T. R. O’Neale, W. R. Roper, D. M. Tonei, L. J. Wright, *Organometallics* **2009**, *28*, 567–572; b) G. R. Clark, G.-L. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167–2177; c) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771–1777.
- [11] Additional examples of metallabenzofurans: a) H. Yamazaki, K. Aoki, *J. Organomet. Chem.* **1976**, *122*, C54–C58; b) R. Birk, U. Grössmann, H.-U. Hund, H. Berke, *J. Organomet. Chem.* **1988**, *345*, 321–329; c) U. Grössmann, H.-U. Hund, H. W. Bosch, H. Schmalke, H. Berke, *J. Organomet. Chem.* **1991**, *408*, 203–218; d) M. I. Bruce, B. C. Hall, B. W. Skelton, E. R. T. Tiekink, A. H. White, N. N. Zaitseva, *Aust. J. Chem.* **2000**, *53*, 99–107.
- [12] See the Supporting Information.
- [13] J. R. Bleeker, R. Behm, Y.-F. Xie, M. Y. Chiang, K. D. Robinson, A. M. Beatty, *Organometallics* **1997**, *16*, 606–623.
- [14] Based on a search of the Cambridge Structural Database, CSD version 5.31 (November 2009).
- [15] See, for examples: a) Q. Wang, L. Liu, C. Lin, H. Sun, W.-X. Zhang, Z. Xi, *Dalton Trans.* **2009**, 10433–10435; b) T. B. Wen, W. Y. Hung, H. H.-Y. Sung, Z. Zhou, I. D. Williams, G. Jia, *Eur. J. Inorg. Chem.* **2007**, 2693–2701; c) T. Yu, X. Sun, C. Wang, L. Deng, Z. Xi, *Chem. Eur. J.* **2005**, *11*, 1895–1902; d) C. S. Chin, M. Kim, H. Lee, S. Noh, K. M. Ok, *Organometallics* **2002**, *21*, 4785–4793; e) R. P. Hughes, H. A. Trujillo, J. W. Egan, Jr., A. L. Rheingold, *J. Am. Chem. Soc.* **2000**, *122*, 2261–2271, and references therein; f) Z. Xi, S. Huo, Y. Noguchi, T. Takahashi, *Chem. Lett.* **2000**, 218–219; g) Z. Xi, R. Fischer, R. Hara, W.-H. Sun, Y. Obora, N. Suzuki, K. Nakajima, T. Takahashi, *J. Am. Chem. Soc.* **1997**, *119*, 12842–12848.
- [16] Jackson–Meisenheimer complexes, also referred to as anionic σ complexes or Meisenheimer complexes, are key intermediates in the S_NAr mechanism of aromatic nucleophilic substitution reactions. They are formed by the covalent addition of nucleophiles to a ring carbon atom of aromatic or heteroaromatic substrates bearing electron-withdrawing substituents and have been characterized as stable or transient species. For details, see: F. Terrier, *Chem. Rev.* **1982**, *82*, 77–152.
- [17] a) E. Rüba, K. Mereiter, R. Schmid, V. N. Sapunov, K. Kirchner, H. Schottenberger, M. J. Calhorda, L. F. Veiros, *Chem. Eur. J.* **2002**, *8*, 3948–3961; b) E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, H. Schottenberger, *J. Organomet. Chem.* **2001**, *637*, 70–74.
- [18] S. Doherty, M. R. J. Elsegood, W. Clegg, D. Mampe, N. H. Rees, *Organometallics* **1996**, *15*, 5302–5308.
- [19] F. H. Antwi-Nsiah, O. Oke, M. Cowie, *Organometallics* **1996**, *15*, 506–520.
- [20] J. G. López-Cortés, A. Samano-Galindo, M. C. Ortega-Alfaro, A. Toscano, H. Rudler, A. Parlier, C. Alvarez-Toledano, *J. Organomet. Chem.* **2005**, *690*, 3664–3668.

Received: February 5, 2010
Published online: April 30, 2010