DOI: 10.1002/chem.201003566

New Highly Stable Metallabenzenes via Nucleophilic Aromatic Substitution Reaction

Ran Lin, Hong Zhang,* Shunhua Li, Jiani Wang, and Haiping Xia*[a]

Abstract: Treatment of the ruthenabenzene [Ru{CHC(PPh_3)CHC(PPh_3)CH}Cl_2(PPh_3)$_2$]Cl (**1**) with excess 8-hydroxyquinoline in the presence of CH_3COONa under air atmosphere produced the S_NAr product [(C_9H_6NO)Ru{CHC(PPh_3)CHC(PPh_3)C}(C_9H_6NO)(PPh_3)]Cl_2 (**3**). Ruthenabenzene **3** could be stable in the solution of weak alkali or weak acid. However, reaction of **3** with NaOH afforded a 7:1 mixture of ruthenabenzenes [(C_9H_6NO)Ru{CHC(PPh_3)CHCHC}(C_9H_6NO)(PPh_3)]Cl (**4**) and [(C_9H_6NO)Ru{CHCHCHC(PPh_3)C}(C_9H_6NO)(PPh_3)]Cl (**5**), presumably involving a P–C bond cleavage of the metallacycle. Complex **3** was also reactive to HCl, which results in a transformation of **3** to ruthenabenzene [Ru{CHC(PPh_3)CHC(PPh_3)C}Cl_2(C_9H_6NO)(PPh_3)]Cl (**6**) in high yield. Thermal stability tests showed that ruthenabenzenes **4**, **5**, and **6** have remarkable thermal stability both in solid state and in solution under air atmosphere. Ruthenabenzenes **4** and **5** were found to be fluorescent in common solvents and have spectral behaviors comparable to those organic multicyclic compounds containing large π-extended systems.

Keywords: 8-hydroxyquinoline · metallabenzene · nucleophilic aromatic substitution reaction · photoluminescence · stability

Introduction

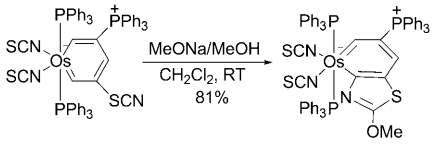
Metallabenzenes are an attractive class of organometallic complexes because they can display aromatic properties and mediate organometallic reactions.[1] As one of the major issues of metallabenzene chemistry, the isolation and characterization of stable metallabenzenes have been extensively investigated.[2–5] Most of the well characterized stable metallabenzenes are those with a transition metal of the third transition series, especially osmium,[3] iridium[4] and platinum.[5] In contrast, isolation of metallabenzenes with a metal of the first or the second transition series has met with limited success,[6–9] although they have been frequently proposed as reactive intermediates.[10] Furthermore, the majority of such species should be stabilized by coordination of π-system to another metal fragment,[6] or have only been detected spectroscopically at low temperature.[7] We have prepared a series of phosphonium-substituted ruthenabenzenes, which represent the first stable examples of non-metal-coordinated metallabenzenes containing a transition metal of the second transition series.[8] The bicyclic species, which were described as tethered metallabenzenes, constitute an addition to this special class of metallabenzenes.[9] In the literatures, there are few studies on the reactivities and properties of metallabenzenes with the first- or second-row transition metals due to the rare examples.[8a,9a,11]

Researches on unique characteristic chemical reactions of metallabenzenes, such as electrophilic aromatic substitution (S_EAr) or nucleophilic aromatic substitution (S_NAr), are of great importance not only to provide strong chemical support for the aromaticity of the metallabenzene ring but also to obtain new interesting organometallic complexes. For example, Roper, Wright, and co-workers have demonstrated that the S_EAr reaction of metallabenzenes could afford the related halo-metallabenzenes.[12] While this manuscript was still in preparation, they also reported the first metallabenzene reactions that involve intermolecular S_NAr of hydrogen by external nucleophiles.[13] Paneque et al. reported that the nucleophilic attack of HO^- or MeO^- to iridaaromatics allowed the formation of Jackson–Meisenheimer complexes.[14] In addition, metallabenzynes, the relative of metallabenzenes, can also undergo S_EAr and nucleophilic aromatic addition reactions.[15] In our previous study, we found that the intramolecular S_NAr reaction of osmabenzene [Os{CHC(PPh_3)CHC(SCN)CH}$(NCS)_2$(PPh_3)$_2$] led to the isolation of the first metallabenzothiazole [Eq. (1)],[16] and the nucleophilic aromatic addition reactions of metallabenzene [M{CHC(PPh_3)CHC(PPh_3)CH}Cl_2(PPh_3)$_2$]Cl (M = Os or Ru) produced the metallacyclohexadiene and η^2-allene-coordinated metallacycles [Eq. (2)].[11] These observations prompted us to search new nucleophilic reagents to construct metallaaromatics with special properties.

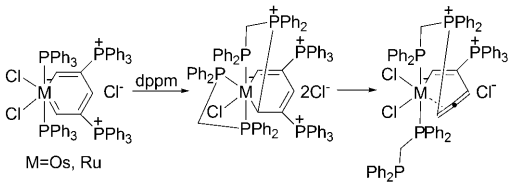
8-Hydroxyquinoline has long been regarded as a versatile and useful bidentate ligand with a variety of applications.[17] Thus we envisioned that related multicyclic complexes with special properties might be formed if 8-hydroxyquinoline

[a] R. Lin, Dr. H. Zhang, Dr. S. Li, J. Wang, 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

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



(1)

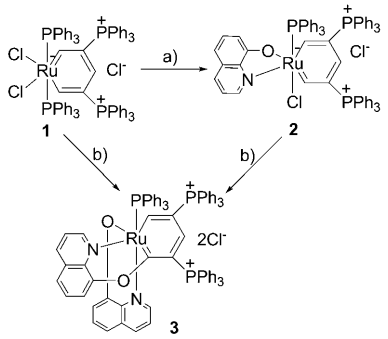


(2)

could act as an external nucleophile to react with our ruthenabenzenes. In this paper, we report the first S_NAr reaction of ruthenabenzene, which was attacked by 8-hydroxyquinoline and generated a multicyclic complex containing a metallabenzene unit. Further treatments of this new multicyclic complex achieved the highly stable metallabenzenes with notable anti-acid or anti-alkali properties. Considering the large π-extended structures of these multicyclic complexes, their photoluminescence properties were also studied. The details of the results are reported in the following section.

Results and Discussion

Reactions of ruthenabenzene with 8-hydroxyquinoline: Treatment of **1** with 1.5 equivalents of 8-hydroxyquinoline in dichloromethane led to the formation of the corresponding monosubstituted ruthenabenzene **2** (Scheme 1). The



Scheme 1. Reactions of ruthenabenzene **1** with 8-hydroxyquinoline. a) 8-hydroxyquinoline (1.5 equiv), CH_2Cl_2, 2 h; b) 8-hydroxyquinoline (5.0 equiv), CH_3COONa (10 equiv), CH_2Cl_2, under air atmosphere, 24 h.

structure of **2** can be deduced easily, as its NMR data is similar to our previously reported ruthenabenzene [Ru{CHC(PPh$_3$)CHC(PPh$_3$)CH}Cl(bipy)(PPh$_3$)]Cl$_2$,[8] which has been structurally characterized by X-ray diffraction. In particular, the $^{31}P\{^1H\}$ NMR spectrum shows three singlet peaks at δ = 36.4 (Ru*P*Ph$_3$), 18.6 (C*P*Ph$_3$) and 18.4 ppm (C*P*Ph$_3$). In the ^1H NMR spectrum, the two signals of RuC*H* appear at δ = 16.8 and 16.4 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the five carbon signals of the metallacycle appear at δ = 294.1 (Ru*C*H), 289.7 (Ru*C*H), 145.5 (γ-*C*H), 116.1 (*C*PPh$_3$) and 114.0 ppm (*C*PPh$_3$).

When the proportion of 8-hydroxyquinoline in this reaction was increased, the expected nucleophilic attack of 8-hydroxyquinoline on a carbon of the metallacycle has not been detected. However, in the presence of CH_3COONa and under air atmosphere, the reaction of complex **1** with excess 8-hydroxyquinoline afforded the S_NAr product **3** (Scheme 1). As suggested by in situ NMR, we defined complex **1** with 5.0 equivalents of 8-hydroxyquinoline in the presence of 10 equivalents CH_3COONa in CH_2Cl_2 under air atmosphere as the standard conditions, which could ensure the complete transformation of **1** in 24 h. The reaction of isolated **2** with excess 8-hydroxyquinoline under the same conditions gave the same result. In both reactions, the product **3** could not be obtained in the absence of CH_3COONa. In addition, the reactions did not proceed when manipulations were carried out under nitrogen atmosphere.

As complex **3** has good solubility in organic solvents, it is difficult to obtain the single crystal of **3** to determine its solid-state structure. Fortunately, the counter anion Cl^- in **3** can be easily replaced with BPh_4^- by treatment of **3** with $NaBPh_4$ to give ruthenabenzene **3′**. The structure of **3′** was confirmed unambiguously by X-ray diffraction. As shown in Figure 1, complex **3′** contains an essentially planar metallabenzene unit. The maximum deviation from the least-squares plane through Ru1 and C1–C5 is 0.0566 (0.0035) Å for C1, and the sum of angles in the six-membered ring is 719.4°, which is very close to the ideal value of 720°. It is interesting that even the seventeen atoms of the metallacycle (Ru, C1–C5) and the 8-hydroxyquinoline ring (N1, O1, and

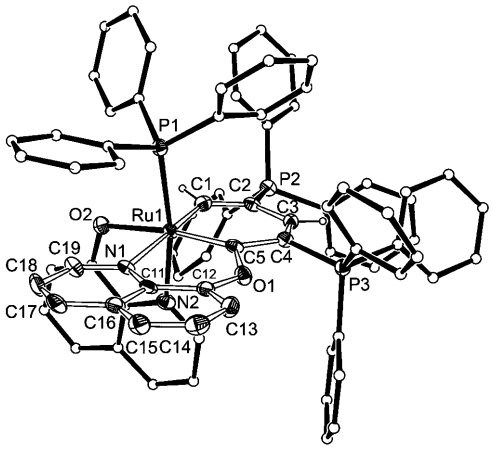
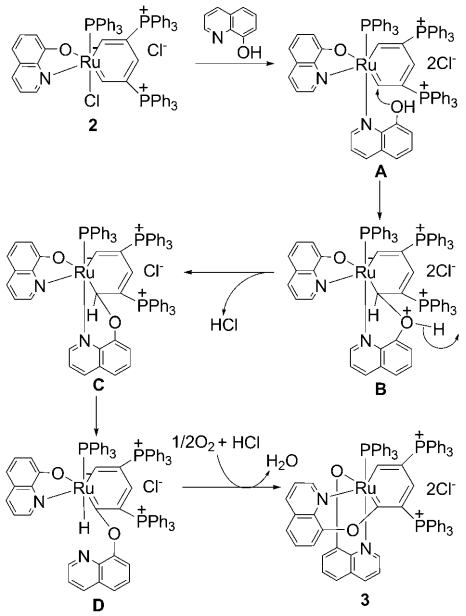


Figure 1. Moleculr structure for the cation of complex **3′** (ellipsoids at the 50% probability level). Counter anion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–P1: 2.3802(15), Ru1–N2: 2.129(5), Ru1–O2: 2.151(4), Ru1–N1: 2.187(5), Ru1–C1: 1.937(6), Ru1–C5: 1.886(5), C1–C2: 1.383(8), C2–C3: 1.419(8), C3–C4: 1.382(7), C4–C5: 1.455(8), P2–C2: 1.794(5), P3–C4: 1.802(5); P1-Ru1-N2: 169.75(13), O2-Ru1-N1: 88.48(16), C1-Ru1-C5: 92.0(2), Ru1-C1-C2: 128.4(4), C1-C2-C3: 123.0(5), C2-C3-C4: 125.2(5), C3-C4-C5: 122.3(5), C4-C5-Ru1: 128.5(4).

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

C11–C19) are approximately coplanar, which is reflected by the mean deviation (0.0726 Å) from the least-squares plane. The Ru1–C5 bond (1.886(5) Å) is appreciably shorter than the Ru1–C1 bond (1.937(6) Å). The similar trend has been observed in Bleeke's iridaphenol [Ir{=C(OH)C(Me)=CHC(Me)=CH}(OTf)(PMe_3)$_3$]OTf (1.916(16) and 2.031(16) Å)[18] and Jia's osmaphenol [Os{=C(OH)CH=C(Me)C($SiMe_3$)=CH)(bipy)(PPh_3)$_2$]OTf (1.921(4) and 2.010(4) Å),[15a] respectively. Probably due to the electronic asymmetry of the substituent groups, the C4–C5 bond (1.455(8) Å) is markedly longer than other C–C bonds of the metallacycle (C1–C2 1.383(8), C2–C3 1.419(8), C3–C4 1.382(7) Å). Overall, the Ru–C and C–C bond distances within the six-membered ring, together with its planar nature, still indicate that the metallacycle has a generally delocalized structure.

On the basis of the characterized structure of **3** and the reaction conditions, a plausible mechanism for the reaction of ruthenabenzene **2** with 8-hydroxyquinoline is proposed in Scheme 2. Ligand substitution in complex **2** with coordination of the N atom of 8-hydroxyquinoline initially gives **A**, which could undergo intramolecular nucleophilic addition with the free hydroxyl group of the 8-hydroxyquinoline ligand to give the O-protonation intermediate **B**. Elimination of HCl from **B** could produce the Jackson–Meisenheimer **C**. Subsequent dissociation of the 8-hydroxyquinoline ligand from metal center and α-H migration from C_α atom of the metallacycle to metal center may produce hydridometallabenzene intermediate **D**. Finally, the oxidation of **D**, followed by the recoordination of the 8-hydroxyquinoline N atom to the ruthenium center would yield ruthenabenzene **3**. It is also possible that an H_2 elimination in B gives **3** directly in the presence of O_2. Consistent with the mechanism, the formation of **3** could not be observed when the reaction was performed under oxygen-free atmosphere. The addition of excess CH_3COONa may facilitate the intramolecular nucleophilic attack of the 8-hydroxyquinoline to aromatic metallacycle.

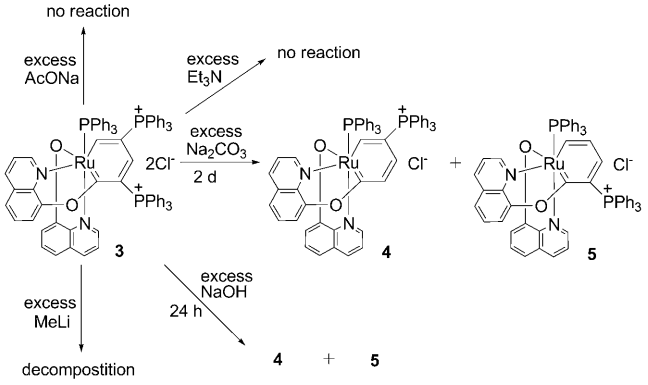


Scheme 2. Plausible mechanism for the S_NAr reaction of ruthenabenzene **2** with 8-hydroxyquinoline.

This mechanism is parallel to our previous reported intramolecular S_NAr reaction of osmabenzene.[16] The convincing evidence that nucleophilic addition may be a reasonable initial step was provided by the isolation of the Jackson–Meisenheimer complexes in the nucleophilic aromatic addition reactions[11,14] and in the intermolecular S_NAr reactions of metallabenzenes.[13] These observations suggest that the nucleophilic reactivity of the metallacycle can be promoted when the electron density of the aromatic ring is significantly decreased by the electron-withdrawing groups.

Reactivity of ruthenabenzene 3 with alkalis or acids: As mentioned above, the excess CH_3COONa has been regarded as one of essential conditions for the formation of ruthenabenzene **3**. Thus, it appears that complex **3** could be stable in the solution with weak alkali. To further investigate the stability/reactivity of this new tethered ruthenabenzene, **3** was subjected to a variety of alkali or acid conditions. As shown in Scheme 3, **3** has good stability in solution in the presence of weak alkali, such as CH_3COONa, $NaHCO_3$, and triethylamine. When excess Na_2CO_3 was added to the solution of **3** in methanol, slow transformation was observed during the course of two days of observation. The transformation proceeded better when the water solution of excess NaOH was added instead. As monitored by in situ NMR spectroscopy, when a solution of **3** in methanol was stirred for 24 h in the presence of two equivalents NaOH, **3** was completely consumed to give a 7:1 mixture of **4** and **5** (Scheme 3).

A pure sample of compound **4** can be obtained from the reaction mixture by column chromatography in 73% yield. The structure of **4** has been determined by X-ray diffraction study, and a view of the cation of **4** is shown in Figure 2. The structural feature associated with the metallacycle of **4**



Scheme 3. Reactions of ruthenabenzene **3** with alkali.

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

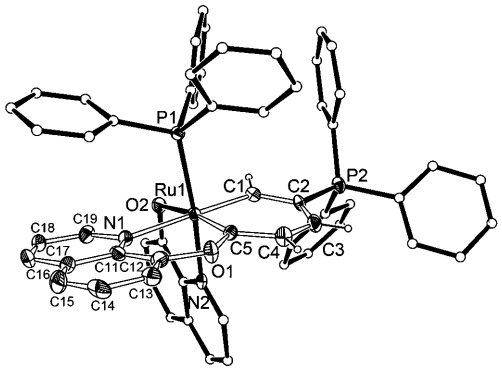
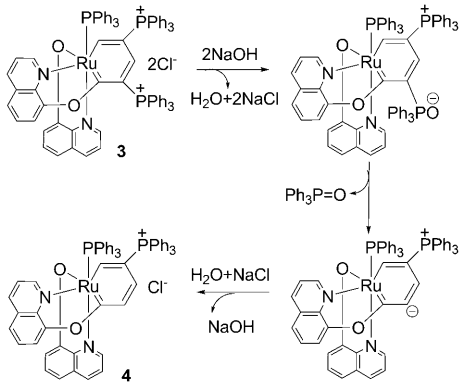


Figure 2. Molecular structure for the cation of complex **4** (ellipsoids at the 50% probability level). Counter anion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1−N2: 2.124(4), Ru1−P1: 2.3593(14), Ru1−O2: 2.174(3), Ru1−N1: 2.183(4), Ru1−C1: 1.962(5), Ru1−C5: 1.880(5), C1−C2: 1.368(6), C2−C3: 1.423(6), C3−C4: 1.355(7), C4−C5: 1.436(6), P2−C2: 1.776(5); N2-Ru1-P1: 169.32(11), O2-Ru1-N1: 89.05(14), C1-Ru1-C5: 90.0(2), Ru1-C1-C2: 129.0(4), C1-C2-C3: 122.3(5), C2-C3-C4: 124.7(5), C3-C4-C5: 123.4(5), C4-C5-Ru1: 129.3(4).

is very similar to that of **3**. The metallacycle and the 8-hydroxyquinoline ring are essentially coplanar (the mean deviation from the least-squares plane through all seventeen atoms is 0.0708 Å). And the Ru1−C5 bond (1.880(5) Å) is also shorter than the Ru1−C1 bond (1.962(5) Å). Although the C−C distances within the six-membered ruthenacyclic ring of **4** show considerable alternation (C1−C2 1.368(6), C2−C3 1.423(6), C3−C4 1.355(7), C4−C5 1.436(6) Å), all of the four-bond distances still fall within the range observed for other metallabenzenes,[2–5] indicating a certain degree of delocalization within the metallacycle system of **4**. Consistent with the solid-state structure, the ^{1}H and ^{13}C NMR chemical shifts of the ring atoms appear in the aromatic region. The ^{1}H NMR spectrum displays the Ru*CH* signal at $\delta = 13.7$ ppm, the RuCHC(PPh_3)C*H* signal at $\delta = 7.4$ ppm and the RuCHC(PPh_3)CHC*H* signal at 6.6 ppm. The $^{13}C\{^{1}H\}$ NMR spectrum shows the five carbon signals of the metallacycle at $\delta = 264.7$ (Ru*C*H), 110.4 (*C*(PPh_3)), 142.2 (γ-*C*H), 119.4 (RuCHC(PPh_3)CH*C*H) and 286.3 ppm (Ru*C*).

Complex **5** can be isolated as a green solid from the reaction mixture by column chromatography in approximately 8% yield. The structure of **5** can be assigned readily, as its characterizing spectroscopic data is similar to those of **4**, which has been confirmed by X-ray diffraction. In terms of chemical composition, complex **5** is almost the same as **4** in that they all contain one six-membered ruthenacyclic ring, one PPh_3 ligand and two 8-hydroxyquinoline groups. The only difference is the position of the phosphonium group of **5** attached to the β-carbon.

A rationale that accounts for the observed results is shown in Scheme 4. The formation of **4** or **5** may involve a P−C bond cleavage of metallacycle. Easy breaking of the P−C bond is not surprising, as the alkaline hydrolysis of phosphonium salts have been studied extensively and there is general agreement about the mechanism of the hydrolysis

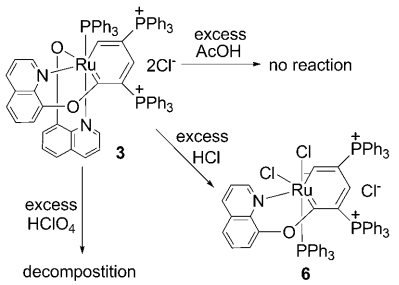


Scheme 4. Plausible mechanism for the formation of ruthenabenzene **4**.

reaction.[19] The favored pathway to form **4** is presumably due to the steric effect introduced by the 8-hydroxyquinoline substituent of the metallacycle.

We studied the reaction of **3** with MeLi as well. Decomposition of **3** was observed, which resulted in a number of phosphorus-containing species which proved difficult to be separated and identified.

Complex **3** can tolerate weak acid AcOH in solution. When excess HCl were allowed to react with **3**, the reaction yielded **6** in four hours (Scheme 5). The in situ ^{1}H NMR experiment showed that similar reaction occurred when excess HF, HBF_4, or H_3PO_4 was added to the solution of **3**, although the reactions were slower and some unreacted **3** was detectable by NMR after four hours.



Scheme 5. Reactions of ruthenabenzene **3** with acids.

Complex **6** is isolated as a green solid in 91% yield. The structure of **6** has been confirmed by X-ray diffraction (Figure 3). The most notable structural feature of **6** is that the metallacycle ring deviates significantly from planarity. The mean deviation from the least-squares plane through the C1−C5 chain is 0.0250 Å. The Ru is out of the plane of the metallacyclic carbon atoms by 0.5243 (51) Å. The 8-hydroxyquinoline ring is out of the plane, which differs from the related complex **3′** and **4**. Despite the relatively long C4−C5 bond length, the lack of significant alternations in the other C−C bond lengths and the Ru−C distances of metallacycle suggest the delocalized structure of **6**, which is similar to those reported nonplanar metallabenzenes.[4m,12,14,15a]

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

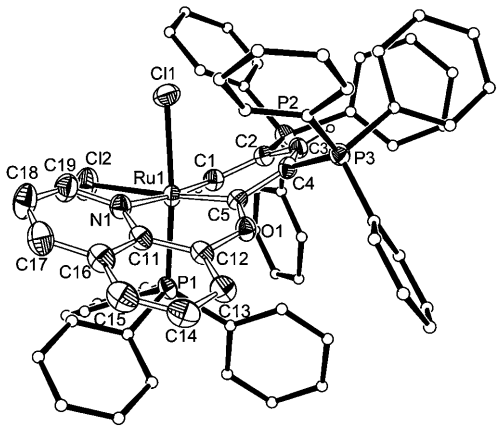


Figure 3. Molecular structure for the cation of complex **6** (ellipsoids at the 50% probability level). Counter anion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1−Cl1: 2.4570(14), Ru1−P1: 2.3393(14), Ru1−Cl2: 2.5160(15), Ru1−N1: 2.215(4), Ru1−C1: 1.921(4), Ru1−C5: 1.881(4), C1−C2: 1.401(6), C2−C3: 1.405(6), C3−C4: 1.388(6), C4−C5: 1.440(6), P2−C2: 1.788(4), P3−C4: 1.790(4); Cl1-Ru1-P1: 173.60(4), Cl2-Ru1-N1: 89.85(10), C1-Ru1-C5: 91.46(17), Ru1-C1-C2: 125.4(3), C1-C2-C3: 123.5(4), C2-C3-C4: 124.3(4), C3-C4-C5: 122.2(4), C4-C5-Ru1: 125.0(3).

The nonplanarity found in metallabenzene complexes has been investigated theoretically via DFT calculations.[20] In addition, the characteristic spectroscopic data related to **6** demonstrate the ruthenabenzene formulation. The ^{1}H NMR spectrum shows two ^{1}H NMR signals at δ = 16.5 and 7.4 ppm for the two CH of the metallacycle. The ^{31}P{^{1}H} NMR spectrum shows three singlet peaks at δ = 46.0 (Ru*P*Ph$_3$), 24.0 (C*P*Ph$_3$), 17.6 ppm (C*P*Ph$_3$). In the ^{13}C{^{1}H} NMR spectrum, the five carbon signals of the metallacycle appear at δ = 292.6 (Ru*C*H), 113.4 (*C*(PPh$_3$)), 154.8 (γ-*C*H), 105.6 (*C*(PPh$_3$)) and 273.2 ppm (Ru*C*).

The reaction of complex **3** with $HClO_4$ has also been carried out. The in situ NMR experiment indicated that addition of the strong oxidizing acid $HClO_4$ to the solution of **3** in methanol caused the completely decomposition of complex **3**. The decomposition destroyed the metallabenzene ring and released triphenylphosphine oxide.

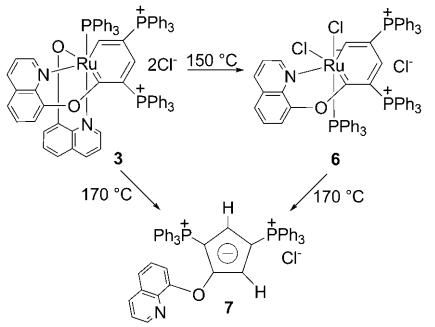
Thermal decomposition reactions of ruthenabenzenes: With the anti-acid and anti-alkali ruthenabenzenes in hand, we turned to examine their thermal stability. The thermal stability tests have been performed in air, and the results are given in Table 1. We have reported the unusually high thermal stability of ruthenabenzene **1**.[8a] As shown in Table 1, these new species of metallabenzenes containing 8-hydroxyquinoline group have even more remarkable stability, especially complexes **4** and **5**. Solid sample of **4** or **5** can be heated at 170 °C for at least five hours without noticeable decomposition. When the temperature was increased to 190 °C, as indicated by in situ NMR, the sample decomposed to form a mixture of species with triphenylphosphine oxide as the dominant product.

The acid-resistant ruthenabenzene **6** is very stable, which remains nearly unchanged in solid state after heated at 150 °C for five hours. When the solid sample of **6** is heated at 170 °C, the decomposition occurs (Scheme 6). The major decomposition product **7** could be isolated by column chromatography. The structure of **7** has been determined by X-ray diffraction study, and the molecular structure is shown in Figure 4. Compound **7** contains a planar five-membered carboncycle with one 8-hydroxyquinoline substituent and two PPh$_3$ substituents. The co-planarity is reflected by the very small mean deviations (0.0017 Å) from the least-squares planes through the five atoms C1, C2, C3, C4, and C5. Compound **7** is closely related to compound **8**, the thermal decomposition product of ruthenabenzene **1**,[8a] which has been preveniently assigned to the few stable cyclopentadienyl ion examples [Eq. (3)]. In previous literatures, there are ample evidences for the ready conversion of metallabenzenes to η^5- or η^1-cyclopentadienyl complexes.[3a,4k–p] It is speculated that the transformation to cyclopentadienyl ion in our metallabenzene systems may be attributed to the presence of bulky phosphonium substituents.

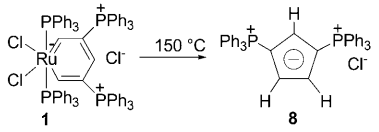
Table 1. Thermal decomposition data of ruthenabenzenes **1**–**6** in solid state.[a]

	100 °C	120 °C	150 °C	170 °C	190 °C
1[8]	●[b]	△[c]	■$_1$[d]	–	–
2	●	△	■$_1$	–	–
3	●	△	■$_2$[e]	–	–
4	●	●	●	●	■$_3$[f]
5	●	●	●	●	■$_3$[f]
6	●	●	●	■$_4$[g]	–

[a] All reactions were carried out for 5 h. [b] ● = Stable. [c] △ = Partly decomposed. [d] ■$_1$ = Completely decomposed, major product is complex **8**. [e] ■$_2$ = Completely decomposed, major product is complex **6**. [f] ■$_3$ = Completely decomposed, major product is Ph_3PO. [g] ■$_4$ = Completely decomposed, major product is complex **7**.



Scheme 6. Thermal decomposition reactions of ruthenabenzenes **3** and **6**.



(3)

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

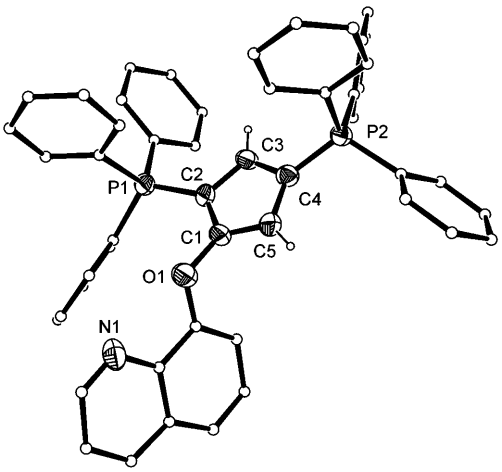


Figure 4. Molecular structure for the cation of complex **7** (ellipsoids at the 50% probability level). Counter anion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1−C2: 1.430(6), C2−C3: 1.407(5), C3−C4: 1.400(6), C4−C5: 1.444(6), O1−C1: 1.398(5), P1−C2: 1.749(4), P2−C4: 1.737(4); C1-C2-C3: 106.0(4), C2-C3-C4: 109.0(4), C3-C4-C5: 107.8(4), C4-C5-C1: 106.7(4), C5-C1-C2: 110.5(4).

The thermal stability of ruthenabenzenes **3**–**6** in solution has also been studied. Comparison of the thermal stability of ruthenabenzene series in DMSO is presented in Table 2. It should be noted that heating solution of **4** and **5** at 120°C did not result in appreciable decomposition.

Table 2. Thermal decomposition data of ruthenabenzenes **3** and **4** in solution.[a]

	100°C	110°C	120°C	140°C
3	●	■$_2$	–	–
4	●	●	●	■$_3$
5	●	●	●	■$_3$
6	●	●	■$_4$	–

[a] For definition see footnote in Table 1.

We have recently reported some noticeable stable metallaaromatics, including osmabenzenes,[3b] osmapyridine,[3c] osmanaphthalyne,[3d] and ruthenabenzenes.[8] Except our prevenient paper, there are only a few reports about thermal stability of metallaaromatics.[4j,k,m,o,5a,21,22] Haley et al. demonstrated that their iridabenzene [Ir{CHCHCHC(Ph)C(Ph)}(CO)(PPh_3)$_2$] is thermally stable to about 200°C, which represents the first and the only documented example of metallabenzenes that are stable above 110°C.[4o] To the best of our knowledge, ruthenabenzenes **4**, **5**, and **6** are the first examples of metallabenzenes with a metal of the first or the second transition series having such remarkable thermal stability both in solid state and in solution under air atmosphere. Thus, it gives new hopes for future development of our ruthenabenzenes in application researches, considering that ruthenium complexes are known for effective catalytic performance, abundant spectral information, and bioactivities.

Photoluminescence properties of the investigated ruthenabenzenes: As suggested by the X-ray crystal structures, the metallacycle and the 8-hydroxyquinoline ring in **3**, **4** or **5** have a degree of delocalization within the coplanar tetracyclic framework. Since a number of organic compounds with conjugated multicycle frameworks are known as efficient fluorophores, the photoluminescence properties of **3**, **4**, and **5** were studied. Although ruthenabenzene **3** in solution was almost nonfluorescent at room temperature, its derivatives **4** and **5** were found to be fluorescent in common solvents (Figure 5). For example, the quantum yields were calculated

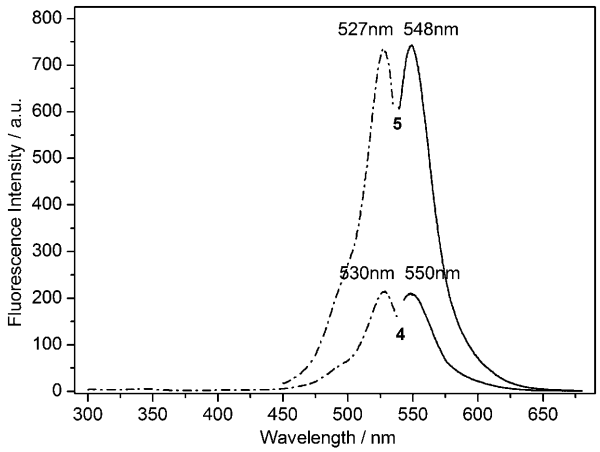


Figure 5. Excitation (dot) and emission (solid) spectra of ruthenabenzenes **4** and **5** in methanol/water (1:1, v/v). [Ru] = 1.0×10^{-4} mol L^{-1}.

to be 1.0% (25°C) and 4.0% (25°C) respectively for **4** and **5** in methanol-water (1:1, v/v) mixture, using rhodamine B as the primary standard for calculation.[23] The long-wavelength absorption and emission of **4** or **5** accorded well with the large π-extended system of the coplanar 8-hydroxyquinoline-ruthenabenzene tetracycle. It is interesting that only a small Stokes' shift of about 20 nm has been observed for **4** or **5**. This is comparable to the spectral behaviors of organic multicyclic compounds such as fluorescein and rhodamine.

The photoluminescence of other related ruthenabenzenes were also examined. Compound **2** in methanol/water exhibited an intense fluorescence (295/500 nm), which is typical of the 8-hydroxyquinoline ligand. As expected, compound **6** with nonplanar metallacycle was almost nonfluorescent in solution at room temperature. Compared with compound **2**, the disappearance of 8-hydroxyquinoline-dominated fluorescence could be attributed to the arylation of the hydroxyl in compound **6**.

Conclusion

The multicyclic complex containing a ruthenabenzene unit **3** was obtained by treatment of ruthenabenzene **1** with excess 8-hydroxyquinoline in the presence of CH_3COONa under

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 3. Crystal data and structure refinement for **3′**, **4**, **6**, and **7**.

	3′·2.5 $C_2H_4Cl_2$·0.25 CH_2Cl_2	**4**	**6**·$C_2H_4Cl_2$·3.5 H_2O	**7**·2 H_2O
formula	$C_{130.25}H_{109.50}B_2Cl_{5.50}N_2O_2P_3Ru$	$C_{59}H_{45}ClN_2O_2P_2Ru$	$C_{70}H_{64}Cl_5NO_{4.50}P_3Ru$	$C_{50}H_{42}ClNO_3P_2$
M_r	2145.27	1012.43	1362.45	802.24
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.9628(4)	26.1400(12)	13.606(3)	9.1489(18)
b [Å]	17.3434(4)	8.6146(3)	14.287(3)	14.506(3)
c [Å]	25.0208(7)	22.7498(11)	19.144(4)	15.494(3)
α [°]	72.775(2)	90	86.08(3)	98.60(3)
β [°]	80.096(2)	113.643(6)	69.60(3)	90.66(3)
γ [°]	84.007(2)	90	82.76(3)	96.77(3)
V [Å^3]	5691.9(3)	4692.9(4)	3458.9(12)	2018.1(7)
Z	2	4	2	2
ρ_{calcd} [g cm^{-3}]	1.252	1.433	1.308	1.320
μ [mm^{-1}]	0.361	0.507	0.536	0.220
F(000)	2227	2080	1402	840
crystal size [mm^3]	0.50×0.40×0.35	0.30×0.25×0.20	0.42×0.25×0.20	0.20×0.15×0.10
θ range [°]	2.29–25.00	2.36–25.00	3.02–25.00	3.21–25.00
reflns collected	51149	20664	44057	15858
independent reflns	20020	8251	12147	7091
observed reflns [$I \geq 2\sigma(I)$]	12511	4489	10871	4513
data/restraints/params	20020/163/1351	8251/132/598	12147/12/775	7091/0/515
GOF on F^2	1.000	0.856	1.001	1.001
R_1/wR_2 [$I \geq 2\sigma(I)$]]	0.0688/0.2128	0.0530/0.0785	0.0575/0.1902	0.0694/0.1654
R_1/wR_2 (all data)	0.1095/0.2259	0.1094/0.0850	0.0628/0.1951	0.1118/0.2027
largest peak/hole [e Å^{-3}]	2.368/−0.690	0.982/−1.090	2.374/−0.534	1.401/−0.731

air atmosphere via the S_NAr reaction. The ruthenabenzene **3** can tolerate weak alkali or weak acid in solution. Reaction of **3** with NaOH or Na_2CO_3 gave a mixture of ruthenabenzene complexes **4** and **5**, presumably through a P–C bond cleavage of the metallacycle. In addition, **3** readily reacted with HCl to yield ruthenabenzene **6**. Thermal stability tests demonstrated that these new species of metallabenzenes have remarkable stability both in solid state and in solution under air atmosphere. Especially, **4**, **5** and **6** can be heated at 150 °C for at least five hours without appreciable decomposition. Complexes **4** and **5** were found to be fluorescent in solution and have similar spectral behaviors to those organic multicyclic compounds. It suggested a degree of electron delocalization within the metallacycle and the 8-hydroxyquinoline ring, which accorded with the X-ray diffraction study.

Experimental Section

General comments: All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. The starting material [Ru{CHC(PPh_3)CHC(PPh_3)CH}Cl_2(PPh_3)$_2$]Cl **(1)** was synthesized by literature procedures.[8] NMR experiments were performed on a Bruker AV-300 spectrometer (^{1}H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz), or a Bruker AV-500 spectrometer (^{1}H 500.2 MHz; ^{13}C 125.8 MHz; ^{31}P 202.5 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85 % H_3PO_4. Elemental analyses data were obtained on an Elementar Analysen Syetem GmbH Vario EL III instrument. Absorption and fluorescence spectra were recorded on a Varian CARY-300 UV/Vis spectrophotometer and a Hitachi F-4500 fluorophotometer, respectively.

[Ru{CHC(PPh_3)CHC(PPh_3)CH}Cl-(C_9H_6NO)(PPh_3)]Cl (2): A mixture of [Ru{CHC(PPh_3)CHC(PPh_3)CH}Cl_2-(PPh_3)$_2$]Cl (**1**) (0.40 g, 0.30 mmol) and 8-hydroxyquinoline (65 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for about 2 h to give a brown solution. The volume of the mixture was reduced to ca. 2 mL under vacuum and was purified by column chromatography (neutral alumina, acetone/methanol 6:1) to give complex **2** as a brown solid (0.21 g, 53 %). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 16.8 (dd, J(P,H) = 15.0, 7.8 Hz, 1H, RuC*H*), 16.4 (dd, J(P,H) = 17.7, 7.8 Hz, 1H, RuC*H*), 8.2–6.6 ppm (m, 52H, PPh_3, C_9H_6NO, RuCHC-(PPh_3)C*H*); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 36.4 (Ru*P*Ph_3), 18.6 (C*P*Ph_3), 18.4 ppm (C*P*Ph_3); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 294.1 (br, Ru*C*H), 289.7 (br, Ru*C*H), 145.5 (t, J(P,C) = 24.2 Hz, RuCHC-(PPh_3)*C*H), 168.1–109.4 (m, PPh_3, C_9H_6NO), 116.1 (dd, J(P,C) = 71.3, 13.5 Hz, RuCH*C*(PPh_3)), 114.0 ppm (dd, J(P,C) = 73.5, 11.3 Hz, RuCH*C*-(PPh_3)); elemental analysis calcd (%) for $C_{68}H_{54}NOP_3Cl_2Ru$: C 70.04, H 4.67, N 1.20; found: C 70.28, H 5.15, N 1.36.

[(C_9H_6NO)Ru{CHC(PPh_3)CHC(PPh_3)C}(C_9H_6NO)(PPh_3)]Cl_2 (3): A solution of [Ru{CHC(PPh_3)CHC(PPh_3)CH}Cl_2(PPh_3)$_2$]Cl (**1**) (0.20 g, 0.15 mmol) and 8-hydroxyquinoline (0.10 g, 0.75 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of CH_3COONa (0.12 g, 1.5 mmol) and CH_3OH (1 mL). The reaction mixture was stirred at room temperature for 24 h under an air atmosphere to give a green suspension. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (3×5 mL). The volume of the filtrate was reduced to about 1 mL under vacuum and was purified by column chromatography (neutral alumina, acetone/methanol 20:1) to give complex **3** as a green solid (0.15 g, 76 %). ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ = 15.9 (d, J(P,H) = 18.5 Hz, 1H, RuC*H*), 8.8–6.3 (m, 58H, PPh_3, C_9H_6NO, RuCHC(PPh_3)C*H*), 7.9 ppm (dd, J(P,H) = 13.5, 18.5 Hz, 1H, RuCHC(PPh_3)C*H*); ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ = 286.6 (br, Ru*C*H), 273.9 (d, J(P,C) = 13.8 Hz, Ru*C*), 154.6 (dd, J(P,C) = 24.9, 17.5 Hz, RuCHC(PPh_3)*C*H), 167.2–110.8 (m, PPh_3, C_9H_6NO), 114.0 (dd, J(P,C) = 78.6, 12.1 Hz, *C*(PPh_3)), 103.9 ppm (dd, J(P,C) = 74.2, 11.3 Hz, *C*(PPh_3)); ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = 31.7 (Ru*P*Ph_3), 26.1 (C*P*Ph_3), 18.8 ppm (C*P*Ph_3); elemental analysis calcd (%) for $C_{77}H_{59}N_2O_2P_3Cl_2Ru$: C 70.64, H 4.54, N 2.14; found: C 70.67, H 4.76, N 1.96.

[(C_9H_6NO)Ru{CHC(PPh_3)CHC(PPh_3)C}(C_9H_6NO)(PPh_3)](BPh_4)$_2$ (3′): A solution of $NaBPh_4$ (68.4 mg, 0.2 mmol) in CH_3OH (0.5 mL) was added slowly to a solution of complex **3** (0.1 g, 0.08 mmol) in CH_3OH (2 mL). The reaction mixture was stirred at room temperature for 5 min to give a green suspension. The green solid was collected by filtration, washed with CH_3OH (2×3 mL), and then dried under vacuum (0.13 g, 88 %). Elemental analysis calcd (%) for $C_{125}H_{99}B_2N_2O_2P_3Ru$: C 80.00, H 5.32, N 1.49; found: C 80.10, H 5.19, N 1.95.

[(C_9H_6NO)Ru{CHC(PPh_3)CHCHC}(C_9H_6NO)(PPh_3)]Cl (4) and [(C_9H_6NO)Ru-{CHCHCHC(PPh_3)C}(C_9H_6NO)(PPh_3)]Cl (5): A solution of NaOH (25.0 mg, 0.63 mmol) in H_2O (1 mL) was added slowly to a so-

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

lution of complex **3** (0.40 g, 0.31 mmol) in CH_3OH (15 mL). The reaction mixture was stirred at room temperature for about 24 h to give a reddish brown solution. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (3×5 mL). The volume of the filtrate was reduced to about 1 mL under vacuum and was purified by column chromatography (neutral alumina, acetone/methanol 20:1) to give complexes **4** and **5** in different color sequentially.

Complex **4** was collected as a yellowish green solid (0.23 g, 73%). ^{1}H NMR plus HMQC (300.1 MHz, $CDCl_3$): δ=13.7 (d, J(P,H)=23.4 Hz, 1H, Ru*CH*), 9.1–6.8 (m, 43H, PPh_3, C_9H_6NO, RuCHC(PPh_3)C*H*), 7.4 (br, 1H, RuCHC(PPh_3)C*H*, obscured by the phenyl signals and confirmed by ^{1}H,^{13}C HMQC), 6.6 ppm (d, J(P,H)=9.1 Hz, 1H, RuCC*H*); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ=286.3 (d, J(P,C)=13.0 Hz, Ru*C*), 264.7 (dd, J(P,C)=14.2, 3.9 Hz, Ru*C*H), 142.2 (d, J(P,C)=23.8 Hz, RuCHC(PPh_3)*C*H), 167.9–109.6 (m, PPh_3, C_9H_6NO), 119.4 (d, J(P,C)=11.2 Hz, Ru*C*CH), 110.4 ppm (d, J(P,C)=76.6 Hz, RuCH*C*(PPh_3)); ^{31}P{^{1}H} NMR (121.5.0 MHz, $CDCl_3$): δ=40.4 (d, J(P,P)=3.6 Hz, Ru*P*Ph_3), 15.4 ppm (d, J(P,P)=3.6 Hz, C*P*Ph_3); elemental analysis calcd (%) for $C_{59}H_{45}ClN_2O_2P_2Ru$: C 69.99, H 4.48, N 2.77; found: C 69.59, H 4.82, N 2.70.

Complex **5** was collected as a green solid (25 mg, 8%). ^{1}H NMR (300.1 MHz, $CDCl_3$): ^{1}H NMR plus ^{1}H,^{1}H COSY and HMQC (300.1 MHz, $CDCl_3$): δ=15.3 (d, J(H,H)=6.9 Hz, 1H, RuC*H*), 9.0–6.4 (m, 44H, PPh_3, C_9H_6NO, RuCHC*HCH*), 7.9 (br, 1H, RuCHC*H*CH, obscured by the phenyl signals and confirmed by ^{1}H,^{13}C HMQC and ^{1}H,^{1}H COSY), 7.5 ppm (br, 1H, RuCHCHC*H*, obscured by the phenyl signals and confirmed by ^{1}H,^{13}C HMQC); ^{13}C{^{1}H} NMR plus DEPT-135 (75.5 MHz, $CDCl_3$): δ=281.6 (d, J(P,C)=13.7 Hz, Ru*C*H), 270.3 (dd, J(P,C)=14.3, 4.1 Hz, Ru*C*), 152.4 (d, J(P,C)=15.8 Hz, RuCHCH*C*H), 167.9–109.6 (m, PPh_3, C_9H_6NO), 120.7 (d, J(P,C)=2.9 Hz, RuCH*C*H, confirmed by ^{1}H,^{13}C HMQC), 96.9 ppm (d, J(P,C)=76.0 Hz, Ru*C*C(PPh_3)); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ=35.2 (s, Ru*P*Ph_3), 23.3 ppm (s, C*P*Ph_3); elemental analysis calcd (%) for $C_{59}H_{45}ClN_2O_2P_2Ru$: C 69.99, H 4.48, N 2.77; found: C 69.59, H 4.38, N 2.60.

[Ru{CHC(PPh_3)CHC(PPh_3)C}Cl_2(C_9H_6NO)(PPh_3)]Cl (6): HCl (1M in diethyl ether, 1.5 mL, 1.5 mmol) was added to a solution of complex **3** (0.30 g, 0.23 mmol) in $CHCl_3$ (10 mL). The reaction mixture was stirred at room temperature for about 4 h to give a deep green solution. The solvent was washed with H_2O (3×5 mL), and the volume of the organic phase was reduced to ca. 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 (0.25 g, 91%). ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ=16.5 (d, J(P,H)=18.5 Hz, 1H, RuCH), 10.3–5.9 (m, 52H, PPh_3, C_9H_6NO, RuCHC(PPh_3)C*H*), 7.4 ppm (m, 1H, RuCHC(PPh_3)C*H*, obscured by the phenyl signals and confirmed by ^{1}H,^{13}C HMQC); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ=292.6 (d, J(P,C)=13.7 Hz, Ru*C*H), 273.2 (d, J(P,C)=12.8 Hz, Ru*C*), 154.8 (dd, J(P,C)=25.7, 17.7 Hz, RuCHC-(PPh_3)*C*H), 155.6–118.01 (m, PPh_3, C_9H_6NO), 113.4 (dd, J(P,C)=80.6, 12.5 Hz, *C*(PPh_3)), 105.6 ppm (dd, J(P,C)=78.6, 11.5 Hz, *C*(PPh_3)); ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ=46.0 (s, Ru*P*Ph_3), 24.0 (s, C*P*Ph_3), 17.6 ppm (s, C*P*Ph_3); elemental analysis calcd (%) for $C_{68}H_{53}NOP_3Cl_3Ru$: C 68.03, H 4.45, N 1.17; found: C 68.19, H 4.75, N 1.27.

[C(C_9H_6NO)C(PPh_3)CHC(PPh_3)CH]Cl (7): A solid sample of complex **3** (0.35 g, 0.27 mmol) was heated at 190°C for 5 h. The mixture was solved in 5 mL of CH_2Cl_2 to give a green solution. The mixture was purified by column chromatography (neutral alumina, acetone/methanol 20:1) to give complex **7** as a light brown solid (0.10 g, 49%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ=8.8–7.1 (m, 36H; PPh_3, C_9H_6NO), 6.2 (m, 1H, CC(PPh_3)C*H*), 5.9 ppm (m, 1H, CC(PPh_3)CHC(PPh_3)C*H*); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ=154.2–113.0 (m, PPh_3, C_9H_6NO), 150.1 (dd, J(P,C)=20.4, 8.9 Hz, *C*C(PPh_3)CHC(PPh_3)CH), 127.1 (t, J(P,C)=13.6 Hz, CC(PPh_3)CHC(PPh_3)*C*H), 107.6 (t, J(P,C)=13.4 Hz, CC-(PPh_3)CHC(PPh_3)CH), 88.2 (dd, J(P,C)=113.4, 19.2 Hz, *C*(PPh_3)), 85.5 ppm (dd, J(P,C)=112.3, 14.4 Hz, *C*(PPh_3)); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ=14.3 (d, J(P,C)=7.5 Hz, C*P*Ph_3), 13.1 ppm (d, J(P,C)=7.5 Hz, C*P*Ph_3); elemental analysis calcd (%) for $C_{50}H_{38}ClNOP_2$: C 78.37, H 5.00, N 1.83; found: C 77.99, H 5.30, N 2.19.

X-ray crystallography: Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 or CH_2ClCH_2Cl solutions layered with *n*-hexane for **3′**, **4**, **6**, and **7** (Table 3). Data collections were performed on an Oxford Gemini S Ultra or a Rigaku R-AXIS SPIDER IP CCD area detector using graphite-monochromated $Mo_{K\alpha}$ 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 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 794265 (**3′**), 794266 (**4**),794267 (**6**) and 794268 (7) 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. 20801046 and 20925208) and Research Fund for the Doctoral Program of Higher Education of China (Nos. 200803841034 and 20090121110010).

[1] For recent reviews, see: a) J. R. Bleeke, *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. Bleeke, *Chem. Rev.* **2001**, *101*, 1205–1227.

[2] Recent examples for the synthesis of rhenabenzene: K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2010**, *122*, 2819–2822; *Angew. Chem. Int. Ed.* **2010**, *49*, 2759–2762.

[3] Recent examples for the synthesis of osmabenzenes: a) P. M. Johns, W. R. Roper, S. D. Woodgate, L. J. Wright, *Organometallics* **2010**, *29*, 5358–5365; b) J. Huang, R. Lin, L. Wu, Q. Zhao, C. Zhu, T. B. Wen, H. Xia, *Organometallics* **2010**, *29*, 2916–2925; c) 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; d) 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; e) H. Zhang, L. Wu, R. Lin, Q. Zhao, G. He, F. Yang, T. B. Wen, H. Xia, *Chem. Eur. J.* **2009**, *15*, 3546–3559; f) L. Gong, Y. Lin, T. B. Wen, H. Xia, *Organometallics* **2009**, *28*, 1101–1111; g) M. A. Esteruelas, A. B. Masamunt, M. Oliván, E. Oñate, M. Valencia, *J. Am. Chem. Soc.* **2008**, *130*, 11612–11613; h) L. Gong, Y. Lin, T. B. Wen, H. Zhang, B. Zeng, H. Xia, *Organometallics* **2008**, *27*, 2584–2589; i) L. Gong, Y. Lin, G. He, H. Zhang, H. Wang, T. B. Wen, H. Xia, *Organometallics* **2008**, *27*, 309–311; j) 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; k) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771–1777; l) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856–2857; m) 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; n) P. Barrio, M. A. Esteruelas, E. Oñate, *J. Am. Chem. Soc.* **2004**, *126*, 1946–1947; o) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem.* **2001**, *113*, 2005–2008; *Angew. Chem. Int. Ed.* **2001**, *40*, 1951–1954.

[4] Recent examples for the synthesis of iridabenzenes: a) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536–5540; b) G. R.

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Clark, G.-L. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167–2177; c) K. Ilg, M. Paneque, M. L. Poveda, N. Rendón, L. L. Santos, E. Carmona, K. Mereiter, *Organometallics* **2006**, *25*, 2230–2236; d) C. S. Chin, H. Lee, M.-S. Eum, *Organometallics* **2005**, *24*, 4849–4852; e) J. R. Bleeke, P. V. Hinkle, M. Shokeen, N. P. Rath, *Organometallics* **2004**, *23*, 4139–4149; f) R. D. Gilbertson, T. L. S. Lau, S. Lanza, H.-P. Wu, T. J. R. Weakley, M. M. Haley, *Organometallics* **2003**, *22*, 3279–3289; g) J. R. Bleeke, P. V. Hinkle, N. P. Rath, *Organometallics* **2001**, *20*, 1939–1951; h) J. R. Bleeke, J. M. B. Blanchard, E. Donnay, *Organometallics* **2001**, *20*, 324–336; i) R. P. Hughes, H. A. Trujillo, J. W. Egan, Jr., A. L. Rheingold, *J. Am. Chem. Soc.* **2000**, *122*, 2261–2271; j) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2000**, *6*, 437–441; Examples for the synthesis of iridabenzenes also including the rearrangements to form cyclopentadienyl complexes: k) M. Paneque, M. L. Poveda, N. Rendón, E. Álvarez, E. Carmona, *Eur. J. Inorg. Chem.* **2007**, 2711–2720; l) H.-P. Wu, D. H. Ess, S. Lanza, T. J. R. Weakley, K. N. Houk, K. K. Baldridge, M. M. Haley, *Organometallics* **2007**, *26*, 3957–3968; m) E. Álvarez, M. Paneque, M. L. Poveda, N. Rendón, *Angew. Chem.* **2006**, *118*, 488–491; *Angew. Chem. Int. Ed.* **2006**, *45*, 474–477; n) H.-P. Wu, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2005**, *11*, 1191–1200; o) H.-P. Wu, S. Lanza, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 2824–2826; p) C. S. Chin, H. Lee, *Chem. Eur. J.* **2004**, *10*, 4518–4522.

[5] Recent examples for the synthesis of platinabenzenes: a) V. Jacob, C. W. Landorf, L. N. Zakharov, T. J. R. Weakley, M. M. Haley, *Organometallics* **2009**, *28*, 5183–5190; b) C. W. Landorf, V. Jacob, T. J. R. Weakley, M. M. Haley, *Organometallics* **2004**, *23*, 1174–1176; c) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem.* **2002**, *114*, 3620–3623; *Angew. Chem. Int. Ed.* **2002**, *41*, 3470–3473; d) V. Jacob, T. J. R. Weakley, M. M. Haley, *Organometallics* **2002**, *21*, 5394–5400.

[6] Metal-coordinated ruthenabenzenes: a) U. Effertz, U. Englert, F. Podewils, A. Salzer, T. Wagner, M. Kaupp, *Organometallics* **2003**, *22*, 264–274; b) 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; c) M. I. Bruce, N. N. Zaitseva, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **2002**, 1678–1686; d) U. Englert, F. Podewils, I. Schiffers, A. Salzer, *Angew. Chem.* **1998**, *110*, 2196–2197; *Angew. Chem. Int. Ed.* **1998**, *37*, 2134–2136; e) W. Lin, S. R. Wilson, G. S. Girolami, *Organometallics* **1997**, *16*, 2356–2361; f) W. Lin, S. R. Wilson, G. S. Girolami, *J. Chem. Soc. Chem. Commun.* **1993**, 284–285; g) H. W. Bosch, H.-U. Hund, D. Nietlispach, A. Salzer, *Organometallics* **1992**, *11*, 2087–2098.

[7] Thermally unstable ruthenabenzenes: a) J. Yand, W. M. Jones, J. K. Dixon, N. T. Allison, *J. Am. Chem. Soc.* **1995**, *117*, 9776–9777.

[8] Non-metal-coordinated ruthenabenzenes: a) H. Zhang, L. Feng, L. Gong, L. Wu, G. He, T. Wen, F. Yang, H. Xia, *Organometallics* **2007**, *26*, 2705–2713; b) 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.

[9] Tethered ruthenabenzenes and ironbenzenes: a) G. R. Clark, T. R. O'Neale, W. R. Roper, D. M. Tonei, L. J. Wright, *Organometallics* **2009**, *28*, 567–572; b) M. I. Bruce, B. C. Hall, B. W. Skelton, E. R. T. Tiekink, *Aust. J. Chem.* **2000**, *53*, 99–107; c) U. Grössmann, H.-U. Hund, H. W. Bosch, H. Schmalle, H. Berke, *J. Organomet. Chem.* **1991**, *408*, 203–218; d) R. Birk, U. Grössmann, H.-U. Hund, H. Berke, *J. Organomet. Chem.* **1988**, *345*, 321–329; e) H. Yamazaki, K. Aoki, *J. Organomet. Chem.* **1976**, *122*, C54–C58.

[10] a) R. P. Hughes, H. A. Trujillo, A. J. Gauri, *Organometallics* **1995**, *14*, 4319–4324; b) J. Yang, J. Yin, K. A. Abboud, W. M. Jones, *Organometallics* **1994**, *13*, 971–978; c) R. P. Hughes, D. J. Robinson, *Organometallics* **1989**, *8*, 1015–1019.

[11] H. Zhang, R. Lin, G. Hong, T. Wang, T. B. Wen, H. Xia, *Chem. Eur. J.* **2010**, *16*, 6999–7007.

[12] S_EAr reactions of metallabenzenes: a) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2008**, *27*, 451–454; b) 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.

[13] G. R. Clark, L. A. Ferguson, A. E. Mclntosh, T. Söhnel, L. J. Wright, *J. Am. Chem. Soc.* **2010**, *132*, 13443–13452.

[14] 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, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898–9899.

[15] a) 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; 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.

[16] 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.

[17] a) Y. Chi, P.-T. Chou, *Chem. Soc. Rev.* **2007**, *36*, 1421–1431; b) P.-T. Chou, Y. Chi, *Eur. J. Inorg. Chem.* **2006**, 3319–3332; c) J. P. Phillips, *Chem. Rev.* **1956**, *56*, 271–297.

[18] J. R. Bleeke, R. Behm, *J. Am. Chem. Soc.* **1997**, *119*, 8503–8511.

[19] a) K. Y. Lee, J. E. Na, M. J. Lee, J. N. Kim, *Tetrahedron Lett.* **2004**, *45*, 5977–5981; b) H.-J. Cristau, P. Mouchet, *Phosphorus Sulfur Silicon Relat. Elem.* **1995**, *107*, 135–144; c) D. G. Gilheany, N. T. Thompson, B. J. Walker, *Tetrahedron Lett.* **1987**, *28*, 3843–3844; d) R. A. McClelland, G. H. McGall, G. Patel, *J. Am. Chem. Soc.* **1985**, *107*, 5204–5209; e) A. Schnell, J. C. Tebby, *J. Chem. Soc. Perkin Trans. 1* **1977**, 1883–1886; f) J. R. Corfield, S. Trippett, *J. Chem. Soc. D* **1970**, 1267a; g) D. W. Allen, S. J. Grayson, I. Harness, B. G. Hutley, I. W. Mowat, *J. Chem. Soc. Perkin Trans. 2* **1973**, 1912–1915; h) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, C. A. VanderWerf, A. Calvin, *J. Am. Chem. Soc.* **1964**, *86*, 2378–2384; i) R. F. Hudson, M. Green, *Angew. Chem.* **1963**, *75*, 47–56; j) G. Aksnes, J. Songstad, *Acta Chem. Scand.* **1962**, *16*, 1426–1432; k) M. Zanger, C. A. VanderWerf, W. E. McEwen, *J. Am. Chem. Soc.* **1959**, *81*, 3806–3807; l) L. Horner, H. Hoffmann, H. G. Wippel, G. Hassel, *Chem. Ber.* **1958**, *91*, 52–57; m) G. W. Penton, C. K. Ingold, *J. Chem. Soc.* **1929**, *1*, 2342–2357.

[20] a) Z. Lin, *Acc. Chem. Res.* **2010**, *43*, 602–611; b) J. Zhu, G. Jia, Z. Lin, *Organometallics* **2007**, *26*, 1986–1995.

[21] J. R. Bleeke, Y.-F. Xie, W.-J. Peng, M. Chiang, *J. Am. Chem. Soc.* **1989**, *111*, 4118–4120.

[22] a) K. J. Weller, I. Filippov, P. M. Briggs, D. E. Wigley, *Organometallics* **1998**, *17*, 322–329; b) P. N. Riley, R. D. Profilet, M. M. Salberg, P. E. Fanwick, I. P. Rothwell, *Polyhedron* **1998**, *17*, 773–779.

[23] T. Karstens, K. Kobs, *J. Phys. Chem.* **1980**, *84*, 1871–1872.

Received: December 10, 2010
Published online: February 24, 2011

 © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim