Cycloaddition

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Stable Iso-osmabenzenes from a Formal [3+3] Cycloaddition Reaction of Metal Vinylidene with Alkynols[**]

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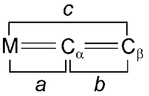
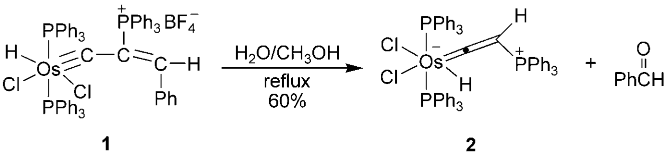
The investigation on the synthesis and reactivity of metal vinylidene complexes has always been an active area,[1] especially given their applications as well-known catalysts for metathesis and carbon–carbon and carbon–heteroatom coupling reactions.[1b,e,2] Compared with other reactions of metal vinylidenes, the cyclization reactions are underdeveloped. Previous studies showed that the vinylidene M=C_α bond participated in cycloadditions (see *a*) as key steps in carbon–carbon coupling reactions,[3] and some cycloaddition products have also been isolated.[4] Interestingly, similar reactions of the metal vinylidene C_α=C_β bond (see *b*) have been realized as well.[5] However, cyclizations of the skeleton of metal vinylidene (M=C_α=C_β) as a unit (see *c*) remain scarce. In fact, the reported cyclization is a formal [3+2] cycloaddition reaction.[5c] To the best of our knowledge, the [3+3] cyclization reactions of metal vinylidene to construct six-membered rings have not been reported.



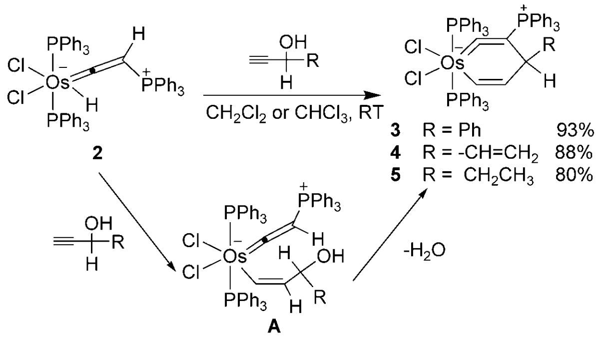
Moreover, since the first isolation of metallabenzene was achieved by Roper and co-workers,[7a] considerable research interest has been attracted in this field.[6,7] Nevertheless, the metallabenzene analogue isometallabenzene, which can be seen as a metal-containing 1,2,4-cyclohexatriene, has not been thoroughly explored. Until now, only the $16e^-$ isometallabenzene [Os{=C=C(Ph)−CH(Ph)−CH=C(CH_2Ph)}Cl($Pi\text{Pr}_3)_2$], prepared by double coupling reactions, was reported by Esteruelas and co-workers in 2004.[8] Herein, we report an unprecedented formal [3+3] cycloaddition reaction between the hydride vinylidene complex [$OsHCl_2${=C=CH(PPh_3)}($PPh_3)_2$] (**2**) and alkynols under mild conditions to give stable $18e^-$ iso-osmabenzenes. The origin of the unexpected stability of these iso-osmabenzene complexes and their isomerization into η^5-cyclopentadienyl complexes through metalated cyclopentadiene intermediates is also described.

Stirring of the osmium hydride alkenylcarbyne complex [$OsHCl_2$(≡C−C(PPh_3)=CHPh)($PPh_3)_2$]BF_4 (**1**)[9] in a mixture of H_2O/CH_3OH (3:2 v/v) at reflux produced the osmium hydride vinylidene complex **2**, which was isolated as a light-yellow solid in 60 % yield (Scheme 1). The other product, PhCHO, was detected by ^{1}H NMR ($\delta = 9.3$ ppm; PhC*H*O) and GC analysis of the reaction mixture (see Figure S1 in the Supporting Information). Complex **2** was characterized by NMR spectroscopy and elemental analysis, and the structure was additionally confirmed by single-crystal X-ray diffraction (Figure S2).



Scheme 1. Preparation of osmium hydride vinylidene **2**.

Complex **2** is thermally stable in the solid state but highly reactive in solution. Treatment of **2** with HC≡CCH(OH)Ph in dichloromethane or chloroform at room temperature led to a fast color change from light yellow to brown red. The unexpected iso-osmabenzene **3** was generated from a formal [3+3] cycloaddition and isolated in high yield (93 %). Similarly, when **2** reacted with HC≡CCH(OH)CH=CH_2 or HC≡CCH(OH)CH_2CH_3 under the same reaction conditions, the other two iso-osmabenzenes, **4** (88 % yield) and **5** (80 % yield), were also formed (Scheme 2).



Scheme 2. Preparation of iso-osmabenzene **3**–**5**.

The structure of **3** was characterized by single-crystal X-ray diffraction analysis.[10] As shown in Figure 1, the six-membered ring is almost planar. The deviations, in Å, from the best plane are 0.0410 (Os1), 0.0003 (C1), 0.0515 (C2), 0.0571 (C3), 0.0022 (C4), and 0.0491 (C5). The Os1=C1 bond

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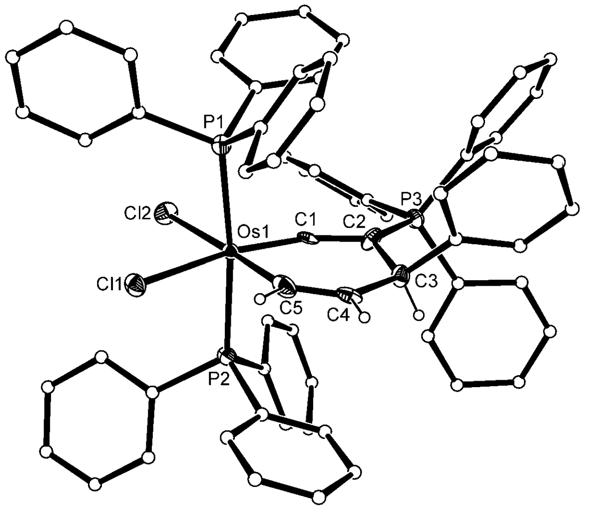


Figure 1. X-ray crystal structure of **3** (ellipsoids shown at the 50% probability level). Some of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Os1–Cl1 2.487(2), Os1–Cl2 2.492(3), Os1–P1 2.393(3), Os1–P2 2.398(3), Os–C1 1.781(11), Os1–C5 2.043(12), C1–C2 1.339(13), C2–C3 1.563(14), C3–C4 1.507(13), C4–C5 1.351(14); C1-Os1-C5 78.3(4), Os1-C1-C2 155.1(8), C1-C2-C3 114.2(9), C2-C3-C4 111.6(9), C3-C4-C5 128.6(10), C4-C5-Os1 131.4(8).

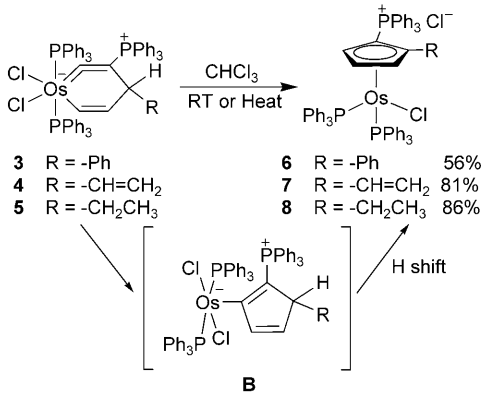
length (1.781(11) Å) is at the low-end of the typical Os=C=CRR′ (1.78–1.90 Å)[11] and Os=$C_{carbene}$ (1.78–2.14 Å) bonds.[12] The Os1–C5 bond length (2.043(12) Å) is within the range observed for typical Os–C_{vinyl} bonds.[13] The C1=C2, C4=C5, C2–C3, and C3–C4 bond lengths are typical for carbon–carbon double and single bonds. The Os–C and C–C bond lengths within the six-membered ring indicate that the metallacycle has a localized nature. The Os1-C1-C2 angle of 155.1(8)° is comparable to that of Esteruelas' iso-osmabenzene (158.5(3)°)[8] and Jia's osmabenzyne (148.7(3)–154.9(9)°)[14] or osmanaphalyne (151.1(5)° and 155.0(3)°).[15]

In keeping with the solid-state structure of **3**, the ^{1}H NMR analysis showed no signal for the carbene proton. Two proton signals for the Os–CH=CH unit were observed at $\delta = 8.3$ and 4.7 ppm, respectively, with a coupling constant of 9.5 Hz, which indicates a *cis* geometry.

Mainly attributed to the chirality of the sp^3-carbon atom C3, the ^{31}P{^{1}H} NMR spectrum of **3** displayed the same characteristic AB spin system as did Esteruelas' isometallabenzene;[8] the resonances were centered at $\delta = -3.4$ (d, ^2J(PP) = 360.5 Hz) and -7.9 ppm (d, ^2J(PP) = 360.5 Hz) for each of the two Os*P*Ph$_3$, respectively. The signal at $\delta = 3.9$(s) ppm was assigned to C*P*Ph$_3$. Unfortunately, the poor solubility of **3** and **4** prevented ^{13}C{^{1}H} NMR characterization. Isoosmabenzenes **4** and **5** have similar NMR spectroscopic characteristics as **3**.

A plausible mechanism for the formation of **3**, **4**, and **5** is shown in Scheme 2. The insertion of terminal alkynes into Os–H bond should afford intermediate **A**. The subsequent dehydration and C–C coupling between the C$_\beta$ of the vinylidene fragment and the hydroxy-linked carbon atom in **A** led to the formal [3+3] cycloaddition iso-osmabenzene products. It should be mentioned that the typical reaction of metal hydride complexes is the insertion of terminal alkynes into their M–H bonds.[16]

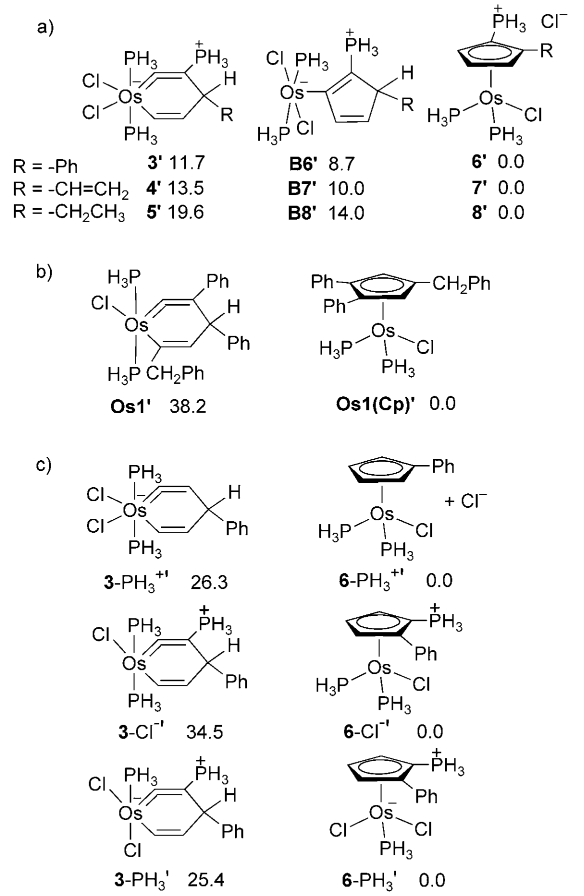
Solid samples of **3**, **4**, and **5** show air and moisture stabilities; they can be heated in air at 100 °C for 5 hours without notable decomposition. In solution, complex **3** is thermally stable to some extent, and tolerant to bases such as Na$_2$CO$_3$ and NaOH; however **3** is sensitive to acids such as HCl and HBF$_4$. In contrast to **3**, complexes **4** and **5** are less stable. When **4** was continuously stirred in chloroform at room temperature, it rearranged slowly into the η^5-cyclopentadienyl complex **7** after three days (Scheme 3). The isomerization of **5**, which led to **8**, was faster and accomplished in quantitative yield within two days. The solution of **3** behaved similarly to give **6**, but very slowly as the transformation took more than one week. By comparing the above-mentioned results, the stability of **3**, **4**, and **5** follows the sequence **3** > **4** > **5**, which is mainly influenced by the substituents on the sp^3-carbon atom.



Scheme 3. Preparation of **6**–**8**.

DFT calculations have been carried out to gain insight into the relative stabilities of **3**, **4**, and **5**. Compounds **3′**, **4′**, and **5′** are model complexes in which the PPh$_3$ ligand is replaced with PH$_3$. The computed relative free energies for **3′**, **4′**, and **5′** with respect to the model η^5-cyclopentadienyl complexes **6′**, **7′**, and **8′** are 11.7, 13.5, and 19.6 kcal mol^{-1} (Scheme 4a), respectively, and are consistent with the experimental observations. For comparison, we also calculated the energy difference for the first iso-osmabenzene [Os{=C=C(Ph)–CH(Ph)–CH=C(CH$_2$Ph)}Cl(P*i*Pr$_3$)$_2$][8] (model complex **Os1′**) relative to the η^5-Cp complex **Os1(Cp)′** (38.2 kcal mol^{-1}, Scheme 4b).

To probe the origin of the relatively high stability of **3′**, we additionally constructed three more model complexes, namely **3**-PH$_3^{+\prime}$, **3**-Cl$^{-\prime}$, and **3**-PH$_3$′, to examine the role of the phosphonium substituent and different electron counts (Scheme 4c). Interestingly, when the phosphonium substituent is replaced by a hydrogen atom, the relative energy of **3**-PH$_3^{+\prime}$ is increased from 11.7 kcal mol^{-1} to 26.3 kcal mol^{-1} compared to **3′**, indicating that the phosphonium substituent plays a crucial role in stabilizing iso-osmabenzene complexes. Moreover, when one Cl$^-$ or PH$_3$ ligand is deliberately removed from **3′** to form a 16e$^-$ iso-osmabenzene **3**-Cl$^{-\prime}$ or



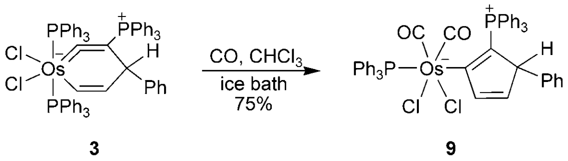
Scheme 4. Relative free energies (kcal mol^{-1}, in the solvent of chloroform) of iso-osmabenzenes compared with Cp complexes.

3-PH$_3$′, respectively, their stabilities relative to the η^5-complexes are decreased to 34.5 and 25.4 kcal mol^{-1}, respectively, suggesting that the contribution to the stability from the 18e$^-$ rule is not negligible. Taken together, both the phosphonium substituent at the C$_\beta$ position and the 18e$^-$ nature of **3** contribute to the high stability.

Additional studies showed that complexes **6**, **7**, and **8** could also be produced by heating **3**, **4**, and **5**, respectively, in chloroform for hours. By changing the counteranion of **8** to BPh$_4$$^-$, complex **8a** was prepared and confirmed by X-ray diffraction (Figure S3). Furthermore, the complexes **6**, **7**, **8**, and **8a** were characterized by NMR spectroscopy and elemental analysis.

It is well known that metallabenzenes can undergo carbene migratory insertion reactions into cyclopentadienyl complexes.[17] A similar process can be detected in the isomerization of isometallabenzenes (Scheme 3). The proposed mechanism shows that it may go through the metalated cyclopentadiene intermediate **B**. As a result of its instability, the 16e$^-$ five-coordinated **B** immediately undergoes H-shift onto the C$_\alpha$ atom of the Os-C$_{vinyl}$ followed by Os−C bond cleavage, giving the stable η^5-cyclopentadienyl complexes **6**, **7**, and **8**. Indeed, the computed data for the metalated cyclopentadiene **B6′**, **B7′**, and **B8′** model complexes are less stable by 8.7, 10.0, and 14.0 kcal mol^{-1} relative to the corresponding η^5-cyclopentadienyl model complexes **6′**, **7′**, and **8′**, respectively (Scheme 4a).

To capture the intermediate in this reaction, CO was introduced to stabilize **B**. A flask containing a solution of **3** was placed in an ice bath and under a CO atmosphere, and the mixture was stirred, thus leading to **9** (Scheme 5). Complex **9** was characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (Figure 2).[10] The formation of **9** suggests that iso-osmabenzenes rearranged via metalated cyclopentadiene intermediates.



Scheme 5. Preparation of **9**.

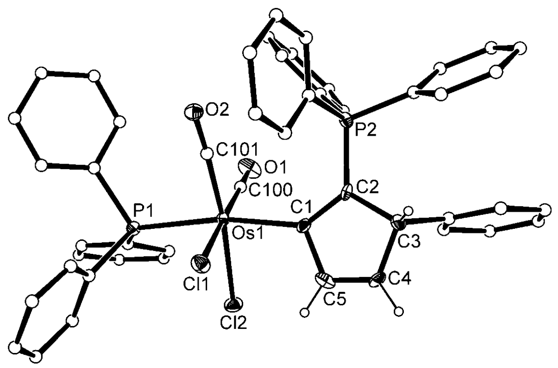
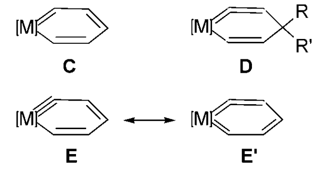


Figure 2. X-ray crystal structure of **9** (ellipsoids shown at the 50% probability level).

At first glance, isometallabenzene **D** is similar to metallabenzene **C** and metallabenzyne **E**, particularly the resonance structure **E′** (Scheme 6). Compared with metallabenzyne **E**, metallabenzene **C** and isometallabenzene **D** have a lower degree of unsaturation. Although metallabenzenes and metallabenzynes are familiar to us, isometallabenzenes are extremely rare. In this regard, isolation of the isometallabenzenes **3**, **4**, and **5** will definitely enrich the chemistry of six-membered metallacycles.



Scheme 6. Metallabenzene, isometallabenzene, and metallabenzyne.

In summary, isometallabenzenes were isolated from the novel [3+3] cycloaddition reactions of a metal vinylidene complex with alkynols in high yields at room temperature.

This method provides a simple and efficient route to prepare stable isometallabenzenes. The origin of the unexpected stability was probed by using DFT calculations, which suggest that both the phosphonium substituent at the C_β position and the $18e^-$ nature of the complex are the stabilizing factors. We also found that these isometallabenzenes could isomerize into η^5-cyclopentadienyl complexes via a metalated cyclopentadiene intermediate. The new reaction pattern between metal vinylidene and alkynols represents a promising synthetic method to construct other metallacycles. Expansion of cyclizations of vinylidene complexes to heteroatom-containing metallacycles is ongoing.

Experimental Section

2: The osmium hydride-alkenylcarbyne complex $[OsHCl_2(\equiv C{-}C(PPh_3){=}CHPh)(PPh_3)_2]BF_4$ (**1**) (506 mg, 0.405 mmol) was stirred in a mixture of CH_3OH (20 mL) and H_2O (30 mL) under reflux for about 12 h to give a light-yellow suspension, which was collected by filtration, washed with methanol and diethyl ether, and then dried under vacuum. Yield: 261 mg, 60 %. ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = -8.0$ (td, $J(P,H) = 15.6$ Hz, $J(P,H) = 4.0$ Hz, 1 H, Os*H*), 7.7–6.6 ppm (m, 45 H, PPh_3), 0.6 ppm (br, 1 H, OsCC*H*PPh_3); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): $\delta = 7.6$ (d, $J(P,P) = 4.9$ Hz Os*P*Ph_3), −1.06 ppm (t, $J(P,P) = 4.9$ Hz, C*P*Ph_3); elemental analysis (%) calcd for $C_{56}H_{47}P_3Cl_2Os$: C 62.62, H 4.41; found: C 62.32, H 4.31.

3: $HC\equiv CCH(OH)Ph$ (55.4 µL, 0.447 mmol) was added to a solution of **2** (400 mg, 0.372 mmol) in CH_2Cl_2 or $CHCl_3$ (15 mL). The reaction mixture was stirred at room temperature for about 1 h at which point a brown-red solution was obtained. A red solid was collected after the solvent was evaporated to dryness under vacuum and the resulting residue was washed by diethyl ether and then dried under vacuum. Yield: 412 mg, 93 %. ^1H NMR (500.2 MHz, $CDCl_3$): $\delta = 8.3$ (dd, $J(H,H) = 9.5$ Hz, $J(H,H) = 2.0$ Hz, 1 H, OsC*H*CHCH(Ph)), 7.5–6.6 (m, 50 H, Ph), 5.2 (m, 1 H, OsCHC*H*CH(Ph)), 4.7 ppm (m, OsCHCHC*H*(Ph)); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): $\delta = 3.9$ (s, C*P*Ph_3), −3.4 (d, $J(P,P) = 360.5$ Hz, Os*P*Ph_3), −7.9 ppm (d, $J(P,P) = 360.5$ Hz, Os*P*Ph_3); elemental analysis (%) calcd for $C_{65}H_{53}Cl_2P_3Os$: C 65.71, H 4.50; found: C 65.70, H 4.33.

For details of the preparation of **4**, **5**, **6**, **7**, **8**, **8a**, and **9**, see the Supporting Information.

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[10] CCDC 796181 (**3**) and CCDC 796183 (**9**) contains 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. See the Supporting Information for details.

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