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Isolation of an Eleven-Atom Polydentate Carbon-Chain Chelate Obtained by Cycloaddition of a Cyclic Osmium Carbyne with an Alkyne

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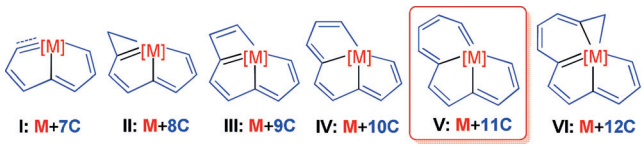
Abstract: *Carbon ligands have long played an important role in organometallic chemistry. However, previous examples of all-carbon chelating ligands are limited. Herein, we present a novel complex with an eleven-atom carbon chain as a polydentate chelating ligand. This species was formed by the [2+2+2] cycloaddition reaction of two equivalents of an alkyne with an osmapentalyne that contains the smallest carbyne bond angle (127.9°) ever observed. Density functional calculations revealed that electron-donating groups play a key role in the stabilization of this polydentate carbon-chain chelate. This process is also the first [2+2+2] cycloaddition reaction of an alkyne with a late-transition-metal carbyne complex. This study not only enriches the chemistry of polydentate carbon-chain chelates, but also deepens our understanding of the chelating ability of carbon ligands.*

The metal–carbon bond is a fundamental feature of organometallic chemistry.[1,2] Many species containing carbon ligands, such as metallocenes,[3] metal carbonyls,[4] metal carbenes,[5] and metal carbynes,[6] play a significant role in organometallic chemistry. However, examples of polydentate ligands with all-carbon chelating atoms (chelating through σ-bonds) are very rare.[7–9] Indeed, reports of CCC-type polydentate ligands are limited, and most of these ligands contain a two-electron N-heterocyclic carbene donor.[7b–g]

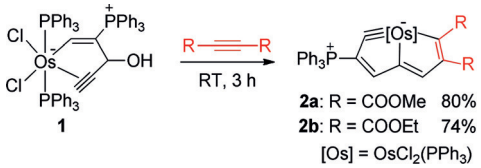
In the past few years, we have reported novel metallaaromatic species, namely metallapentalynes and metallapentalenes (**I** in Scheme 1), that contain a seven-atom carbon chain as the chelating group.[8] Thereafter, with the extension of the chelating carbon chain, a series of organometallic frameworks were constructed (**II**, **III**, **IV**, and **VI** in Scheme 1).[9] These species exhibit diverse properties. For instance, the planar Möbius-aromatic seven-carbon framework **I** shows aggregation-enhanced near-infrared photoluminescence,[8a] whereas the twelve-carbon framework **VI** gives rise to a broad absorption in the near-infrared region and exhibits significant photothermal properties.[9d] Structurally, these frameworks can be viewed as a series of long carbon chains coordinated to a transition metal. Therefore, the term "carbolong chemistry" has been used to describe the chemistry of these frameworks.[9d] However, in the family of the carbolong complexes, the eleven-carbon framework (**V** in Scheme 1) has not been synthesized thus far.



Scheme 1. Representative frameworks of carbolong complexes.

We previously reported the synthesis of the first five-membered metal carbyne complex, osmapentalyne.[8a,10] In this complex, the bond angle of the carbyne carbon atom (129.8°) is much smaller than that observed in the first six-membered metal carbyne, osmabenzyne (148.7°),[10a] and both of them are far from the ideal value of 180°. The extremely small bond angle of osmapentalyne makes it highly reactive. We found that osmapentalyne reacted with nucleophiles and electrophiles to form a series of osmapentalene derivatives.[8b,11] However, our attempts to construct the eleven-carbon framework **V** in a [2+2+2] cycloaddition reaction of two equivalents of an alkyne with the reported osmapentalynes failed.[9b,12] In this work, we synthesized a new osmapentalyne, which has the smallest bond angle (127.9°) at the carbyne carbon reported thus far. Subsequently, the first eleven-carbon framework **V** was synthesized by a [2+2+2] cycloaddition reaction of this cyclic metal carbyne complex with two equivalents of an alkyne. The isolation of the eleven-carbon species completes the sequence of carbolong complexes.

Treatment of osmium complex **1**[13] with an internal alkyne, dimethyl acetylenedicarboxylate (DMAD), at room temperature for 3 h afforded osmapentalyne **2a**, which was isolated as a yellow solid in 80% yield (Scheme 2). Compared to the reported osmapentalynes with high thermal stability,[8a]



Scheme 2. Synthesis of osmapentalynes **2a** and **2b**.

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complex **2a** could only be stored at room temperature for a few weeks in the solid state. Osmapentalyne **2b** was also synthesized under similar conditions.

The solid-state structure of **2a** was determined by X-ray diffraction.[14] As shown in Figure 1, complex **2a** contains

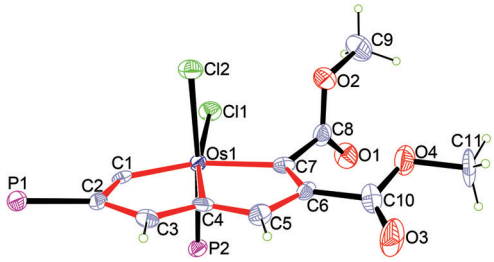


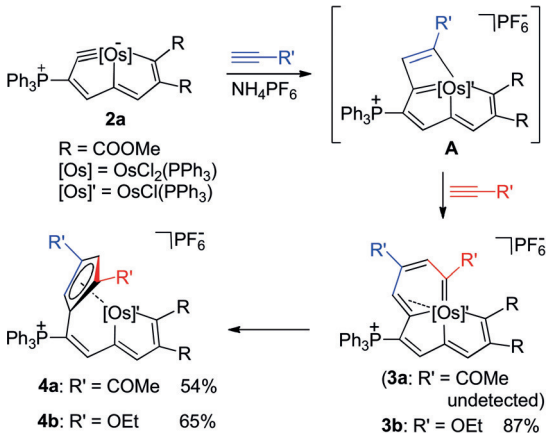
Figure 1. X-ray crystal structure of **2a**. Ellipsoids set at 50% probability. The phenyl moieties in PPh_3 are omitted for clarity.

a metal–carbon triple bond in a five-membered ring (5MR). The length of this triple bond was found to be 1.850(6) Å, which is similar to that of the first osmapentalyne (1.845(3) Å).[8a] The C–C bond lengths (1.373–1.426 Å) in the fused 5MRs are similar to those of benzene, indicating a delocalized structure. Furthermore, **2a** features a nearly planar osmapentalyne unit, as reflected by the mean deviation (0.0407 Å) from the least-squares plane of Os1 and C1–C7 and the sums of the bond angles in the two 5MRs (539.6° and 539.9°).

Complexes **2a** and **2b** were further characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS). In the ^{13}C NMR spectrum of **2a**, the resonance of the carbyne carbon atom was observed at $\delta = 325.8$ ppm, which is in the range of the signals observed for osmapentalynes ($\delta = 319.7$–330.8 ppm).[8a,15] The H3 and H5 proton resonances in the fused 5MRs of **2a** appeared in the aromatic region at $\delta = 7.73$ and 9.39 ppm, respectively. In the HRMS spectrum, the molecular ion peak of **2a** was observed at 1013.1138, which is in agreement with the calculated value for $[M+Na]^+$ (1013.1112).

Notably, the carbyne bond angle (127.9(5)°) of **2a** is the smallest among the metal carbyne species studied to date.[8a] In addition, the single phosphine and two chloride ligands on the osmium center of **2a** offer less steric protection of the Os≡C bond in **2a**, which most likely leads to its higher reactivity. Therefore, we examined reactions of **2a** with alkynes to probe the possibility of [2+2+2] cycloaddition reactions towards an eleven-carbon framework **V** (Scheme 1).

In the presence of NH_4PF_6, treatment of **2a** with 3-butyn-2-one ($HC{\equiv}CCOCH_3$) at room temperature for two days afforded complex **4a** in 54% isolated yield based on **2a** (Scheme 3). Complex **4a** was characterized by single-crystal X-ray diffraction (Figure 2), which clearly showed that a Cp unit is coordinated to the osmium center. The C–C bond lengths in this Cp ring range from 1.394 to 1.473 Å. Therefore, complex **4a** can be viewed as an osmacyclopentadiene and a half-osmacene connected by two sp^2-hybridized carbon atoms. Notably, this is the first example of a [2+2+2] cycloaddition reaction of an alkyne with a late-transition-metal carbyne complex.



Scheme 3. Reactions of osmapentalyne **2a** with alkynes.

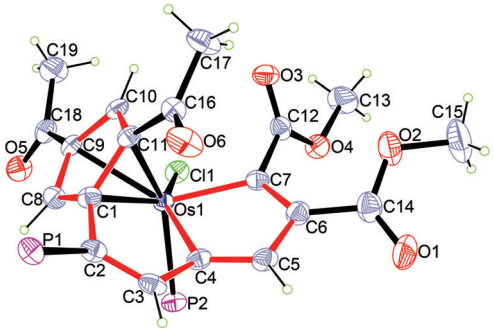


Figure 2. X-ray crystal structure of the cation of complex **4a**. Ellipsoids set at 50% probability. The phenyl moieties in PPh_3 are omitted for clarity.

We inferred that **4a** was formed by a tandem cycloaddition reaction of **2a** with two molecules of the alkyne. As shown in Scheme 3, the first alkyne molecule reacts with **2a** in a [2+2] cycloaddition reaction to give intermediate **A**, which contains a metallacyclobutadiene unit. This process is similar to the previously reported reaction of an osmapentalyne with an alkyne.[9b] Subsequently, the second alkyne inserts into the metallacyclobutadiene unit and forms the six-membered ring (6MR) intermediate **3**, which undergoes elimination to give the final complex **4a**. A detailed mechanism for the formation of **4** is depicted in Scheme S1 in the Supporting Information.

To isolate the eleven-carbon intermediate, we studied the reaction of osmapentalyne **2a** with an electron-donating alkyne to stabilize the 6MR metallabenzene structure.[16] In the presence of NH_4PF_6, osmapentalyne **2a** reacted with two molecules of HC≡COEt at room temperature to give complex **3b** (Scheme 3) after 5 h, which is the first example of an eleven-carbon framework isolated in the family of carbolong complexes. Interestingly, under reflux at 60 °C for two days, complex **3b** underwent an elimination reaction to give the η^1-cyclopentadienyl intermediate, which then rearranged to form the thermally stable η^5-Cp complex **4b** (Scheme S1). The analogous formation of Cp complexes from metallabenzenes has previously been proposed and confirmed.[17]

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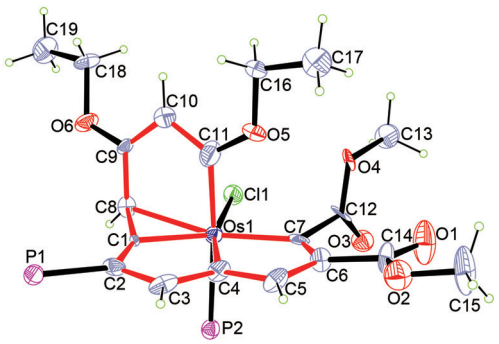

Figure 3. X-ray crystal structure of the cation of complex **3b**. Ellipsoids set at 50% probability. The phenyl moieties in PPh_3 are omitted for clarity.

The solid-state structure of **3b** was determined by single-crystal X-ray diffraction, and one of the two independent molecules with similar structures in the unit cell is shown in Figure 3. Unexpectedly, the 6MR in complex **3b** is extremely distorted, and the dihedral angle between the Os1/C8/C9/C10/C11 and the Os1/C1/C8 plane is 102.7°. However, the two 5MRs are nearly coplanar, as reflected by the small mean deviation from the least-squares plane (0.0380 Å). The Os1–C8 bond (2.253(6) Å) is clearly longer than the Os1–C1 (1.949(6) Å) and Os1–C11 (2.023(7) Å) bonds. The nearly equal Os–C bond lengths (Os1–C1 1.949(6) Å, Os1–C4 2.049(7) Å, Os1–C7 2.030(6) Å) and the C–C bond lengths (1.391–1.420 Å) in the fused 5MRs indicate the delocalized nature of this osmapentalene unit in complex **3b**.

Structurally, complex **3b** can be viewed as an eleven-atom carbon chain coordinated to the osmium center. The 6MR in **3b** is not coplanar with the osmapentalene unit, in contrast to the planar structures observed for other members of the carbolong family. Density functional theory (DFT) calculations showed that this non-coplanar structure of **3b** is more stable than the corresponding planar one (Scheme S2 and Figure 4). Therefore, the framework of **3b** also represents the first non-planar structure in the carbolong family.

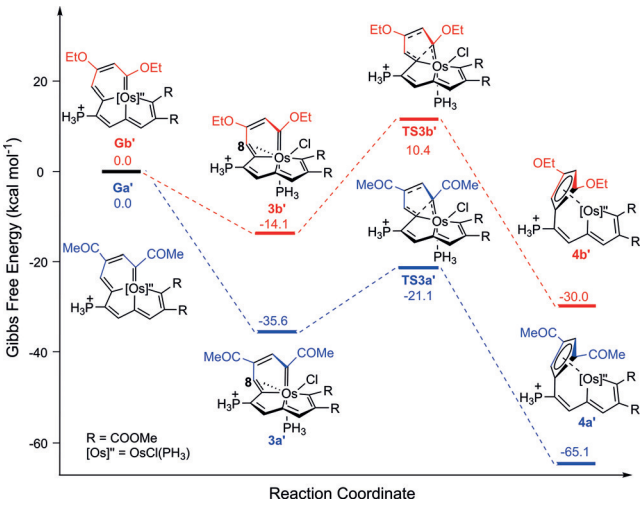

Figure 4. Energy profile (kcal mol^{-1}) for the conversion of the planar 6MR intermediate **G′** into Cp complex **4′**. The pathways for derivatives with electron-donating and electron-withdrawing groups in the 6MR are shown in red and blue, respectively.

The NMR spectroscopic data of complex **3b** are consistent with its X-ray structure. In particular, in its ^{1}H NMR spectrum, the resonances of H3 and H5 were observed at shifts of $\delta = 9.35$ and 8.84 ppm, respectively, which are similar to those of the proton resonances for the osmapentalenes.[8b,18] In the ^{13}C NMR spectrum, the resonances for C1 and C11 were observed at $\delta = 241.6$ and 236.2 ppm, respectively. In addition, the molecular ion peak in the HRMS spectrum of **3b** was observed at 1095.2381, which is in agreement with the calculated value (1095.2386). The solid-state structure of **4b** was also corroborated by NMR spectroscopy and HRMS. The NMR data of **4b** are similar to those of **4a** (see the Supporting Information).

In the reactions of complex **2a** with alkynes, the electron-donating group on the alkyne plays a crucial role in the stabilization of the 6MR in **3b**. To gain more insight into the substituent effect in these reactions, we performed DFT calculations on simplified models with PH_3 groups in place of the PPh_3 groups. Figure 4 shows the energy profile calculated for the conversion of the planar 6MR intermediate **G′** into the final complex **4′** (a full energy profile for this reaction is shown in Figure S1). Interestingly, the non-planar structure **3′** is more stable than the planar structure **G′**, irrespective of whether the substituent on the ring is electron-withdrawing (**3a′**) or electron-donating (**3b′**). The calculated Os1–C8 bond length in **3b′** (2.249 Å) is close to that (2.253 Å) determined from its X-ray structure, which is obviously shorter than that in **3a′** (2.586 Å) and indicates a stronger interaction between the Os1 and C8 atoms in **3b′**. Moreover, the energy barrier for the conversion of **3b′** into **4b′** was calculated to be 24.5 kcal mol^{-1}, which is higher than that for the formation of **4a′** from **3a′** (14.5 kcal mol^{-1}). These values indicate that electron-donating groups increase the energy barrier for the conversion of **3′** into **4′**, which is consistent with the experimental observation that only **3b** was isolated and converted into **4b** at reflux.

In conclusion, we have described the synthesis of a new osmapentalyne with the smallest carbyne bond angle ever reported. Thereafter, the first eleven-atom carbon chain chelating to a transition metal was obtained by the first [2+2+2] cycloaddition of a late-transition-metal carbyne complex with an alkyne. DFT calculations showed that the electron-donating group on the alkyne plays a crucial role in the stabilization of the 6MR intermediate. The non-planar eleven-carbon framework is an important member in the carbolong family because it expands our understanding of the chelating ability of carbon ligands. In addition, a [2+2] cycloaddition reaction between metal carbyne and alkyne has been proposed as a key step in alkyne metathesis. Therefore, this study provides a new perspective for the application of late-transition-metal carbyne species as catalysts in alkyne metathesis or alkyne polymerization reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C ligands · chelation · cycloaddition · metallacycles · osmium

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