

Alternation of Metal-Bridged Metallacycle Skeletons: From Ruthenapentalene to Ruthenapentalene and Ruthenaindene Derivative

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The reaction of ruthenapentalene with one equivalent of isocyanide led to the formation of a rare ruthenapentalene complex by nucleophilic addition. When excess isocyanides were used, the metal-bridged ruthenaindene derivatives can be isolated and were formed by one carbon of isocyanide insertion into the ruthenacycle. Complexes **3** represent the first metallaindene derivatives with a second-row transition metal at the bridgehead position. The transformations from ruthenapentalene *via* ruthenapentalene to ruthenaindene derivatives are of interest and can be extended to the syntheses of other polycyclic ruthenacycles. These unique metallacycles exhibit considerable stability and broad spectral absorption spanning the visible spectrum, and enabling their potential applications in photoelectric materials.

Keywords metallacycle, ruthenium, indene, isocyanide, ring-expansion

Introduction

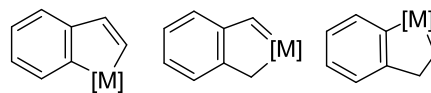
Metallacycles have attracted much interest because of their importance in fundamental chemistry and their promising applications in many fields.^[1] Incorporation of a transition metal fragment into a cyclic compound can significantly influence the structure and electronic properties of the compound. In this way, unique metallacycles exhibiting interesting properties have been synthesized, including metallabenzenes,^[2] metallabenzynes,^[3] metallapentalynes,^[4] metallapentalenes,^[5] and dimetalla[n]annulenes.^[6]

Indene and its derivatives are important structures in natural products,^[7] biologically active compounds^[8] and functional materials.^[9] Replacement of a carbon atom in an indene framework with a transition-metal atom produces a metallaindene, which can show significant reactivity toward unsaturated substrates.^[10] Metallaindenes that have been structurally characterized are typically those with a non-ring junction carbon atom in the five-membered ring replaced by a transition-metal (I, Scheme 1).^[11-15] In contrast, transition metal bridged metallaindenes, in which a ring-junction carbon is replaced by a metal atom, have rarely been observed. Recently, we reported the first metal bridged metallaindene, osmaindene (II, Scheme 1),^[16] and we have now studied second-row transition metals as the bridge-head metal atom in metallaindenes. Metal-bridged ruthenaindene derivatives have been isolated for the first time by the

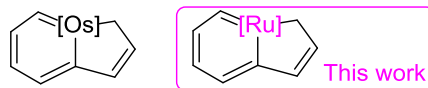
reactions of ruthenapentalene with isocyanides. The reaction proceeds by a nucleophilic addition to form a rare bridgehead ruthenapentalene, and this is followed by an unprecedented ring-expansion reaction of the ruthenacyclic compound.

Scheme 1 Metallaindenes with transition metals located at different positions.

Type I: Non-metal-bridged metallaindenes



Type II: Metal-bridged metallaindenes



Experimental

All syntheses were performed under an N₂ atmosphere using standard Schlenk techniques, unless otherwise stated. Diethyl ether was distilled from sodium/benzophenone and dichloromethane from calcium hydride under N₂ prior to use. The starting materials ruthenapentalene **1** was synthesized according to previously published procedures.^[17] Other reagents were

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used as received from commercial sources without further purification. Column chromatography was performed on silica gel (200-300 mesh) in air. Nuclear magnetic resonance (NMR) spectroscopy was performed at room temperature using a Bruker Advance II 400 spectrometer, or a Bruker Ascend III 600 spectrometer. The ^1H and ^{13}C NMR chemical shifts (δ) are reported relative to tetramethylsilane, and the ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 . The absolute values of the coupling constants are given in hertz (Hz). Elemental analyses were performed on a Vario EL III elemental analyser. Absorption spectra were recorded on a UV-2550 UV-Vis spectrophotometer. The STL808T1-15W fiber-coupled laser system (Stone Company) was used in photothermal experiments and the temperature data were collected by using an FLIR A35 FOV 24 thermal imaging camera. Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD Area Detector with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All of the data were corrected for absorption effects using the multi-scan technique.

For full synthetic details and spectra for ruthenapentalenes **2** and ruthenaindene derivatives **3**, and the X-ray crystallographic details for **2a** and **3a**, see Electronic Supplementary Information (ESI). CCDC-1849259 (**2a**) and CCDC-1849261 (**3a**) contain the supplementary crystallographic data for this paper.

Results and Discussion

Treatment of ruthenapentalyne **1**^[17] with one equivalent of cyclohexyl isocyanide led to the formation of a complex **2a**. The reaction proceeds by the nucleophilic addition of isocyanide to the Ru-C carbyne in ruthenapentalyne **1**. Under similar conditions, **1** reacted with one equivalent of 2-naphthyl isocyanide to produce the analogue **2b** (Scheme 2). Both complexes were characterized by NMR spectroscopy and elemental analysis.

The structure of **2a** was confirmed by single crystal X-ray diffraction. The crystal structure of **2a** showed that it contains a ruthenapentalene skeleton bearing a cyclohexyl isocyanide substituent at the α -carbon (Figure 1). The bond lengths of Ru1-C1 (2.106(4) \AA) and Ru1-C7 (1.995(5) \AA) are comparable with those in previous reported ruthenapentalenes which are between 1.907(2) \AA and 2.103(3) \AA .^[17] The carbon-carbon bond lengths of the metallabicyclic unit fall in the range of 1.376(6) \AA and 1.419(6) \AA , which are between the single and double C-C bond lengths. The metallabicyclic unit of **2a** is approximately planar; the mean deviation from the least-squares plane of Ru and C1-C7 is 0.017 \AA . These data reflect the electronic delocalization within the metallacycles. The bond distances of C1-C11 (1.357(7) \AA) and C11-N1 (1.170(7) \AA) confirm the presence of a cyclohexyl isocyanide substituent in the ruthenapentalene. The C1-C11-N1 angle of 171.8(6) $^\circ$ indi-

cates the nearly linear structure at C11 of the cyclohexyl isocyanide substituent.

Scheme 2 Formation of ruthenapentalenes **2** and ruthenaindene derivatives **3**.

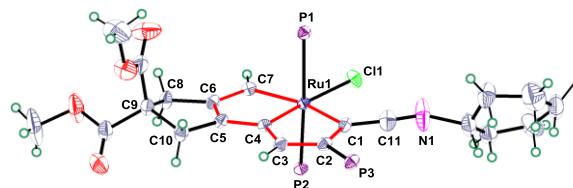
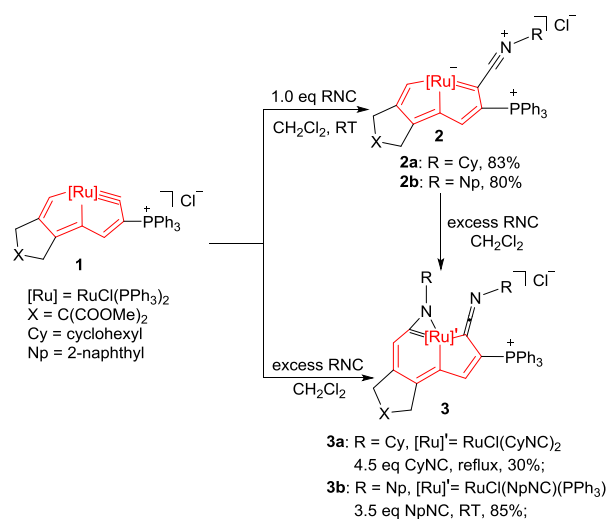


Figure 1. X-ray molecular structure for the cation of **2a** (thermal ellipsoids set at 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity.

Complex **2a** was further characterized by NMR spectroscopy. The ^{31}P NMR spectrum showed a RuPPh_3 signal at 22.98 ppm, and a signal from CPh_3 at 8.65 ppm. In the ^1H NMR spectrum, a phosphorus coupled triplet signal at 16.81 ppm is assigned to the proton at C7. The signal from the proton at C3 appears in the aromatic region with a value of 7.30 ppm. The ^{13}C NMR spectrum displays metal-bonded carbon atoms in the typical downfield regions for C7 (280.0 ppm), C1 (279.9 ppm) and C4 (222.6 ppm). The remaining carbon signals of the ruthenapentalene moiety are observed at 174.3 (C6), 168.4 (C5), 151.9 (C3), 119.5 (C2) ppm, respectively. The signal corresponding to C11 is observed at 111.0 ppm, as expected for a typical isocyanide carbon.^[18]

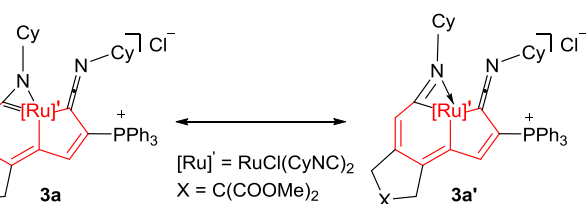
Although a wide variety of metalla-aromatic complexes are known, most documented examples contain third-row transition metal centers^[2-5, 19] and second-row transition metal aromatic complexes, especially those containing ruthenium are limited. To date, well-defined aromatic ruthenacycles were only known for ruthenabenzene and their derivatives,^[20] and the more recently reported ruthenapentalynes and ruthen-

napentalenes.^[17] Ruthenapentalenes **2** represent an important supplement to the rare aromatic ruthenacycle family.

Interestingly, treatment of ruthenapentalene **1** with excess cyclohexyl isocyanide or 2-naphthyl isocyanide in dichloromethane gave rise to complexes **3a** and **3b**, respectively (Scheme 2). The identities of these two products were characterized by their NMR spectra. Further insertion of one carbon of isocyanide into the Ru-C bond occurred, resulting in the formation of the ring-expanded ruthenaindene products. This was confirmed by the crystal structure of **3a** (Figure 2). Complexes **3** can also be obtained from **2** under similar conditions by the addition of excess isocyanide.

Single crystal X-ray diffraction showed that **3a** contains a metallaindene unit with one Ru atom located at the bridgehead position (Figure 2). Complex **3a** has an essentially planar ruthenaindene unit, which is reflected by the small mean deviation (0.067 Å) from the least-squares plane. The sum of the angles in the six-membered and five-membered rings (719.8° and 539.1°, respectively) are very close to the ideal values of 720° and 540°, respectively. Notably, the ruthenaindene ring is fused with an azacyclopropene unit. These rings (composed of Ru1, C1–C8 and N2) are approximately coplanar, as reflected by the mean deviation from the least-squares plane (0.071 Å). The three Ru–C bond lengths (Ru1–C1 2.126(3) Å, Ru1–C4 2.110(3) Å, Ru1–C8 2.085(3) Å) are nearly equal. The C–C bond lengths (1.355(5)–1.444(4) Å) in the metallacycle are within the range of typical single and double carbon-carbon bond lengths. The bond length of C8–N2 is 1.214(4) Å, which suggests a carbon-nitrogen double bond,^[16,21] implying the contribution of resonance structure **3a'** in **3a** (Scheme 3). The bond lengths of C1–C12 (1.324(4) Å), C12–N1 (1.213(4) Å) and the C1–C12–N1 angle of 173.1(4)°, are comparable to those of linear C=C=N substituents.^[16,21]

Scheme 3 The resonance structures of **3a**.



The structure of **3a** was further characterized by NMR spectroscopy. The only single signal at 13.70 ppm in the ³¹P NMR spectrum is attributable to the CPh₃. In the ¹H NMR spectrum, the doublet resonance signal (6.52 ppm) and single signal (5.86 ppm) are assigned to C3H and C7H, respectively. In the ¹³C NMR spectrum, the chemical shift of ruthenium-bonded C8 (190.1 ppm) is downfield from that of C1 (136.3 ppm), suggesting that C8 shows more carbene character than C1. The remaining carbon signals of the ruthenaindene moiety are observed at 120.2 (C2), 150.3 (C3), 189.8 (C4), 167.3

(C5), 147.9 (C6) and 80.3 (C7) ppm. In comparison to the NMR of **3a**, the ³¹P NMR spectrum of **3b** shows two singlet signals at 15.34 ppm and 16.35 ppm, which are assigned to CPh₃ and RuPPh₃ respectively, indicating one PPh₃ ligand is not substituted by isocyanide. The R group of the isocyanide influence the behavior of the ligand substitution due to the steric effect.

Structurally characterized ruthenaindenes are rare and are all limited to those in which the ruthenium is at the non-bridgehead position.^[12] The structure of **3** allows its identification as a unique ruthenaindene with a bridge-head ruthenium atom. The formation of **3**, realized by the unprecedented ring-expansion of ruthenapentalene or ruthenapentalene, is an example of an efficient method with which to synthesize new polycyclic ruthenacycles.

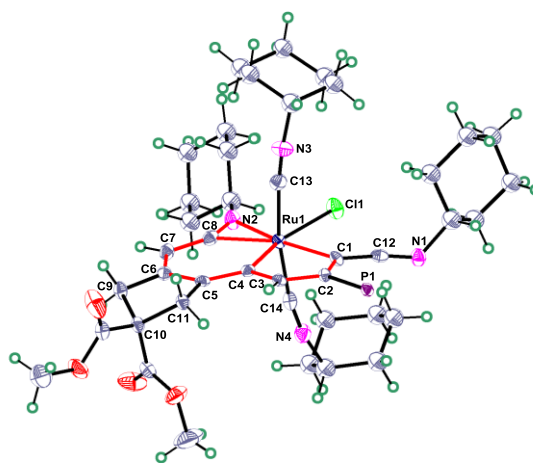
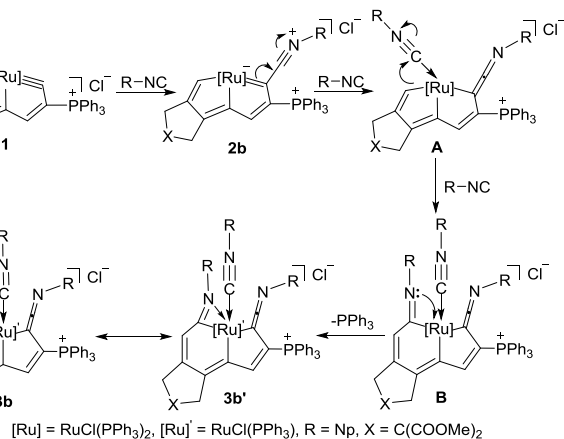


Figure 2. X-ray molecular structure for the cation of **3a** (thermal ellipsoids set at 50% probability). The phenyl moieties in PPh₃ have been omitted for clarity.

A plausible mechanism for the formation of **3** is proposed for 2-naphthyl isocyanide and is shown in Scheme 4. First, the nucleophilic addition of one equivalent of isocyanide to the ruthenapentalene **1** affords ruthenapentalene **2b**. Then the intramolecular arrangement of **2** and coordination of an isocyanide to the ruthenium center generates the intermediate **A**. This is followed by the insertion of the isocyanide into the Ru-C bond resulting in the formation of intermediate **B**. Notably, the insertion reaction selectively occurred at the C7 position rather than C1 may due to the steric effect of R group on C=C=N and phosphonium substituent adjacent to C1. Reactions such as cycloaddition and insertion tend to attack at the less steric site in our previous works.^[5b, 5d-g, 16] The displacement of PPh₃ and coordination of nitrogen in exocyclic imine group to the ruthenium center, and the aromatization of the six-membered metallacycle would afford the final ruthenaindene derivative **3b**. Previously, in the formation of osmaindene derivative, an η²-iminoketenyl

osmpentalene intermediate was isolated,^[16] but in our case, no such species was observed. The less diffuse d orbitals of ruthenium, compared to those of osmium, suggest a weaker electron-back donation of ruthenium to the carbon,^[22] which results in the unfavorability of the formation of a ruthenium η^2 -coordination species.

Scheme 4 The proposed mechanism of the formation of ruthenaindene derivatives **3b**.



In the solid state, ruthenaindene derivatives **3a** and **3b** are air-stable. Their thermal stabilities are also remarkable; both remain nearly unchanged when heated at 100 °C in air for 3 h. The UV-vis absorption spectra of complexes **2** and **3** are shown in Figure 3. In the visible region, an absorption maximum for **2b** is observed at 562 nm, which is red-shifted by approximately 80 nm compared with that of **2a**. Complex **3a** has an absorption maximum at 621 nm, while complex **3b** exhibits broad absorption in the range of 500-700 nm. The results indicate the R group on the isocyanide made a significant contribution on the absorption properties.

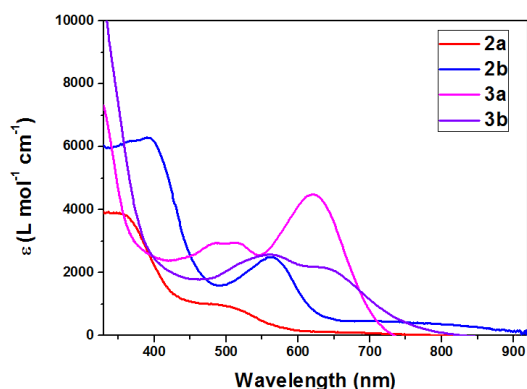


Figure 3. UV-vis absorption spectra of **2** and **3** (1.0×10^{-4} M) in CH_2Cl_2 at room temperature.

As **2b** shows a broad absorption between 700 nm and 900 nm, its photothermal behavior was further examined by measuring the temperature of its solution under NIR laser irradiation (808 nm, 1.0 W cm^{-2}).^[5f, 23] As shown in Figure 4, the temperature of the EtOH so-

lution containing **2b** (1.0 mg mL^{-1}) significantly increased from 28 °C to 56 °C within 3 min, while the solvent (without **2b**) shows a negligible temperature change (<4 °C) under similar conditions. Thus **2b** shows good photothermal properties.

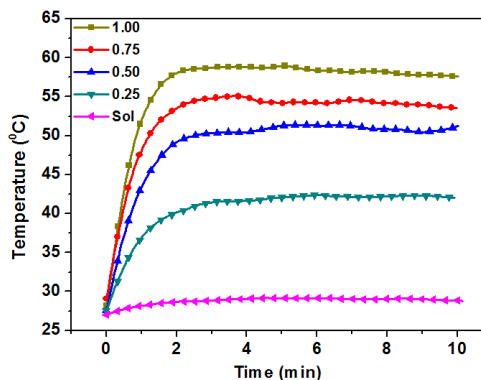


Figure 4. Temperature curves of solutions of **2b** in EtOH at different concentrations (0.00, 0.25, 0.50, 0.75 and $1.00 \text{ mg}\cdot\text{mL}^{-1}$) irradiated with an 808 nm laser at a power density of $1.0 \text{ W}\cdot\text{cm}^{-2}$.

Conclusions

In summary, we describe the preparation and characterization of a type of novel metal-bridged ruthenaindene derivatives, which is the first reported metallaindene with a second-row transition metal at the bridge-head position. The formation of ruthenaindene derivative is derived from the ruthenapentalene *via* a rare ruthenapentalene. The interesting transformation of metallacycle skeletons in the reactions provides an effective methodology for the construction of polycyclic metallacycles. The unique structures, broad absorption spanning the whole visible region together with considerable stability suggest the promising applications of these ruthenacycles in the material field.

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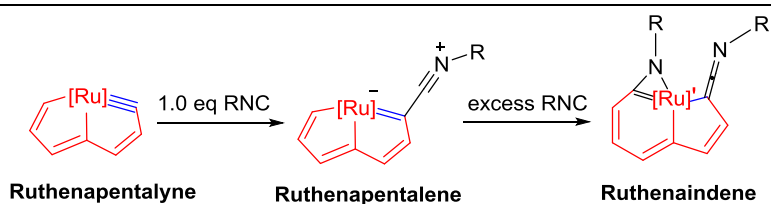
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Entry for the Table of Contents

Page No.

Alternation of Metal-Bridged Metal-cycle Skeletons: From Ruthenapentalyne to Ruthenapentalene and Ruthenaindene Derivative

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The first reported metal-bridged ruthenaindene derivatives have been achieved by the ring-expansion reaction of ruthenapentalyne through a rare ruthenapentalene.

Accepted Article