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Concise Report

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Alternation of Metal-Bridged Metallacycle Skeletons: From Ruthenapentalyne to Ruthenapentalene and Ruthenaindene Derivative[†]

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ABSTRACT The reaction of ruthenapentalyne 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 bridge-head position. The transformations from ruthenapentalyne 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, enabling their potential applications in photoelectric materials.

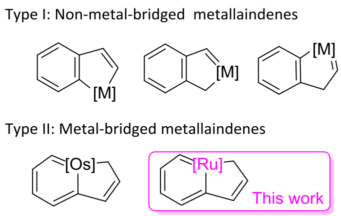
KEYWORDS metallacycle, ruthenium, indene, isocyanide, ring-expansion

Introduction

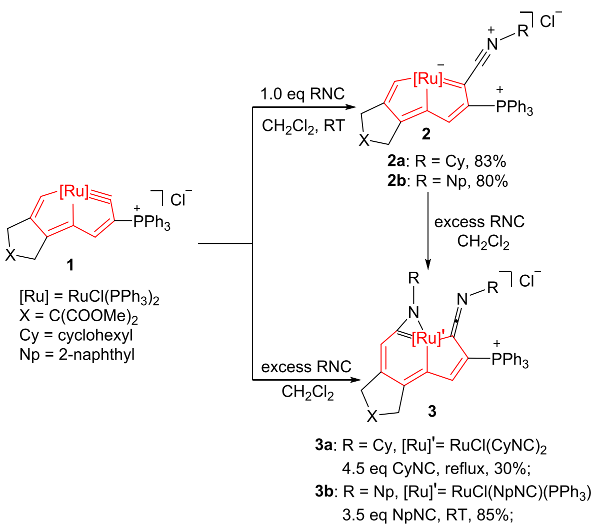
Metallacycles have attracted much interest because of their importance in fundamental chemistry and their promising applications in many fields.[1] Incorporation of a transition metal fragment into a cyclic compound can significantly influence the structure and electronic properties of the compound. 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 ruthenapentalyne 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



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



Results and Discussion

Treatment of ruthenapentalyne **1**[17] with one equivalent of cyclohexyl isocyanide led to the formation of 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) Å) and Ru1—C7 (1.995(5) Å) are comparable with those in previous reported ruthenapentalenes which are between 1.907(2) Å and 2.103(3) Å).[17] The carbon-carbon bond lengths of the metallabicycle fall in the range of 1.376(6) Å and 1.419(6) Å, 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 Å. These data reflect the electronic delocalization within the metallacycles. The bond distances of C1—C11 (1.357(7) Å) and C11—N1 (1.170(7) Å) confirm the presence of a cyclohexyl isocyanide substituent in the ruthenapentalene. The C1–C11–N1 angle of

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[†] Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

171.8(6)° indicates the nearly linear structure at C11 of the cyclohexyl isocyanide substituent.

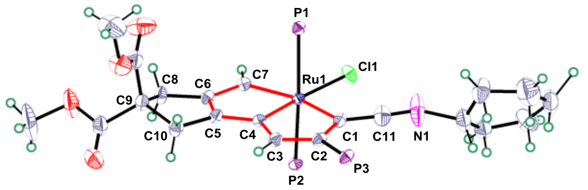


Figure 1 X-ray molecular structure for the cation of **2a** (thermal ellipsoids set at 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity.

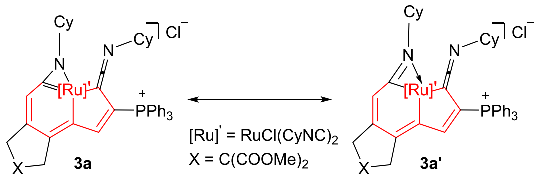
Complex **2a** was further characterized by NMR spectroscopy. The ^{31}P NMR spectrum showed a Ru*P*Ph$_3$ signal at *δ* 22.98, and a signal from C*P*Ph$_3$ at *δ* 8.65. In the ^{1}H NMR spectrum, a phosphorus coupled triplet signal at *δ* 16.81 assigned to the proton at C7. The signal from the proton at C3 appears in the aromatic region with a value of *δ* 7.30. The ^{13}C NMR spectrum displays metal-bonded carbon atoms in the typical downfield regions for C7 (*δ* 280.0), C1 (*δ* 279.9) and C4 (*δ* 222.6). The remaining carbon signals of the ruthenapentalene moiety are observed at *δ* 174.3 (C6), 168.4 (C5), 151.9 (C3), 119.5 (C2), respectively. The signal corresponding to C11 is observed at *δ* 111.0, 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 ruthenabenzenes and their derivatives,[20] and the more recently reported ruthenapentalynes and ruthenapentalenes.[17] Ruthenapentalenes **2** represent an important supplement to the rare aromatic ruthenacycle family.

Interestingly, treatment of ruthenapentalyne **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 bridge-head 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) is 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 *δ* 13.70 in the ^{31}P NMR spectrum is attributable to the C*P*Ph$_3$. In the ^{1}H NMR spectrum, the doublet resonance signal (*δ* 6.52) and single signal (*δ* 5.86) are assigned to C3*H* and C7*H*, respectively. In the ^{13}C NMR spectrum, the chemical shift of ruthenium-bonded C8 (*δ* 190.1) is downfield from that of C1 (*δ* 136.3), suggesting that C8 shows more carbene character than C1. The remaining carbon signals of the ruthenaindene moiety are observed at *δ* 120.2 (C2), 150.3 (C3), 189.8 (C4), 167.3 (C5), 147.9 (C6) and 80.3 (C7). In comparison to the NMR of **3a**, the ^{31}P NMR spectrum of **3b** shows two singlet signals at *δ* 15.34 and 16.35, which are assigned to C*P*Ph$_3$ and Ru*P*Ph$_3$, respectively, indicating one PPh_3 ligand is not substituted by isocyanide. The R group of the isocyanide influences 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 an unique ruthenaindene with a bridge-head ruthenium atom. The formation of **3**, realized by the unprecedented ring-expansion of ruthenapentalyne or ruthenapentalene, is an example of an efficient method with which new polycyclic ruthenacycles can be synthesized.

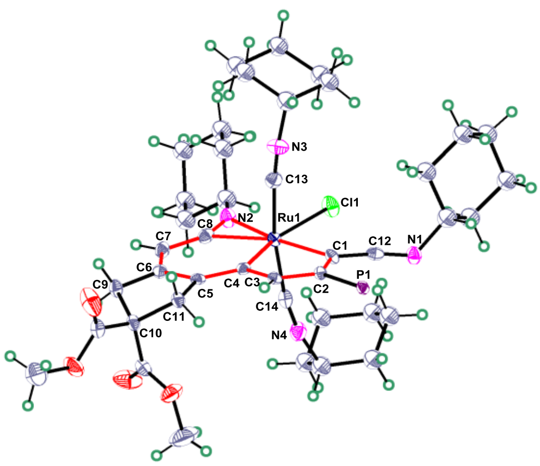
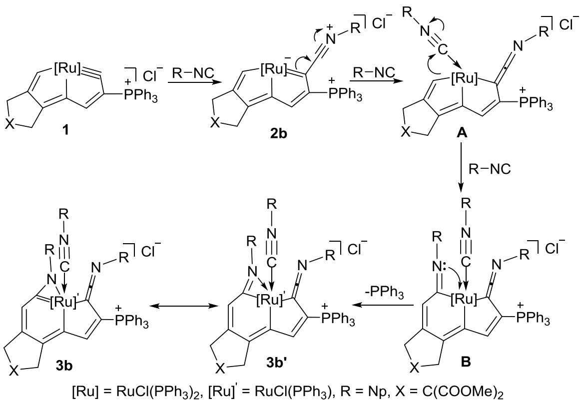


Figure 2 X-ray molecular structure for the cation of **3a** (thermal ellipsoids set at 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity.

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 ruthenapentalyne **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, which may be 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-5g,16] The displacement of PPh_3 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 η^2-iminoketenyl osmapentalene 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 derivative **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 to the absorption properties.

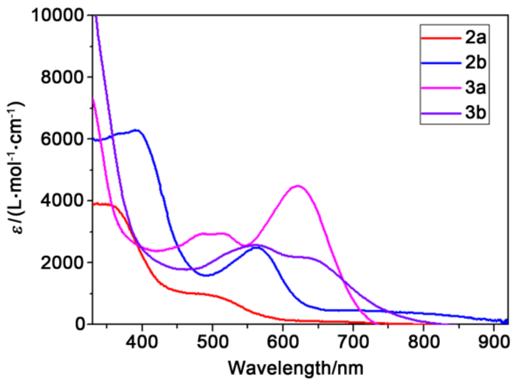


Figure 3 UV-vis absorption spectra of **2** and **3** (1.0×10^{-4} mol/L) in CH_2Cl_2 at room temperature.

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

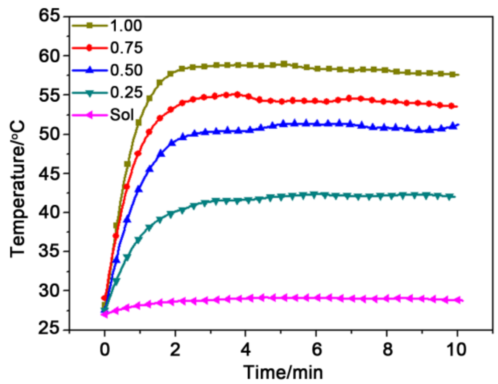


Figure 4 Temperature curves of solutions of **2b** in EtOH at different concentrations (0.00, 0.25, 0.50, 0.75 and 1.00 mg·mL^{-1}) irradiated with an 808 nm laser at a power density of 1.0 W·cm^{-2}.

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 ruthenapentalyne *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 filed.

Experimental

All syntheses were performed under an N_2 atmosphere using standard Schlenk techniques, unless otherwise stated. Diethyl ether was distilled from sodium/benzophenone and dichloromethane from calcium hydride under N_2 prior to use. The starting materials ruthenapentalyne **1** was synthesized according to previously published procedures.[17] Other reagents were 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 ^{1}H 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 Mo Kα radiation (λ=0.71073 Å). All of the data were corrected for absorption effects using the multi-scan technique.

For full 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.

Synthesis and characterization of ruthenapentalene 2a: To a dichloromethane solution (10 mL) of complex **1** (300 mg, 0.25 mmol) was added cyclohexyl isocyanide (31 μL, 0.25 mmol). The mixture was stirred for 30 min at room temperature to give an orange solution. Then the solution was evaporated under vacuum to approximately 3 mL, and the residue was washed with diethyl ether to give **2a** as an orange solid (272 mg, 83%). ^{1}H NMR (600.1 MHz, CD_2Cl_2) δ: 16.81 (t, *J*(P,H)=6 Hz, 1H, C^7*H*), 7.30 (d, *J*(P,H)=5 Hz, 1H, C^3*H*), 7.09—7.77 (46H, H of PPh_3 and above mentioned C^3*H*), 3.54 (s, 6H, COOC*H*$_3$), 3.27 (t, *J*(H,H)=4 Hz, 2H, C^{10}*H*), 1.46 (br, 2H, C^8*H*), 3.13, 1.60, 1.58 plus 1.44—0.99 (11H, H of Cy); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2) δ: 22.98 (s, Ru*P*Ph$_3$), 8.65 (s, C*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC) δ: 280.0 (m, C7), 279.9 (m, C1), 222.6 (dt, *J*(P,C)=25 Hz, *J*(P,C)=6 Hz, C4), 174.3 (t, *J*(P,C)=5 Hz, C6), 171.0 (s, *C*OOCH$_3$), 168.4 (s, C5), 151.9 (d, *J*(P,C)=22 Hz, C3), 143.4 –119.5 (other aromatic carbons), 119.5 (d, *J*(P,C)=87 Hz, C2), 111.0 (d, *J*(P,C)=9 Hz, C11), 64.3 (s, C9), 57. 0 (s), 32.9 (s), 24.6 (s) plus 23.9 (s, 6C of Cy), 52.9 (s, COO*C*H$_3$), 37.8 (s, C8), 37.7 (s, C10). Anal. Calcd for $C_{75}H_{68}Cl_2NO_4P_3Ru$: C, 68.65; H, 5.22; N, 1.07; Found: C, 68.38; H, 5.21; N, 1.09.

Synthesis and characterization of ruthenapentalene 2b: A similar reaction procedure of **2a** was applied except for replacing cyclohexyl isocyanide by 2-naphthyl isocyanide (38 mg, 0.25 mmol), leading to the formation of **2b** as a reddish brown solid (271 mg, 80%). ^{1}H NMR (600.1 MHz, CD_2Cl_2) δ: 18.07 (t, *J*(P,H)=6 Hz, 1H, C^7*H*), 7.33 (d, *J*(P,H)=5 Hz, 1H, C^3*H*), 6.96—7.80 (53H, H of PPh$_3$, H of Np and above mentioned C^3*H*), 3.57 (s, 6H, COOC*H*$_3$), 3.40 (br, 2H, C^{10}*H*), 1.46 (br, 2H, C^8*H*); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2) δ: 20.22 (s, Ru*P*Ph$_3$), 10.82 (s, C*P*Ph$_3$); ^{13}C {^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC) δ: 288.1 (m, C7), 288.0 (m, C1), 226.7 (dt, *J*(P,C)=24 Hz, *J*(P,C)=5 Hz, C4), 174.3 (t, J(P,C)=4 Hz, C6), 171.0 (s, *C*OOCH$_3$), 168.3 (s, C5), 154.2 (d, *J*(P,C)=23 Hz, C3), 125.5—143.9 (other aromatic carbons), 119.1 (d, *J*(P,C)=87 Hz, C2), 114.3(d, *J*(P,C)=11 Hz, C11), 64.2 (s, C9), 52.9 (s, COOCH$_3$), 37.8 (s, C8), 37.4 (s, C10). Anal. Calcd for $C_{79}H_{64}Cl_2NO_4P_3Ru$: C, 69.96; H, 4.76; N, 1.03; Found: C, 69.82; H, 4.39; N, 0.99.

Synthesis and characterization of ruthenapentalene 3a. Method 1: To a solution of complex **1** (300 mg, 0.25 mmol) in dichloromethane (10 mL) was added cyclohexyl isocyanide (140 μL, 1.13 mmol). The mixture was heated to reflux and stirred for 1 h to give a dark blue solution. The solution was concentrated to approximately 5 mL, then purified by column chromatography (silica gel, 200—300 mesh, eluent: dichloromethane/methanol=45/1) to obtain **3a** as a dark blue solid (84 mg, 30%). **Method 2**: Treatment of isolated **2a** (300 mg, 0.23 mmol) in dichloromethane (10 mL) with cyclohexyl isocyanide (99 μL, 0.80 mmol) by the similar procedure of **Method 1** can also give rise to **3a** (92 mg, 36%). ^{1}H NMR (400.0 MHz, CD_2Cl_2) δ: 7.80—7.60 (15H, H of PPh$_3$), 6.52 (d, *J*(P,H)=10 Hz, 1H, C^3*H*), 5.86 (s, 1H, C^7*H*), 4.90 (tt, *J*(H,H)=11 Hz, *J*(H,H)=3 Hz, 1H, Cy), 3.50 (br, 2H, Cy) plus 1.22—2.37 (41H, Cy), 3.61 (s, 6H, COOC*H*$_3$), 3.42 (s, 2H, C^{11}*H*), 3.12 (s, 2H, C^9*H*); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2) δ: 13.70 (s, C*P*Ph$_3$); ^{13}C {^{1}H} NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC) δ: 190.1 (s, C8), 189.8 (s, C4), 171.5 (s, *C*OOCH$_3$), 167.3 (s, C5), 165.9 (d, *J*(P,C)=6 Hz, C12), 150.3 (d, *J*(P,C)=22 Hz, C3), 147.9 (s, C6), 142.0 (br, RuCyNC), 136.3 (s, C1), 134.9—127.9 (other aromatic carbons), 120.2 (d, *J*(P,C)=88 Hz, C2), 85.0 (s), 84.9 (s), 57.7 (s), 57.6 (s) plus 21.6—33.9 (24C of Cy), 80.3 (s, C7), 60.8 (s, C10), 52.9 (s, COO*C*H$_3$), 42.7 (s, C9), 40.4 (s, C11). Anal. Calcd for $C_{60}H_{71}Cl_2N_4O_4PRu$: C, 64.62; H, 6.42; N, 5.02; Found: C, 64.89; H, 6.08; N, 5.13.

Synthesis and characterization of ruthenapentalene 3b. Method 1: To a solution of complex **1** (300 mg, 0.25 mmol) in dichloromethane (10 mL) was added 2-naphthyl isocyanide (134 mg, 0.88 mmol). The mixture was stirred at RT for 3 h. Then, the solution was concentrated to approximately 3 mL, and washed by diethyl ether to form a brown solid (298 mg, 85%). **Method 2**: Treatment of isolated **2b** (300 mg, 0.22 mmol) in dichloromethane (10 mL) with 2-naphthyl isocyanide (85 mg, 0.55 mmol) by the similar procedure of **Method 1** can also give rise to **3b** (272 mg, 88%). ^{1}H NMR (600.1 MHz, CD_2Cl_2) δ: 8.32—7.11 (51H, H of PPh$_3$, H of Np), 6.39 (s, 1H, C^7*H*), 6.36 (d, *J*(P,H)=10 Hz, 1H, C^3*H*), 3.89 (s, 3H, COOC*H*$_3$), 3.77 (d, *J*(H,H)=22 Hz, 1H, C^9*H*), 3.68 (s, 3H, COOC*H*$_3$), 3.60 (d, *J*(H,H)=22 Hz, 1H, C^9*H*), 3.17 (d, *J*(H,H)=16 Hz, 1H, C^{11}*H*), 2.67 (d, *J*(H,H)=16 Hz, 1H, C^{11}*H*); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2) δ: 16.35 (s, Ru*P*Ph$_3$), 15.34 (s, C*P*Ph$_3$); ^{13}C {^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC) δ: 198.2 (d, *J*(P,C)=11 Hz, C8), 198.0 (d, *J*(P,C)=11 Hz, C4), 172.3 (s, C5), 171.5 and 171.2 (s, *C*OOCH$_3$), 169.1 (s, C6), 166.4 (d, *J*(P,C)=7 Hz, C12), 153.8 (d, *J*(P,C)=20 Hz, C3), 139.4 (s, C1), 123.8 (br, RuNpN*C*), 148.8—122.0 (other aromatic carbons and above mentioned C1, RuNpN*C*), 118.9 (d, *J*(P,C)=88 Hz, C2), 86.4 (s, C7), 57.7 (s, C10), 53.9 (s, COO*C*H$_3$), 43.0 (s, C9), 40.4 (s, C11). Anal. Calcd for $C_{83}H_{63}Cl_2N_3O_4P_2Ru$: C, 71.19; H, 4.53; N, 3.00; Found: C, 70.99; H, 4.14; N, 3.29.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.201800362.

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