

Electronic Supplementary Information for:

**Intramolecular cyclization of a diruthenium complex: insight into the
mechanism of heteroatom-directed intramolecular C-H/olefin
coupling reactions**

Dawei Gong,^{ac} Bowen Hu,^a Jing Shi^a and Dafa Chen^{*ab}

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Experimental Section

A. Chemicals and Reagents

All manipulations were carried out under an inert N₂(g) atmosphere using a Schlenk line. Solvents were distilled from appropriate drying agents under N₂ before use. All reagents were purchased from commercial sources. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use. $\{(C_5H_4N)(\mu_2-\eta^5:\eta^1-C_9H_5)\}Ru_3(CO)_9$ (**1**) was prepared as described previously.^{S1}

B. Physical methods

The ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer. ¹H NMR chemical shifts were referenced to residual solvent as determined relative to Me₄Si ($\delta = 0$ ppm). IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. X-ray diffraction studies were carried out in a Xcalibur E X-ray single crystal diffractometer. Data collections were performed using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption.^{S2} Solution, refinement and geometrical calculations for all crystal structures were performed by SHELXTL.^{S3}

C. Synthetic methods

Synthesis of $\{(C_5H_4N)(\mu_3-\eta^5,\eta^2,\eta^1-C_9H_5CHCH_2CH_2CH_2CH=CH_2)\}Ru_2(CO)_4$ (**2**)

A solution of 0.200 g (0.27 mmol) of **1** and 0.219 g (2.7 mmol) of 1, 5-hexadiene in 10 mL toluene was refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was placed in an Al₂O₃ column. Elution with EtOAc/petroleum ether (v : v = 20 : 1) to give 0.095 g (60.4%) of **2** as orange crystals. Mp: 180 °C (dec). Anal. Calcd for C₂₄H₁₉NO₄Ru₂: C, 49.1; H, 3.3; N, 2.4. Found: C, 49.3; H, 3.2; N, 2.2. ¹H NMR (400 Hz, CDCl₃): δ [7.68 (d, $J = 8.0$ Hz, 1H), 7.58 (td, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.42 (m, 2H), 7.29 (m, 1H), 7.19 (m, 2H), 6.87 (m, 1H)] (Py-H and Ar-H), 4.85 (s, 1H, Cp-H), [3.59 (d, $J = 13.0$ Hz, 1H), 3.48 (d, $J = 8.4$ Hz, 1H), 3.15 (m, 1H), 2.87 (m, 1H), 2.32 (m, 2H), 2.15-1.97 (m, 2H), 1.34-1.14 (m, 2H)] (CHCH₂CH₂CH₂CH=CH₂). IR(ν_{CO} , cm⁻¹, CH₂Cl₂): 2023 (s), 1955 (s), 1900 (s).

Synthesis of $\{(C_5H_4N)(\mu_2-\eta^3,\eta^5-C_9H_5CCH_2CH_2CH_2CCH_2)\}Ru_2(CO)_4$ (**3**)

A solution of 0.500 g (0.85 mmol) of **2** in 10 mL toluene was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was placed in an Al₂O₃ column. Elution with EtOAc/petroleum ether (v : v = 20 : 1) to give 0.380 g (76.3 %) of **3** as orange crystals. Mp: 180°C (dec). Anal. Calcd for C₂₄H₁₇NO₄Ru₂: C, 49.2; H, 2.9; N, 2.4. Found: C, 49.5; H, 3.2; N, 2.3. ¹H NMR (400 Hz, CDCl₃): δ [8.48 (d, $J = 5.2$ Hz, 1H), 7.72 (t, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.24 (m, 1H), 7.12 (t, $J = 8.0$ Hz, 1H), 7.01 (t, $J = 8.4$ Hz, 1H)] (Py-H and Ar-H), 4.35 (s, 1H, Cp-H), [3.16 (m, 1H), 2.64 (m, 1H),

2.47 (m, 1H), 2.31 (m, 2H), 1.96 (m, 2H), 1.50 (m, 1H)] (CCH₂CH₂CH₂C=CH₂). IR(ν_{CO} , cm⁻¹, CH₂Cl₂): 2002 (s), 1958 (s), 1928 (m), 1904 (s).

Catalytic reaction of 3-(2-pyridyl)indene with 1,5-hexadiene

A solution of 0.173 g (1 mmol) of 3-(2-pyridyl)indene, 0.164 g (2 mmol) of 1,5-hexadiene, and 0.064 g (0.1 mmol) of Ru₃(CO)₁₂ in 10 mL toluene was refluxed for 12 h. The solvent and 1,5-hexadiene were removed under reduced pressure, and the residue was placed in an Al₂O₃ column. Elution with EtOAc/petroleum ether ($v : v = 10 : 1$) to give 0.090 g (48.9 %) of [(C₅H₄N)(C₉H₆)]Ru(CO)₂ and 0.057 g (recovery yield : 33.0%) of 3-(2-pyridyl)indene.

Catalytic reaction of 2-phenylpyridine with 1,5-hexadiene

A solution of 0.155 g (1 mmol) of 2-phenylpyridine, 0.164 g (2 mmol) of 1,5-hexadiene, and 0.064 g (0.1 mmol) of Ru₃(CO)₁₂ in 10 mL toluene was refluxed for 12 h. The solvent and 1,5-hexadiene were removed under reduced pressure, and the residue was placed in an Al₂O₃ column. Elution with EtOAc/petroleum ether ($v : v = 10 : 1$) to give 0.090 g (51.5 %) of [(C₅H₄N)(C₆H₄)]Ru(CO)₂ and 0.039 g (recovery yield : 25.3%) of 2-phenylpyridine.

D. Crystallographic Details for 2

A total of 8580 reflections ($-20 \leq h \leq 20$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$) were collected at $T = 293(2)$ K in the range of 2.99 to 25° of which 3759 were unique ($R_{\text{int}} = 0.0234$); MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.362 and -0.331 eÅ⁻³, respectively. The least squares refinement converged normally with residuals of $R(F) = 0.0244$, $wR(F^2) = 0.0485$ and a GOF = 1.048 ($I > 2\sigma(I)$). C₂₄H₁₉NO₄Ru₂, Mw = 587.54, space group C2/c, Monoclinic, $a = 17.6013(5)$, $b = 15.0254(4)$, $c = 17.6493(6)$ Å, $\beta = 113.718(4)^\circ$, $V = 4273.4(2)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.826$ Mg/m³.

E. Crystallographic Details for 3

A total of 14062 reflections ($-19 \leq h \leq 13$, $-11 \leq k \leq 9$, $-37 \leq l \leq 37$) were collected at $T = 296(2)$ K in the range of 2.24 to 25° of which 4026 were unique ($R_{\text{int}} = 0.0312$); MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.623 and -0.695 eÅ⁻³, respectively. The least squares refinement converged normally with residuals of $R(F) = 0.0471$, $wR(F^2) = 0.1131$ and a GOF = 1.098 ($I > 2\sigma(I)$). C₂₄H₁₇NO₄Ru₂, Mw = 585.53, space group P 21/c, Monoclinic, $a = 16.155(5)$, $b = 9.626(3)$, $c = 31.755(7)$ Å, $\beta = 120.579(11)^\circ$, $V = 4251(2)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.830$ Mg/m³.

References

(S1)Chen, D.; Zhang, X.; Xu, S.; Song, H.; Wang, B. *Organometallics* **2010**, *29*, 3418.

(S2)Blessing, R. H. *Acta Crystallogr. A* **1995**, *51*, 33-38.

(S3)Sheldrick, G. M. *SHELXTL* release 6.1.4 ed.; Bruker AXS Inc.: Madison, Wisconsin, 53719, USA, 2003.

IR Spectra

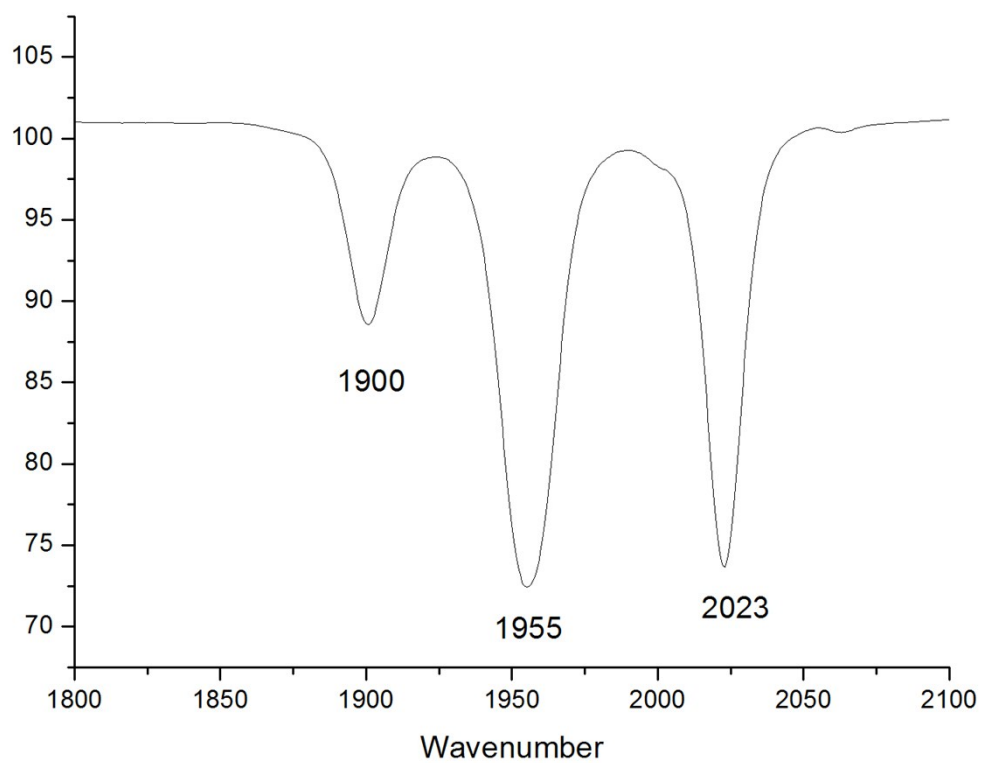


Figure S1. IR spectrum of **2** in CH_2Cl_2 .

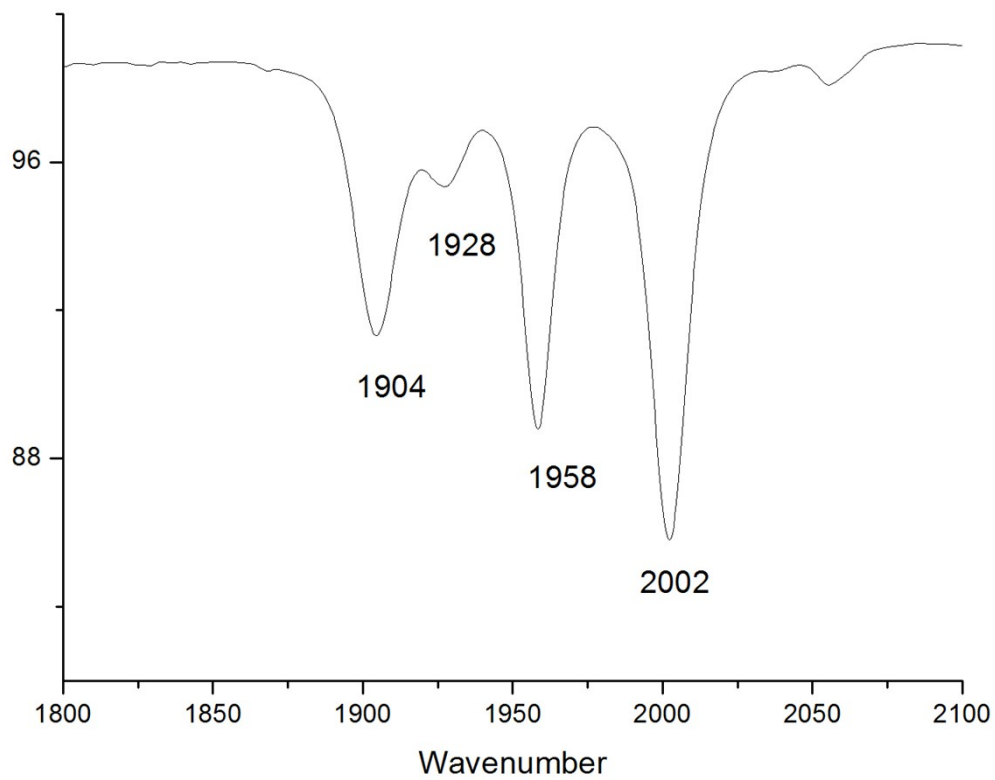


Figure S2. IR spectrum of **3** in CH_2Cl_2 .

1H NMR Spectra

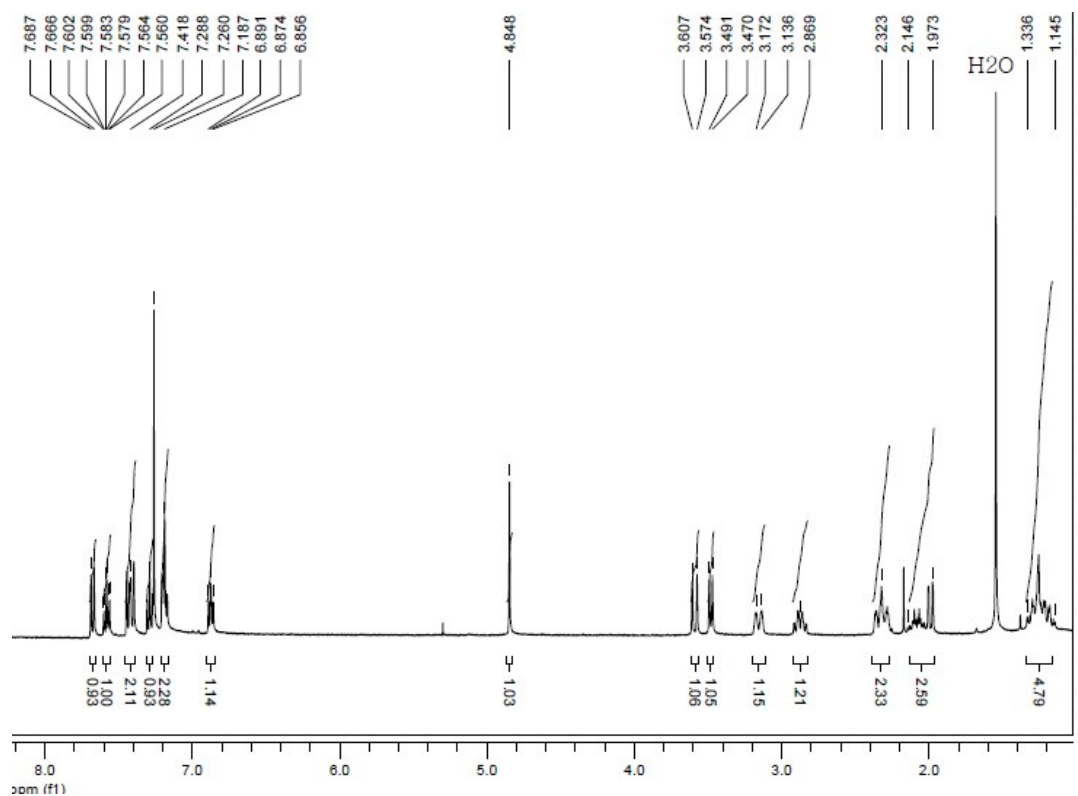


Figure S3. ¹H NMR spectrum of **2** in CH₂Cl₂.

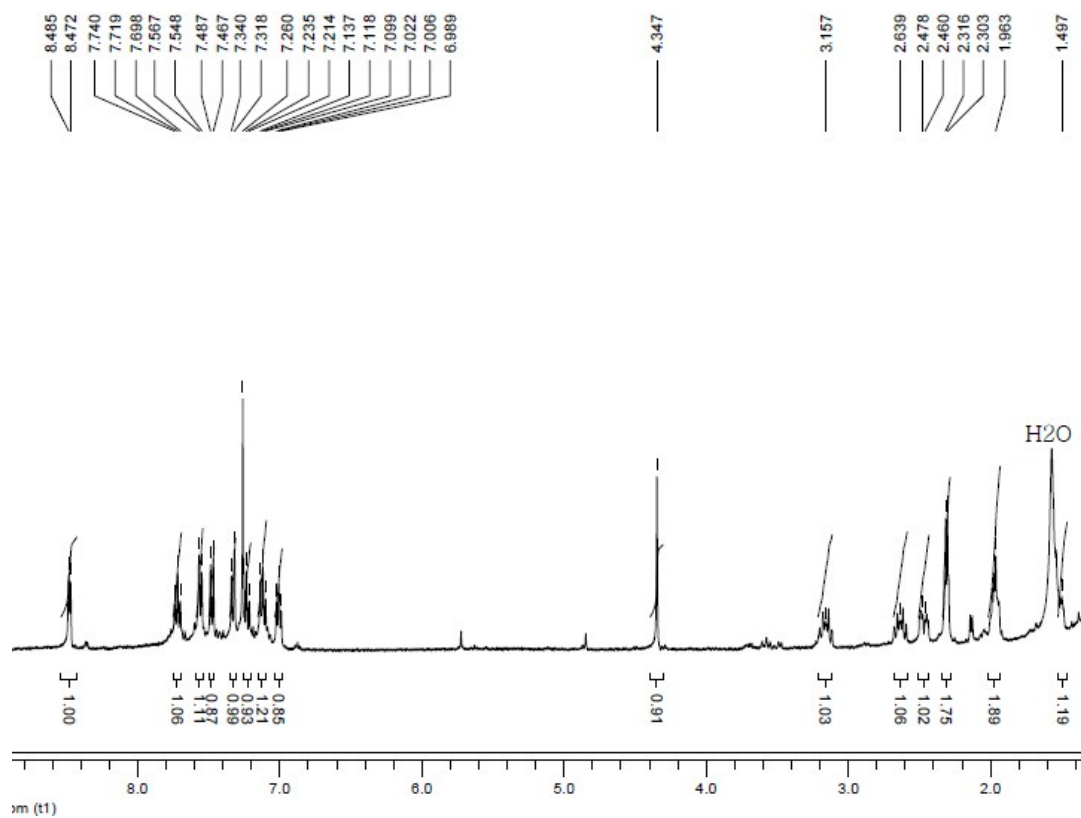


Figure S4. ¹H NMR spectrum of **3** in CH₂Cl₂.