Supporting Information

Solvent-Free Photochemical Formation of Cubane-type Ru Complexes

from Organometallic Ionic Liquids with Cyanoborate Anions

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1. Experimental Procedures

General

[Ru(Cp)(C₆H₆)]Cl and K[BC₄H₉(CN)₃] were prepared using previously reported methods.^{S1,S2} K[BC₈H₁₇(CN)₃] (30 mg, 6% yield) was synthesized using the same method as K[BC₄H₉(CN)₃], starting from K[BC₈H₁₇F₃] (500 mg, 2.27 mmol). A peak at $\delta = -20.4$ in the ¹¹B NMR spectrum was assigned to the isomer K[BC₈H₁₇(NC)(CN)₂], which disappeared after heating at 120°C for 2 h. The spectral data of the anions matched previously reported values.^{S3 1}H NMR (400 MHz, CD₃CN): $\delta = 0.48$ (m, 2H, BCH₂C₇H₁₅), 0.91 (m, 3H, C₇H₁₄CH₃), 1.32 (m, 12H, CH₂C₆H₁₂CH₃). ¹¹B NMR (128 MHz, CD₃CN): $\delta = -30.6$ (s, *B*C₈H₁₇).

¹H and ¹¹B NMR spectra were recorded on a Bruker Avance 400 spectrometer. FT-IR spectra were obtained using a Thermo Nicolet iS5 FT-IR spectrometer with an attenuated total reflectance (diamond) accessory. Raman spectroscopy was performed using a JASCO NRS-7100 laser Raman spectrometer. PXRD patterns were measured on a Rigaku SmartLab diffractometer using Cu Ka radiation. Differential scanning calorimetry was performed on the Q100 differential scanning calorimeter at a scan rate of 10 K min⁻¹. Thermogravimetric-differential thermal analysis measurements were performed on a Rigaku TG8120 in a nitrogen atmosphere at a scan rate of 3 K min⁻¹ using an aluminum pan and an aluminum oxide reference. Viscosity measurements were performed using a TA Instruments DHR-1 rheometer with an 8 mm diameter parallel plate geometry. UV irradiation was performed using a Hamamatsu LC-L1V3 Lightning Cure UV-LED (365 ± 5 nm, >600 mW cm⁻²) at an approximately 1-cm distance. For neat-state photoreactions, the liquid sample was sandwiched between quartz plates on a 10°C cooling plate, with a typical sample thickness of 10 µm or less.

[Ru(Cp)(C₆H₆)]BC₈H₁₇(CN)₃ (**1a**)

An aqueous solution of $[Ru(Cp)(C_6H_6)]Cl$ (49 mg, 0.18 mmol) was added to an aqueous solution of K $[BC_8H_{17}(CN)_3]$ (51 mg, 0.21 mmol), and the mixture was stirred for 30 min. The mixture was extracted five times with dichloromethane, and the combined organic layers were washed with water and dried using anhydrous magnesium sulfate. After filtration, the solvent was removed using a rotary evaporator, and the product was dried in vacuo for 2 h. The residue was dissolved in acetonitrile and passed through a short alumina column (eluent: acetonitrile). The solvent was again removed using a rotary evaporator, and the residue was further dried in vacuo for 2 h, yielding a pale yellow liquid (63 mg, 80% yield). ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 0.37$ (m, 2H, BC*H*₂C₇H₁₅), 0.86 (t, 3H, BC₇H₁₄C*H*₃, *J* = 6.82 Hz), 1.25 (m, 12H, BCH₂C₆*H*₁₂CH₃), 5.49 (s, 5H, Cp-*H*₅), 6.24 (s, 6H, Ar-*H*₆).¹¹B NMR (128 MHz, DMSO-*d*6): δ = -30.6 (s, *B*C₈H₁₇). ¹³C NMR (100 MHz, CDCl₃): δ =14.2 (s, *C*H₃) 22.3–32.9 (m, *C*H₂), 80.8 (s, Cp-*C*₅), 86.1 (s, Ar-*C*₆). FT–IR (cm⁻¹): 724, 824, 828, 890, 897, 955, 1009, 1017, 1082, 1417, 1441, 2201 (CN), 2849, 2918, 3084. Anal. Calcd. for C₂₂H₂₈N₃BRu: C, 59.20; H, 6.32; N, 9.41. Found: C, 58.38; H, 6.43; N, 9.30.

$[Ru(Cp)(C_6H_6)]BC_4H_9(CN)_3$ (1b)

K[BC₄H₉(CN)₃] (71 mg, 0.39 mmol) was dissolved in a small amount of water. A solution of [Ru(Cp)(C₆H₆)]Cl (72 mg, 0.26 mmol) was then added, and the mixture was stirred at room temperature for 30 min. After five extractions with dichloromethane, the combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered, and the solvent removed using a rotary evaporator. The product was dried under vacuum for 2 h, yielding a yellowish-white liquid (87 mg, 87% yield). The product crystallized upon storage at -40°C. The melting point of the solid was 321.3 K ($\Delta H_m = 13.4$ kJ mol⁻¹, $\Delta S_m = 41.5$ J mol⁻¹ K⁻¹). A glass transition ($T_g = 222.3$ K) was observed upon cooling from the melt. The T_g/T_m ratio of 0.69 is consistent with the empirical rule for molecular liquids ($T_g/T_m = 2/3$).^{20,21} ¹H NMR (400 MHz, DMSO- d_6): $\delta = 0.38$ (m, 2H, BCH₂C₃H₇), 0.86 (t, 3H, BC₃H₆CH₃, J = 7.16 Hz), 1.27 (m, 4H, BCH₂C₂H₄CH₃), 5.48 (s, 5H, Cp-H₅), 6.24 (s, 6H, Ar-H₆). ¹¹B NMR (128 MHz, (CD₃)₂SO): $\delta = -30.7$ (s, *B*C₄H₉). ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.1$ (s, *C*H₃) 19.9–30.1 (m, *C*H₂), 80.8 (s, Cp-C₅), 86.1 (s, Ar-C₆). FT–IR (cm⁻¹): 751, 828, 847, 917, 947, 967, 1075, 1418, 1441, 2201 (CN), 2849, 2918, 2953, 3084, 3088. Anal. Calcd. for C₁₈H₂₀N₃BRu: C, 55.40; H, 5.1; N, 10.77. Found: C, 55.17; H, 4.81; N, 10.89.

$[Ru(Cp){BC_8H_{17}(CN)_3}]_4$ (2a)

Compound **1a** (10 mg, 0.022 mmol) was dissolved in methanol (2 mL) and irradiated with UV light under nitrogen for 1 h. The precipitated yellow solid was collected by filtration and dried under vacuum at room temperature for 4 h, affording 4 mg (50% yield) of the desired product. ¹H NMR (400 MHz, CDCl₃): δ = 0.64–0.75 (m, 8H, BC₆H₁₂CH₂CH₃), 0.90 (t, 12H, BC₇H₁₄CH₃ *J* = 6.84 Hz), 1.25–1.44 (m, 48H, BC₆H₁₂C₂H₅), 4.14 (s, 20H, Cp-H₅). ¹³C NMR (100 MHz, CDCl₃): δ =14.2 (s, *C*H₃) 22.8–32.5 (m, *C*H₂), 68.6 (s, Cp-*C*₅). FT–IR (cm⁻¹): 809, 832, 893, 951, 990, 1036, 1098, 1460, 2228, 2853, 2922. Anal. Calcd. for C₆₄H₈₈B₄N₁₂Ru₄: C, 52.19; H, 6.02; N, 11.41. Found: C, 51.21; H, 5.76; N, 11.21.

[Ru(Cp){BC₄H₉(CN)₃}]₄ (**2b**)

A solution of **1b** (5 mg, 0.013 mmol) in methanol (2 mL) was irradiated with UV light under nitrogen for 1 h. The precipitated yellow solid, **2b**, was collected by filtration and dried under vacuum at room temperature for 4 h (2 mg, 50% yield). X-ray structure analysis was unsuccessful owing to the facile loss of solvate molecules. ¹H NMR (400 MHz, CDCl₃): δ = 0.68–0.72 (m, 2H, BCH₂C₃H₇), 0.94 (t, 3H, BC₃H₆CH₃, *J* = 7.06 Hz), 1.44–1.45 (m, 4H, BCH₂C₂H₄CH₃), 4.17 (s, 5H, Cp-H₅). ¹³C NMR (100 MHz, CDCl₃): δ =14.0 (s, CH₃) 17.7–30.2 (m, CH₂), 68.6 (s, Cp-C₅). FT–IR (cm⁻¹): 585, 809, 832, 947, 990, 1075, 1098, 1194, 1221, 1345, 1375, 1410, 1456, 2228 (CN), 2914, 2957. Anal. Calcd. for C₄₈H₅₆B₄N₁₂Ru₄: C, 46.17; H, 4.52; N, 13.46. Found: C, 46.29; H, 4.14; N, 13.19.

Single-crystal X-ray structure determination

Single crystals of three polymorphs (α -, β -, and γ -forms) were obtained by recrystallizing **2a**. The α -form was obtained by allowing methanol vapor to diffuse into a dichloromethane solution, whereas the β - and γ -forms were both prepared by diffusing methanol into dichloromethane solutions at -9° C. The γ -form was a pseudo-polymorph that contained solvate molecules (either dichloromethane or methanol). To prevent the loss of these solvate molecules, oil-coated crystals were used for measurements. Structure analysis was performed using a Bruker APEX II Ultra diffractometer (MoK α), and data analysis was performed with SHELXL^{S4}. Because the solvate molecules could not be located, SQUEEZE was applied, and the void volume containing these solvate molecules was calculated using PLATON.^{S5} The crystallographic parameters are listed in **Table S1**.

Powder X-Ray Diffraction

High-resolution variable-temperature PXRD experiments were performed using synchrotron radiation at SPring-8, BL02B2. A synchrotron radiation X-ray wavelength of 0.8 Å was selected with a double Si(111) crystal monochromator. X-ray wavelength was calibrated using the standard reference material CeO₂ (NIST 674b). Crystalline powder samples of **2a** were packed in a 0.3-mm glass capillary tube. The PXRD patterns were recorded at room temperature. The diffraction pattern was captured using six MYTHEN silicon microstrip photon-counting detectors alongside a flat panel detector, with measurements performed in transmission geometry.^{S6} The measurement temperature was controlled by blowing nitrogen gas.

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2. Figures and Tables



Fig. S1. DSC curves of (a) 1a and (b) 1b.



Fig. S2. ¹H NMR spectra of **1b** measured in CDCl₃ before and after photoirradiation for 1 h: (a) spectrum at 10 °C in the liquid phase; (b) enlarged spectra under the following conditions: (i) liquid phase at 40 °C, (ii) liquid phase at 10 °C (enlarged view of (a)), and (iii) solid phase at 10 °C.



Fig. S3. FT-IR spectra of (a) **1a** before and after UV irradiation, (b) an enlarged view of (a), and (c) **1b** before and after UV irradiation. The asterisk indicates CO₂ absorption.



Fig. S4. Raman spectrum of 2a.



Fig. S5. UV-vis spectral changes upon photoirradiation of (a) **1a** for 15 min and (b) **1b** for 30 min. The samples were sandwiched between two quartz plates for the measurements. The spectra after photoirradiation are saturated below 400 nm.



Fig. S6. TG curves for 1a, 1b, 2a, and 2b measured under nitrogen atmosphere.



Fig. S7. ¹H NMR spectral changes upon photoirradiation of 1a in CDCl₃.



Fig. S8. Temperature dependence of the viscosities of 1a and 1b.



Fig. S9. (a) Photographs of **2b** sandwiched between quartz plates before and after the photoreaction: (i) in the liquid state and (ii) in the solid state. (b) Polarized optical micrographs of the photoproducts (top: without the polarizer, bottom: under crossed Nicols). Photoirradiation was performed at 10 °C. In (b)(i), a microcrystalline film is observed, while (b)(ii) highlights the heterogeneity of the product, which contains unreacted solid and possibly dissociated ligand, appearing as bubble-like features.



Fig. S10. ORTEP diagrams of the molecular structures of (a) α -2a and (b) β -2a. Hydrogen atoms are omitted. One of the disordered components is shown in a lighter color.



Fig. S11. Arrangements of the tetranuclear clusters in (a) α -2a, (b) β -2a, and (c) γ -2a. The Cp rings and hydrogen atoms are omitted.



Fig. S12. PXRD patterns of 2a obtained from the neat reaction and from the solution-phase reaction, measured at room temperature ($\lambda = 0.8$ Å). The patterns for α -2a, β -2a, and γ -2a, simulated from the single-crystal structure analysis data obtained at -183° C, are also shown for comparison.



Fig. S13. UV-vis spectrum of 2a in CH_2Cl_2 (8.15 × 10⁻³ M).



Fig. S14. ¹¹B NMR spectrum of 1a.



Fig. S15. ¹¹B NMR spectrum of 1b.



Fig. S16. ¹³C NMR spectrum of 1a. The asterisk indicates the solvent peak.



Fig. S17. ¹³C NMR spectrum of 2a. The asterisk indicates the solvent peak.



Chemical shift (ppm)

Fig. S18. ¹³C NMR spectrum of 1b. The asterisk indicates the solvent peak.



Fig. S19. ¹³C NMR spectrum of 2b. The asterisk indicates the solvent peak.

	<i>α</i> -2a	β-2a	γ-2 a
Empirical formula	$C_{64}H_{88}Ru_4N_{12}B_4$	$C_{64}H_{88}Ru_4N_{12}B_4$	$C_{64}H_{88}Ru_4N_{12}B_4$
Formula weight	1472.98	1472.98	1468.95
Crystal system	monoclinic	cubic	tetragonal
Space group	$P2_{1}/c$	Ia3d	ΙĀ
a [Å]	13.185(5)	34.657(3)	14.005(3)
<i>b</i> [Å]	25.185(9)	34.657(3)	14.005(3)
<i>c</i> [Å]	21.033(8)	34.657(3)	19.628(5)
β[°]	98.321(4)	90	90
<i>V</i> [Å ³]	6911(4)	41627(12)	3849.8(19)
Ζ	4	24	2
Temperature [K]	90	90	90
$ ho_{ m calcd} [m g \ m cm^{-3}]$	1.416	1.41	1.267
<i>F</i> (000)	3008	18048	1496
Reflns collected	33300	90746	8369
Independent reflns	12201	2871	3036
Parameters	971	193	191
<i>R</i> (int)	0.0226	0.042	0.0256
$R_{1a}, R_{w}^{b} (I > 2\sigma (I))$	0.0377, 0.0952	0.0415, 0.1026	0.0221, 0.0515
R_{1a}, R_{w}^{b} (all data)	0.0473, 0.1018	0.0545, 0.1176	0.0241, 0.0523
Goodness of fit	1.072	1.115	1.085
$\Delta ho_{ m max,min}$ [e Å ⁻³]	2.286, -0.775	1.029, -0.886	0.365, -0.194

Table S1. Crystallographic parameters

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}R_{w} = [\Sigma w (F_{o}{}^{2} - F_{c}{}^{2})^{2} / \Sigma w (F_{o}{}^{2})^{2}]^{1/2}.$