Electronic Supplementary Information

Metallo-supramolecular assembly of protic pincer-type complexes: encapsulation of dinitrogen and carbon disulfide into multiproton-responsive diruthenium cage

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Experimental Details

General procedures. All manipulations were performed under an atmosphere of argon using standard Schlenk technique unless otherwise specified. Solvents were dried by refluxing over sodium benzophenone ketyl (THF, toluene, pentane and hexane) and distilled before use. Dehydrated acetone and benzene were purchased from Wako Pure Chemical Industries and used as received. The deuteriated solvents were dried over P_2O_5 and subjected to trap-to-trap distillation and subsequent three freeze–pump–thaw degassing cycles. [Ru(cod)(cot)],[1] DPPBz[2] and 5-*tert*-butylisophthaloyl dichloride[3] were prepared according to the literature. Other reagents were used as received. ^{1}H (399.78 MHz), $^{13}C\{^{1}H\}$ (100.53 MHz) and $^{31}P\{^{1}H\}$ (161.83 MHz) NMR spectra were obtained on a JEOL JNM-ECX-400 spectrometer. ^{1}H NMR shifts are relative to the signal of the residual $CHCl_3$ (δ_H 7.26), $CHDCl_2$ (δ_H 5.32), C_6D_5H (δ_H 7.15) and CHD_2CN (δ_H 1.94) respectively. $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR shifts are referenced to CD_2Cl_2 (δ_C 53.5) and phosphoric acid (δ_P 0.0), respectively. Raman spectra were recorded on a JASCO NRS-4100 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer.

Synthesis of 4-*tert*-butyl-2,6-bis(5-*tert*-butylpyrazol-2-yl)-1-bromobenzene (Br–$LH_2\cdot 0.5H_2O$). A mixture of potassium *tert*-butoxide (10.01 g, 89.19 mmol) and 3,3-dimethyl-2-butanone (pinacolone) (9.081 g, 90.66 mmol) in toluene (150 mL) was stirred at room temperature for 1 h. 5-*tert*-Butylisophthaloyl dichloride (6.808 g, 20.14 mmol) was added to the mixture at 0 °C and the mixture was stirred for additional 1 h. After the mixture was neutralized with aqueous 1 M HCl, the organic layer was separated, and washed with water (50 mL × 3), brine (50 mL × 2) and dried over sodium sulfate. Evaporation of the solvent under reduced pressure afforded 4-*tert*-butyl-2,6-bis(1,3-dioxo-4,4-dimethylpentyl)-1-bromobenzene as sticky yellow solid. To a boiling solution of the crude diketone in ethanol (100 mL) in an open flask was added hydrazine monohydrate (6.136 g, 122.6 mmol) over the course of 10 min. After the mixture was allowed to reflux for additional 2 h, the white precipitate, **Br–LH_2**$\cdot 0.5H_2O$, that formed was collected by filtration, washed with ethanol (100 mL), water (10 mL), ethanol (10 mL), dichloromethane (10 mL) and dried in vacuo (2.864 g, 6.127 mmol, 30% over 2 steps). ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 9H; ^{t}Bu), 1.40 (s, 18H; ^{t}Bu), 6.41 (s, 2H; aryl), 7.52 (s, 2H; aryl). Anal. Calcd for $C_{24}H_{33}BrN_4O_{0.5}$: C, 61.80; H, 7.35; N, 12.01. Found: C, 61.79; H, 7.61; N, 12.11.

Synthesis of [RuBr(1,5-cod)(LH_2)]·THF (1·THF). A mixture of

[Ru(cod)(cot)] (336.0 mg, 1.065 mmol), **Br–LH$_2$**·0.5H$_2$O (498.7 mg, 1.069 mmol) and 1,5-cyclooctadiene (1.320 mL, 10.74 mmol) in THF (30 mL) was heated at 50 °C for 16 h. After evaporation of the solvent in vacuo, the residue was extracted with hot hexane (50 mL). The filtrate was concentrated to ca. 10 mL under reduced pressure, THF (1 mL) was added to the concentrated solution. Keeping the solution at –30 °C yielded **1**·THF as red crystals (540.8 mg, 0.7320 mmol, 69%). A solvating THF molecule was confirmed NMR spectroscopy and combustion analysis. Crystals suitable for X-ray analysis were obtained by recrystallization from hot diethyl ether. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.39 (s, 18H; *t*Bu), 1.44 (s, 9H; *t*Bu), 1.72–1.80, 1.87–1.88, 1.96–2.03, 2.41–2.47, 2.53–2.63, 5.46–5.47 (m, 2H each; cod), 6.55 (d, ^4J(H,H) = 2.1 Hz, 2H; pyrazole CH), 7.54 (s, 2H; phenyl CH), 10.19 (br s, 2H; NH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 28.9, 29.9, 31.7, 31.8, 32.2, 34.5, 86.4, 93.7, 98.1, 117.1, 136.9, 144.2, 157.2, 162.0, 199.9. Anal. Calcd for $C_{36}H_{53}BrN_4ORu$: C, 58.52; H, 7.23; N, 7.58. Found: C, 58.24; H, 7.21; N, 7.61.

Synthesis of K[(Ru(LH)(μ-dppbz))$_2$(μ-Br)] (2). To a solution of **1**·THF (0.0911 g, 0.123 mmol) and 1,3-bis(diphenylphosphano)benzene (DPPBz; 0.0566 g, 0.127 mmol) in toluene (6 mL) was added a solution of potassium bis(trimethylsilyl)amide (0.5 M, 0.250 mL, 0.125 mmol) in toluene. The mixture was stirred at room temperature for 1 h, then heated at 100 °C for 14 h. After removal of the solvent under reduced pressure, the residue was extracted with benzene (2 mL). Slow addition of pentane (50 mL) to the filtrate afforded **2**·benzene as orange crystals. A thoroughly dried sample lost the co-crystalized benzene (0.0601 g, 0.0306 mmol, 50%). ^{1}H NMR (C$_6$D$_6$): δ 1.13, 1.48, 1.72 (s, 18H each; *t*Bu), 6.33–6.37 (m, 8H; aryl), 6.54 (d, ^4J(H,H) = 2.4 Hz, 2H; pyrazole CH), 6.64–6.87 (m, 38H; aryl), 7.11 (br, 2H; aryl), 7.20 (d, ^4J(H,H) = 1.8 Hz, 2H; aryl), 7.68 (d, ^4J(H,H) = 1.5 Hz, 2H; aryl), 8.86 (quin, *J*(H,P) = 4.8 Hz, 2H; PC(CH)CP), 10.01 (d, ^4J(H,H) = 2.2 Hz, 2H; NH). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 30.5 (s). Anal. Calcd for $C_{108}H_{112}BrKN_8P_4Ru_2$: C, 65.94; H, 5.74; N, 5.70. Found: C, 65.85; H, 6.00; N, 5.58.

Synthesis of [(Ru(NCN-LH)(1,3-dppbz))$_2$(μ-N$_2$)]·2H$_2$O (3·2H$_2$O). To a mixture of **1** (0.0748 g, 0.101 mmol) and DPPBz (0.0465 g, 0.104 mmol) in toluene (5 mL) was added a solution of potassium bis(trimethylsilyl)amide (0.5 M, 0.210 mL, 0.105 mmol) in toluene. The mixture was stirred at room temperature for 1 h, then heated at 100 °C for 14 h. After cooling to room temperature, the solution was filtered off and evaporated to dryness. The resultant solid was dissolved in THF (10 mL), then

N_2 (1 atm) was introduced to the solution through freeze–pump–thaw cycles (three times). The reaction mixture was stirred at room temperature for 1 h. After removal of the solvent in vacuo, subsequent recrystallization from THF–hexane (5 mL/50 mL) afforded **3**$\cdot 2H_2O$ as yellow crystals (0.0164 g, 0.00858 mmol, 17%). Crystals suitable for X-ray analysis were obtained by recrystallization from toluene. ^{1}H NMR (C_6D_6): δ 1.43 (s, 18H, ^{t}Bu), 1.58 (s, 36H, ^{t}Bu), 6.39 (s, 4H, pyrazole CH), 6.53–6.85 (m, 44H, aryl), 7.08–7.10 (m, 2H, aryl), 7.20–7.22 (m, 4H, aryl), 8.68 (quin, J_{HP} = 5.5 Hz, 2H, PC(CH)CP). The NH signals were not observed. ^{31}P{^{1}H} NMR (C_6D_6): δ 32.6 (s). Raman (solid, cm^{-1}): 2083 ($\nu_{\mathrm{N\equiv N}}$). Anal. Calcd for $C_{108}H_{116}N_{10}O_2P_4Ru_2$: C, 67.84; H, 6.11; N, 7.33. Found: C, 68.13; H, 6.38; N, 7.63. ^{15}N-labelled compound, **3-^{15}N$_2$**, was prepared by stirring of **2** in acetone under $^{15}N_2$ atmosphere. Raman (solid, cm^{-1}): 2016 ($\nu_{\mathrm{^{15}N\equiv ^{15}N}}$).

Synthesis of [(Ru(LH)(μ-dppbz))$_2$(μ-η^1:η^2-CS$_2$)]·2H$_2$O (4·2H$_2$O). To a solution of **2** (0.0207 g, 0.0105 mmol) in acetone (3 mL) was added carbon disulfide (3.2 μL, 0.0530 mmol). The mixture was stirred at room temperature for 20 h. After evaporation of the solvent under reduced pressure, the resultant solid was extracted with toluene (5 mL). Slow addition of pentane (15 mL) to the filtrate afforded **4**$\cdot 2H_2O$ as reddish purple crystals (0.0150 g, 0.00780 mmol, 74%). Crystals of **4**·2THF suitable for X-ray analysis were obtained by recrystallization from THF–hexane. ^{1}H NMR (CD_2Cl_2, –40 °C): δ 1.03, 1.36, 1.37, 1.39, 1.43, 1.49 (s, 9H each; *t*Bu), 6.08, 6.19, 6.43, 6.58 (s, 1H each; aryl), 6.24–6.38 (m, 6H; aryl), 6.50–6.52 (m, 4H; aryl), 6.64–6.84 (m, 20H; aryl), 6.90–7.06 (m, 18H; aryl), 7.29–7.32 (m, 2H; aryl), 7.35 (s, 2H; aryl), 9.87 (br s, 1H; NH), 13.46 (br s, 1H; NH). ^{31}P{^{1}H} NMR (CD_2Cl_2, –40 °C): δ 20.0 (br s), 31.0 (s). Anal. Calcd for $C_{109}H_{116}N_8O_2P_4S_2Ru_2$: C, 66.78; H, 5.96; N, 5.71. Found: C, 67.03; H, 5.76; N, 5.45.

Crystallography. Diffraction experiments were performed on a Rigaku Saturn CCD area detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Single crystals suitable for X-ray analyses were mounted on a fiber loop. Intensity data ($6° < 2\theta < 55°$) collected at 93 K were corrected by Lorentz polarization effects and for absorption. Structure solution and refinements were performed with the CrystalStructure program package.[4] The heavy-atom positions were determined by a direct method program (SIR92[5]) and the remaining non-hydrogen atoms were found by subsequent Fourier syntheses and refined by full-matrix least-squares techniques against F^2 using the SHELXL-2014/7 program.[6] One of the phenyl groups in

3$\cdot$2$H_2O$$\cdot$1.5(toluene) were placed at two disordered positions with 50% occupancies and the carbon atoms therein were refined isotropically. The hydrogen atoms except for those in the co-crystalized water molecules in **3**$\cdot$2$H_2O$$\cdot$1.5(toluene) were included in the refinements with a riding model. The ISOR command was used for a partially disordered *t*-butyl carbon atom in **4**$\cdot$2THF to adjust the atomic displacement parameters to realistic values. The co-crystalized diethyl ether (**1**), pentane (**2**), and toluene (**3**) molecules were severely disordered and could not modeled successfully. The remaining electron density in the solvent accessible voids was therefore accounted for with the PLATON SQUEEZE procedure.[7] The numbers of the co-crystalized molecules were estimated from the contribution of the electrons removed from the unit-cell contents, and detailed information can be found in the CIF files (see _platon_squeeze_details). The highly disordered co-crystalizing diethyl ether in **1** perhaps caused the poor R_{int} value.

References

1. (*a*) A. F. Hill, H. Neumann, J. Wagler, *Organometallics*, 2010, **29**, 1026–1031; (*b*) E. Rafter, T. Gutmann, K. Philippot, F. Löw, G. Buntkowsky, B. Chaudret, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* 2013, **3**, 595–599.
2. P. W. Miller, M. Nieuwenhuyzen, J. P. H. Charmant, S. L. James, *Inorg. Chem.* 2008, **47**, 8367–8379.
3. A. Bugarin, B. T. Connell, *Organometallics*, 2008, *27*, 4357–4369.
4. *CrystalStructure 4.1: Crystal Structure Analysis Package*, 2000–2015.
5. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
6. G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3–8.
7. A. L. Spek, *Acta Crystallogr., Sect. C*, 2015, **71**, 9–18.

Fig. S1 Crystal structure of **1**$\cdot$$Et_2O$. The CH hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level.

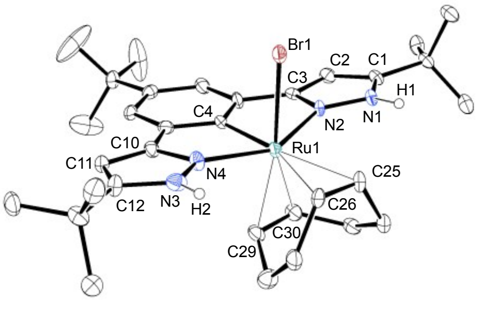


Fig. S2 ^{1}H NMR spectrum of Br–LH$_2$.

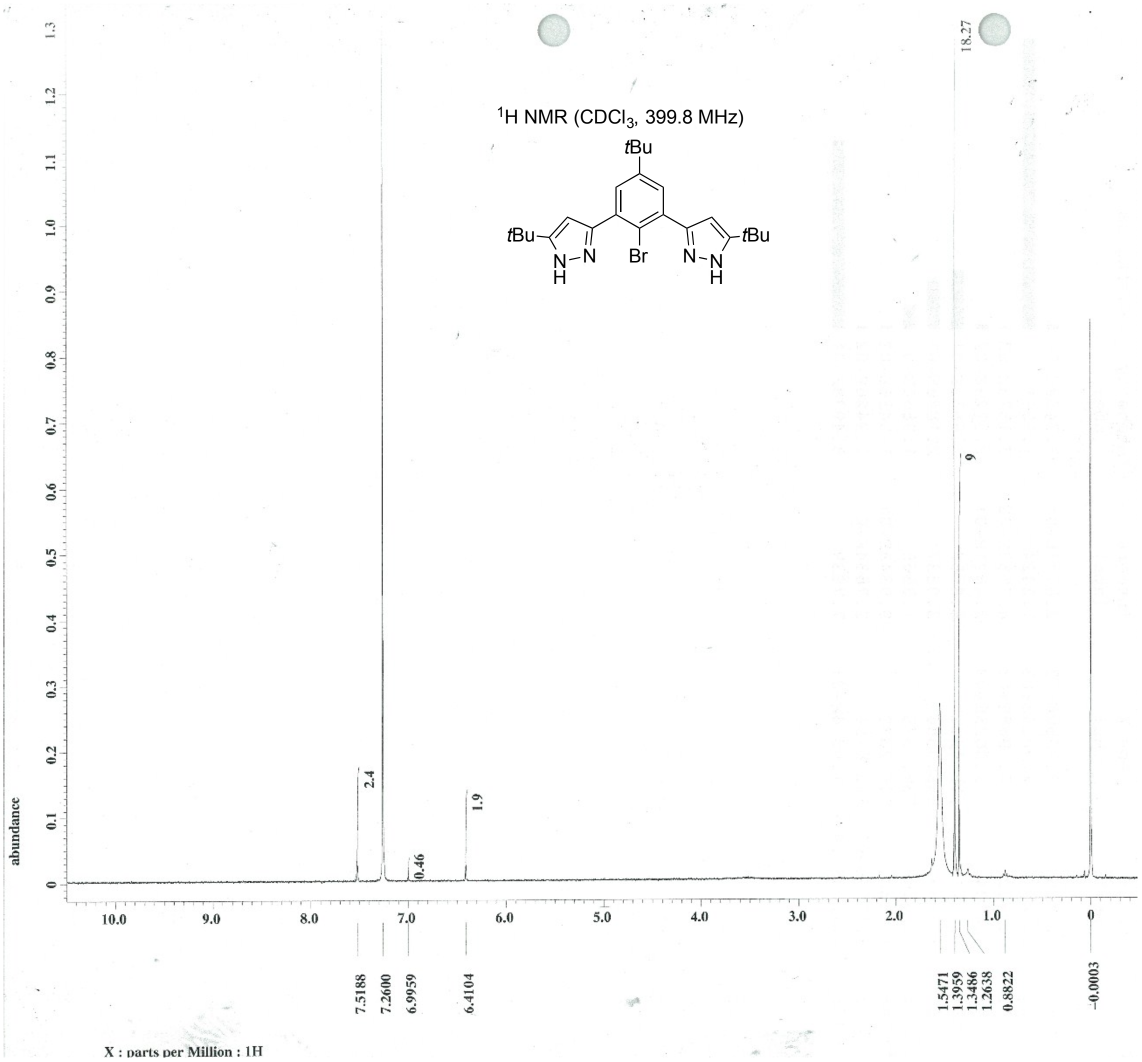


Fig. S3 ^{1}H NMR spectrum of **1**.

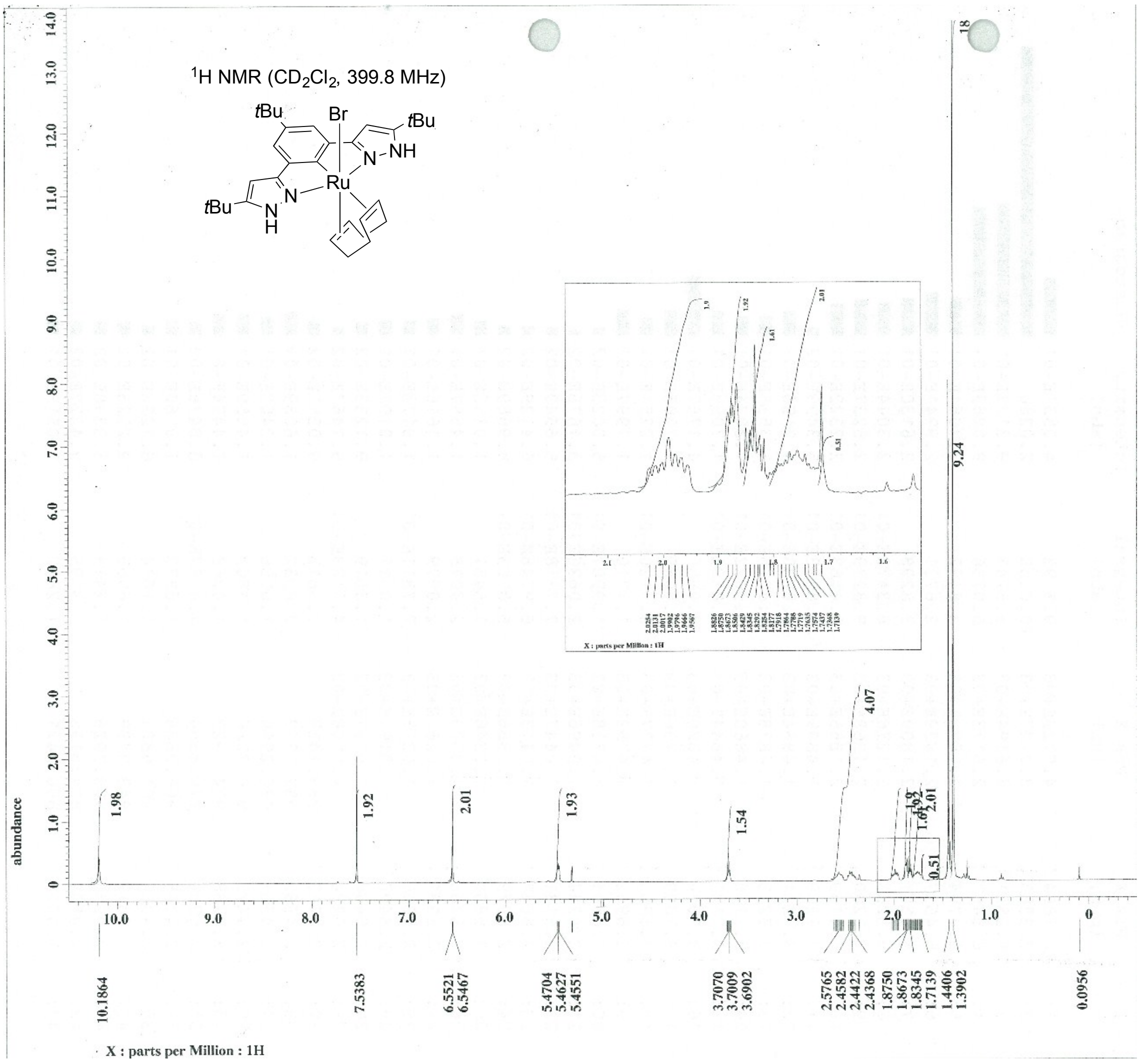


Fig. S4 $^{13}C\{^1H\}$ NMR spectrum of **1**.

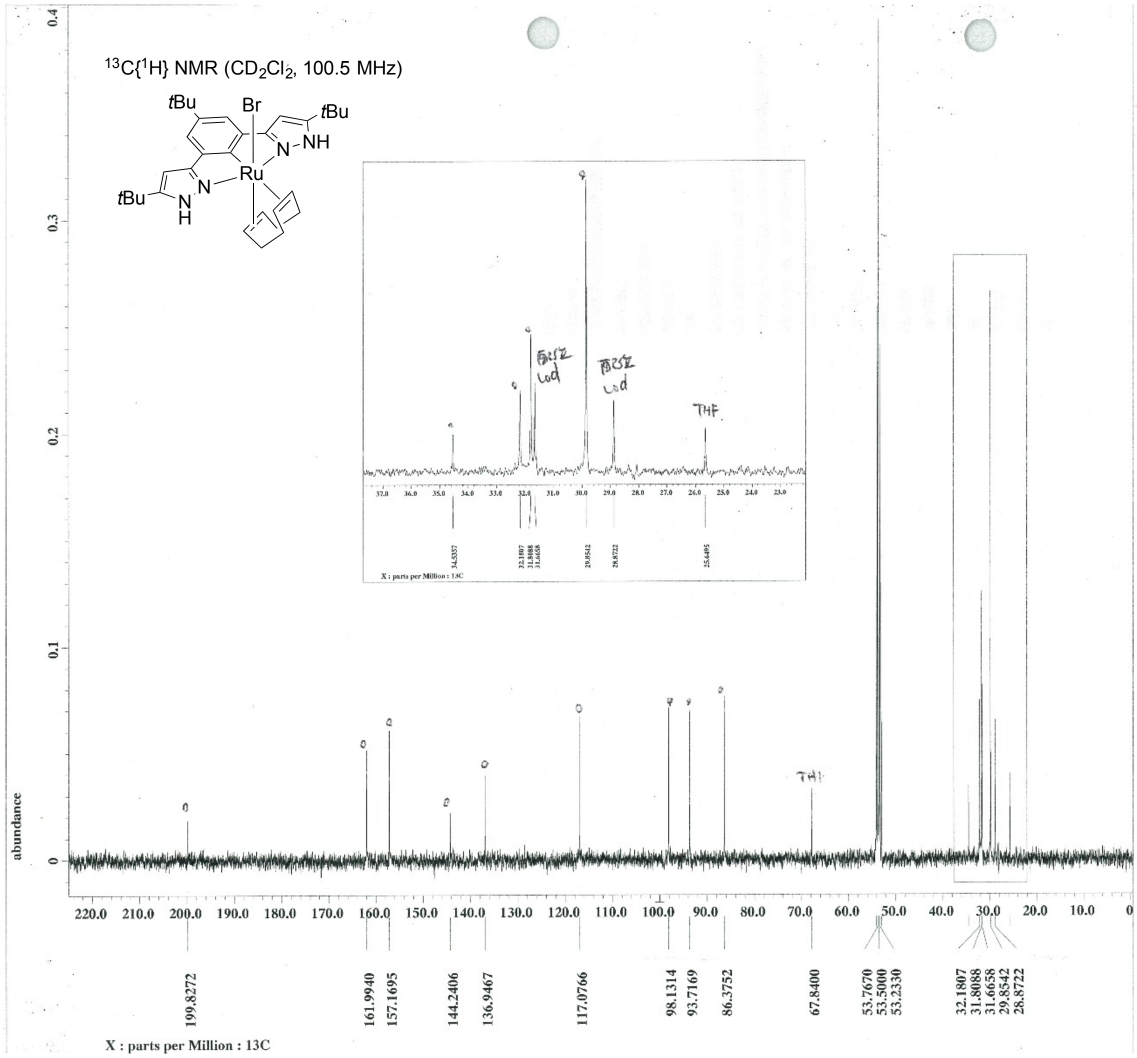


Fig. S5 ^{1}H NMR spectrum of **2**.

^{1}H NMR (C_6D_6, 399.8 MHz)

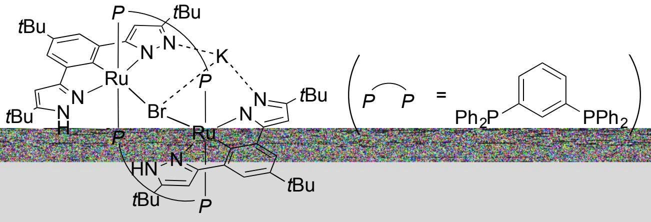


Fig. S6 $^{31}P\{^1H\}$ NMR spectrum of **2**.

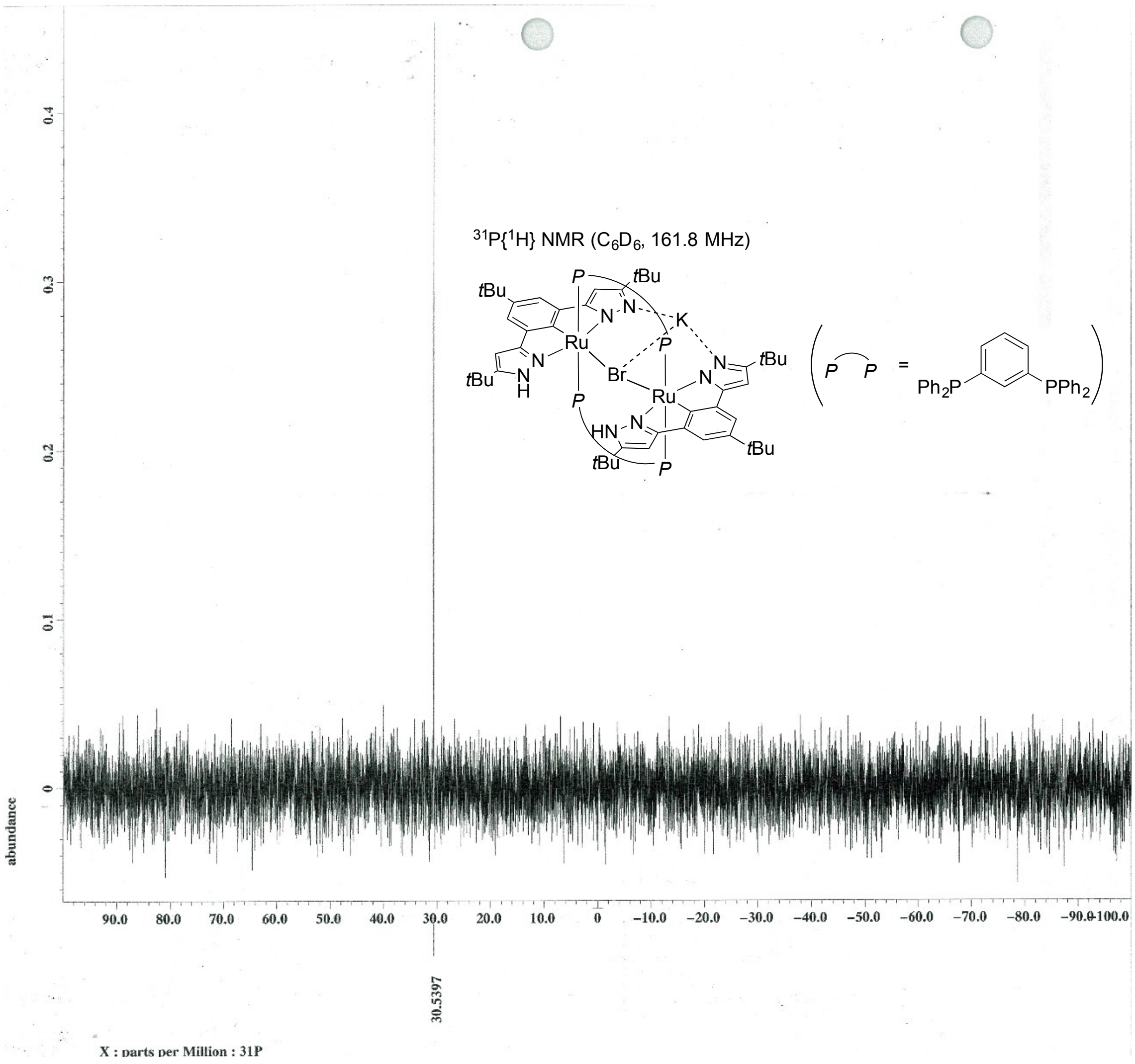


Fig. S7 ^{1}H NMR spectrum of **3**.

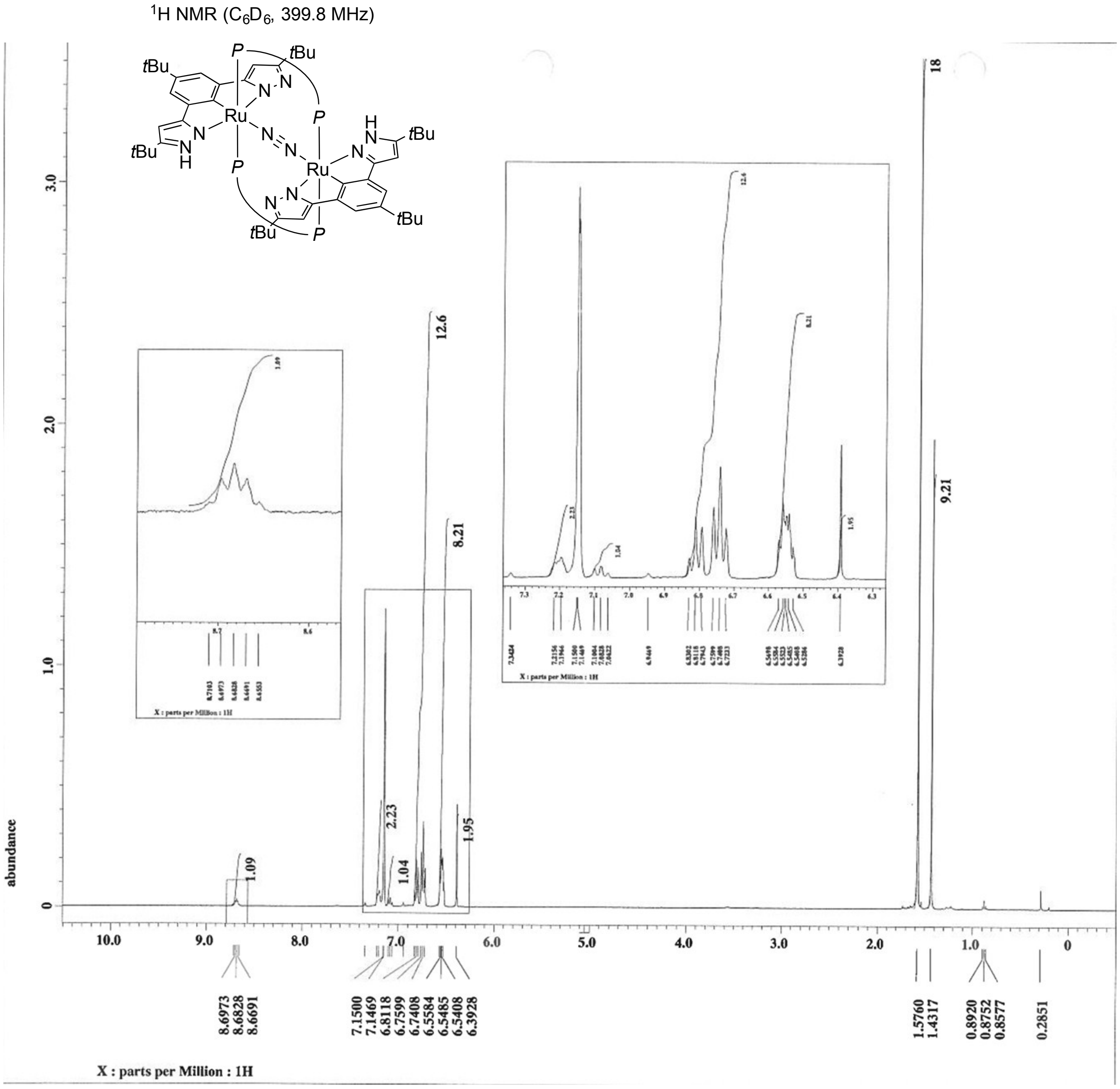


Fig. S8 $^{31}P\{^1H\}$ NMR spectrum of **3**.

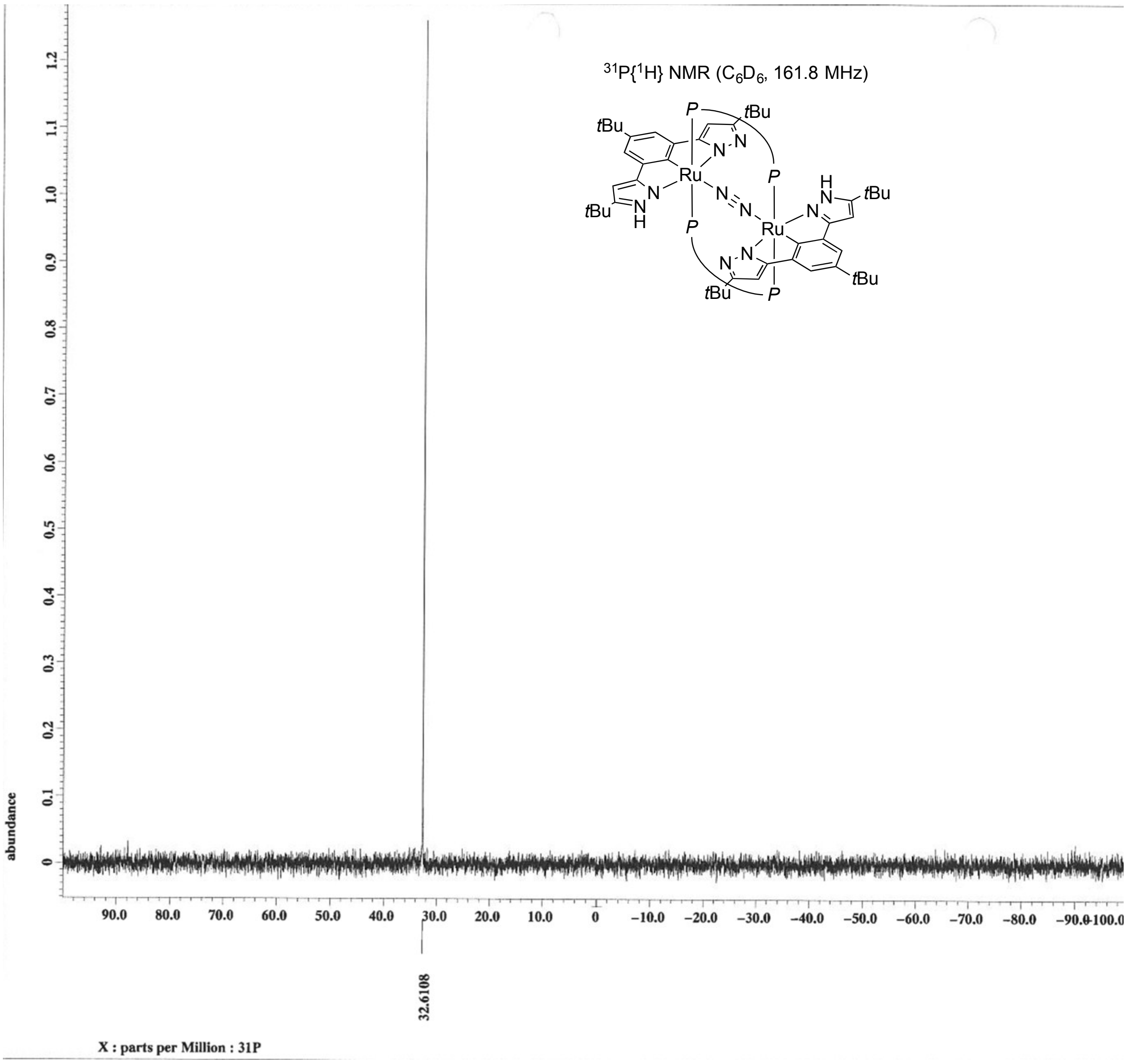
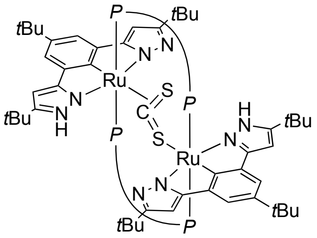


Fig. S9 ^{1}H NMR spectrum of **4**.

^{1}H NMR (CD_2Cl_2, –40 °C, 399.8 MHz)



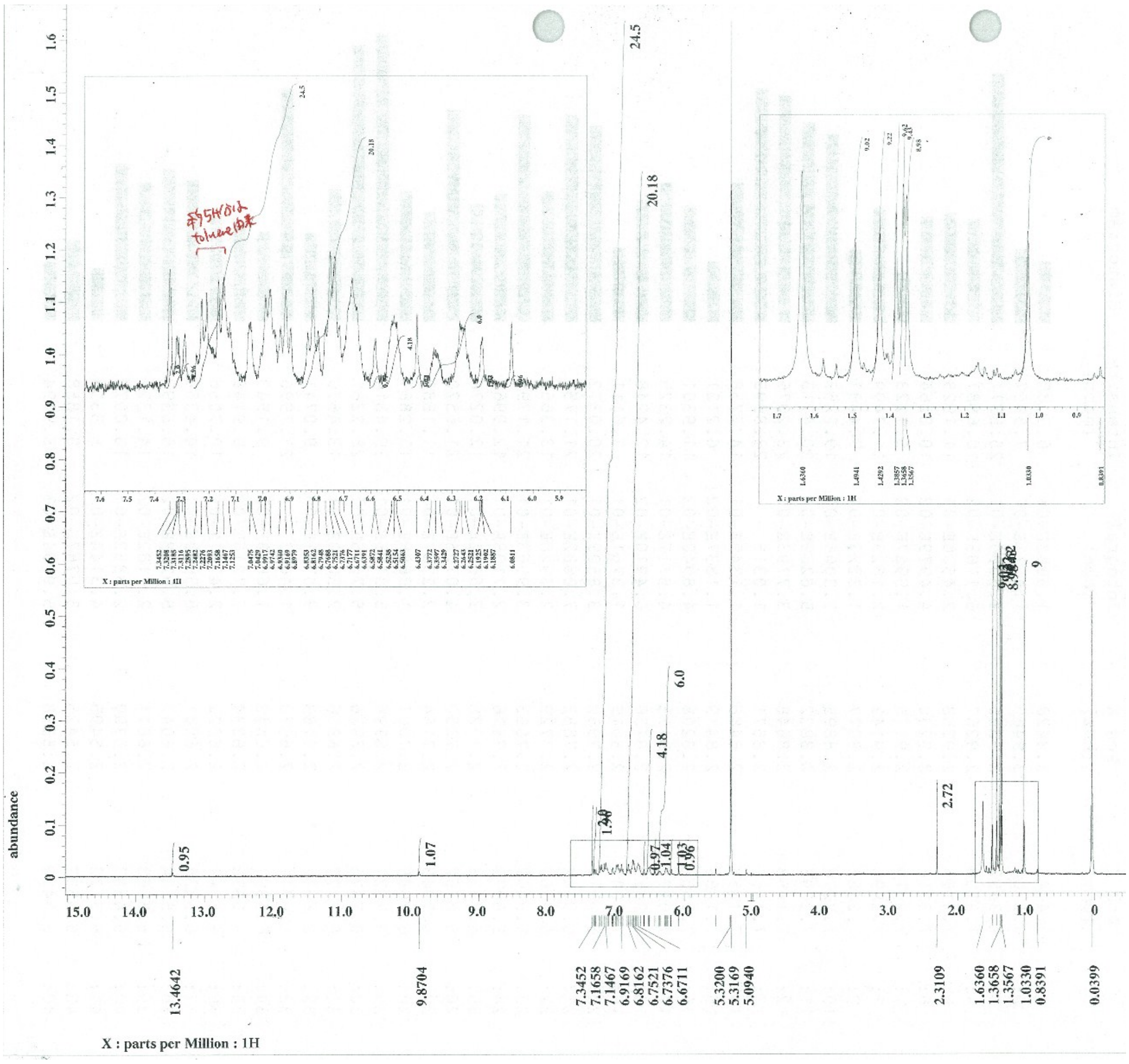


Fig. S10 $^{31}P\{^{1}H\}$ NMR spectrum of **4**.

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, –40 °C, 161.8 MHz)