

Supplementary Data

Reactions of $\text{TpRu}(\text{CO})(\text{NCMe})(\text{Ph})$ with Electron-Rich Olefins: Examples of Stoichiometric C-S, C-O and C-H Bond Cleavage

Laurel A. Goj^a, Marty Lail^a, Karl A. Pittard^a, Kimberly C. Riley^a, T. Brent Gunnoe^{*a}, and Jeffrey L. Petersen^b

^aDepartment of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

^bC. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045

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1.0 Experimental

1.1 General Methods

All procedures were performed under inert atmosphere (dinitrogen) in an Innovative Technologies Company glovebox or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer $\{O_2(g) < 15 \text{ ppm for all reactions}\}$. Benzene and hexanes were purified by reflux over sodium followed by distillation. Benzene- d_6 and $CDCl_3$ were degassed by three freeze-pump-thaw cycles and stored over 4Å molecular sieves. 1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer (operating frequencies for ^{13}C NMR spectra were 100 and 75 MHz, respectively) and referenced to TMS using resonances due to residual protons in the deuterated solvents or the ^{13}C resonances of the deuterated solvents. Resonances due to the Tp ligand are listed by chemical shift and multiplicity only (all coupling constants for the Tp ligand are 2 Hz). Gas chromatography was performed on a Hewlett Packard 5890 GC using a J&W SE-30 capillary column, split inlet, and an FID detector. Chromatograms were produced using Perkin-Elmer Total Chrome 6.2 software. All IR spectra were acquired using a Mattson Genesis II FTIR as thin films on KBr plates. Styrene, ethyl vinyl sulfide, diethyl sulfide, diphenyl sulfide, ethyl phenyl sulfide and 2,3-dihydrofuran were obtained from Sigma Aldrich and used as received. $TpRu(CO)(NCMe)(Ph)$ (**1**) was synthesized according to literature procedures.¹

1.2 Experimental Data

$[TpRu(CO)(\mu\text{-SEt})_2]$ (**2**). A pressure tube charged with $TpRu(CO)(Ph)(NCMe)$ (**1**) (0.300 g, 0.65 mmol) and ethyl vinyl sulfide (3.3 mL, 32 mmol) was heated at 100 °C for

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2 hours. During this time the solution turned dark orange. The mixture was allowed to cool to room temperature and hexanes (~ 1 mL) were added. The pale yellow precipitate was collected by vacuum filtration and dried *in vacuo* (0.067 g, 24%). Single crystals for the X-ray diffraction study were grown by slow diffusion of hexanes into a methylene chloride solution of complex **2**. ^1H NMR (CDCl_3 , δ): 9.34, 7.85, 7.63, 7.58 (12H total, 2:2:4:4 integration, each a d, Tp 3 or 5 position *CH*), 6.53, 6.16 (6H total, 2:4 integration, each a t, Tp 4 position *CH*), 2.48 (2H, m, *SCHHCH*₃), 2.33 (2H, m, *SCHHCH*₃), 0.47 (6H, t, $J = 8$ Hz, *SCH*₂*CH*₃). ^{13}C NMR (CDCl_3 , δ): 207.6 (RuCO), 143.4, 143.2, 135.7, 135.2 (Tp 3 or 5 position), 105.9 (Tp 4 position, coincidental overlap), 28.9 (*SCH*₂*CH*₃), 17.9 (*SCH*₂*CH*₃). IR (cm^{-1}): $\nu_{\text{CO}} = 1929$, $\nu_{\text{BH}} = 2482$.

TpRu(CO)(NCMe)(C≡CCH₂CH₂OH) (3). A pressure tube charged with **1** (0.340 g, 0.740 mmol) and 2,3-dihydrofuran (3.0 mL, 39 mmol) was heated to 80 °C for 72 hours. The dark brown solution was allowed to cool to room temperature, and the volatiles were removed *in vacuo*. The dark residue was dissolved in methylene chloride and passed through a column of silica gel. The initial yellow band was collected, and the volatiles were removed *in vacuo*. The yellow solid was collected and dried (0.094 g, 28 %). ^1H NMR (C_6D_6 , δ): 8.17, 7.66, 7.51, 7.40, 7.36, 7.22 (6H total, 1:1:1:1:1:1 integration, each a d, Tp 3 or 5 position *CH*), 6.13 (1H, br s, *OH*), 6.00, 5.87, 5.83 (3H total, 1:1:1 integration, each a t, Tp 4 position *CH*), 4.55 (1H, m, *CH*₂*CHHOH*), 4.36 (1H, m, *CH*₂*CHHOH*), 2.38 (2H, m, *CH*₂*CH*₂*OH*), 1.63 (3H, s, *NCCH*₃). ^{13}C NMR (C_6D_6 , δ): 236.8 (RuC≡C), 200.6 (RuCO), 179.8 (RuC≡C), 146.5, 144.8, 139.1, 135.4, 134.9, 134.8 (each a dt, $^1J_{\text{CH}} = 181\text{-}191$ Hz, $^{2,3}J_{\text{CH}} = 7$ Hz, Tp 3 or 5 position), 120.1 (RuN≡CCH₃) 106.3, 106.2, 105.2 (each a dt, $^1J_{\text{CH}} = 176$ Hz, $^2J_{\text{CH}} = 9$ Hz, Tp 4 position),

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76.9 (t, $^1J_{\text{CH}} = 148$ Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 26.7 (t, $^1J_{\text{CH}} = 132$ Hz, $\text{CH}_2\text{CH}_2\text{OH}$), 22.3 (q, $^1J_{\text{CH}} = 129$ Hz, $\text{RuN}\equiv\text{CCH}_3$). In addition to the above characterization data, an APT confirmed the assignments of the ^{13}C NMR spectrum. IR (cm^{-1}): $\nu_{\text{CO}} = 1916$, $\nu_{\text{BH}} = 2481$, $\nu_{\text{OH}} = 3336$. Anal. Calcd. (Found) for $\text{C}_{17}\text{H}_{27}\text{BN}_7\text{O}_2\text{Ru}$: C, 42.49 (42.36); H, 4.01 (4.01); N, 21.68 (21.36).

^1H NMR homonuclear decoupling analyses of $\text{TpRu}(\text{CO})(\text{NCMe})(\text{C}\equiv\text{CCH}_2\text{CH}_2\text{OH})$ (3) (see Figure S1). ^1H NMR homonuclear decoupling experiments were performed to confirm the assignment of the resonances at 4.55, 4.36 and 2.38 ppm. Due to the small difference in chemical shift, the resonances at 4.55 and 4.36 were irradiated simultaneously. ^1H NMR (acetone- d_6 , δ) Irradiation of resonance at 2.38 ppm: 4.55 (1H, d, $^2J_{\text{HH}} = 8.4$ Hz), 4.36 (1H, d, $^2J_{\text{HH}} = 8.4$ Hz). ^1H NMR (acetone- d_6 , δ) Irradiation of resonance at 4.45 ppm: 2.23 (1H, d, $^2J_{\text{HH}} = 3.6$ Hz), 2.21 (1H, d, $^2J_{\text{HH}} = 3.9$ Hz).

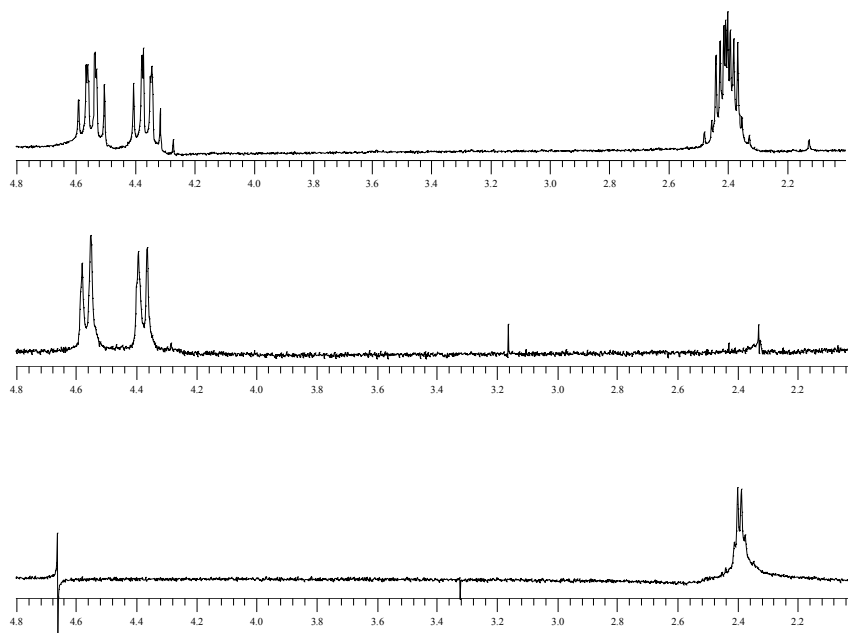


Figure S1. Homonuclear decoupling experiments for $\text{TpRu}(\text{CO})(\text{NCMe})(\text{C}\equiv\text{CCH}_2\text{CH}_2\text{OH})$ (**3**). The top spectrum (2.2 to 4.8 ppm) shows the ^1H NMR spectrum of **3**. The middle spectrum shows the result of irradiation of the resonance at 2.38 ppm (resonances at 4.55 and 4.36 ppm are doublets). The bottom spectrum depicts the result of irradiation of the resonances at 4.55 and 4.36 ppm (the resonance at 2.38 ppm is an *AB* pattern).

NMR tube reaction of $\text{TpRu}(\text{CO})(\text{NCMe})(\text{Ph})$ (1**) and ethyl vinyl sulfide.** A screwcap NMR tube was charged with $\text{TpRu}(\text{CO})(\text{NCMe})(\text{Ph})$ (**1**) (20.0 mg, 0.043 mmol), ethyl vinyl sulfide (9.0 μL , 0.087 mmol), hexamethylbenzene (< 1 mg, internal standard), and 0.7 mL of C_6D_6 . The solution was heated to 80 $^\circ\text{C}$ for 18 hours. Comparison of the initial ^1H NMR spectrum at room temperature and a ^1H NMR spectrum after heating revealed formation $[\text{TpRu}(\text{CO})(\mu\text{-SEt})_2]$ (**2**) (78 %), and styrene (~60 %). The IR spectrum revealed the presence of two stretches at $\nu_{\text{CO}} = 1929, 1965 \text{ cm}^{-1}$. Attempts to isolate and characterize the second, paramagnetic, ruthenium product were unsuccessful.

NMR tube reaction of TpRu(CO)(NCMe)(Ph) (1) and diethyl sulfide. A screwcap NMR tube was charged with TpRu(CO)(NCMe)(Ph) (1) (20.0 mg, 0.043 mmol), diethyl sulfide (5.0 μ L, 0.048 mmol), hexamethylbenzene (< 1 mg, internal standard), and 0.7 mL of C₆D₆. The solution was heated to 80 °C for 18 hours. Comparison of the initial ¹H NMR spectrum at room temperature and a ¹H NMR spectrum after heating revealed likely formation of paramagnetic ruthenium product(s) (*i.e.*, absence of resonances due to the TpRu complexes) and no new observable organic compounds.

NMR tube reaction of TpRu(CO)(NCMe)(Ph) (1) and diphenyl sulfide. A screwcap NMR tube was charged with TpRu(CO)(NCMe)(Ph) (1) (20.0 mg, 0.043 mmol), diphenyl sulfide (8.0 μ L, 0.048 mmol), hexamethylbenzene (< 1 mg, internal standard), and 0.7 mL of C₆D₆. The solution was heated to 80 °C for 18 hours. Comparison of the initial ¹H NMR spectrum at room temperature and a ¹H NMR spectrum after heating revealed likely formation of paramagnetic ruthenium product(s) (*i.e.*, absence of resonances due to the TpRu complexes) and no new observable organic compounds.

NMR tube reaction of TpRu(CO)(NCMe)(Ph) (1) and ethyl phenyl sulfide. A screwcap NMR tube was charged with TpRu(CO)(NCMe)(Ph) (1) (20.0 mg, 0.043 mmol), ethyl phenyl sulfide (6.0 μ L, 0.048 mmol), hexamethylbenzene (< 1 mg, internal standard), and 0.7 mL of C₆D₆. The solution was heated to 80 °C for 18 hours. Comparison of the initial ¹H NMR spectrum at room temperature and a ¹H NMR spectrum after heating revealed likely formation of paramagnetic ruthenium product(s)

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(*i.e.*, absence of resonances due to the TpRu complexes) and no new observable organic compounds.

NMR tube reaction of TpRu(CO)(NCMe)(Ph) (1) and 2,3-dihydrofuran. A screwcap NMR tube was charged with TpRu(CO)(NCMe)(Ph) (**1**) (15.0 mg, 0.033 mmol), 2,3-dihydrofuran (25.0 μ L, 0.326 mmol), hexamethylbenzene (< 1 mg, internal standard), and 0.7 mL of C₆D₆. The solution was heated to 80 °C for 23 hours. Comparison of the initial ¹H NMR spectrum at room temperature and a ¹H NMR spectrum after heating revealed formation of two new ruthenium products in a ratio of 2:1, with the major product identified as TpRu(CO)(NCMe)(C \equiv CCH₂CH₂OH) (**3**). Repeated attempts to isolate and characterize the second ruthenium complex failed.

1.3 Reference

(1) Lail, M.; Arrowood, B. N.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2003**, *125*, 7506-7507.

2.0 X-Ray Report for [TpRu(CO)(μ -SEt)]₂ (2)

2.1 Structure

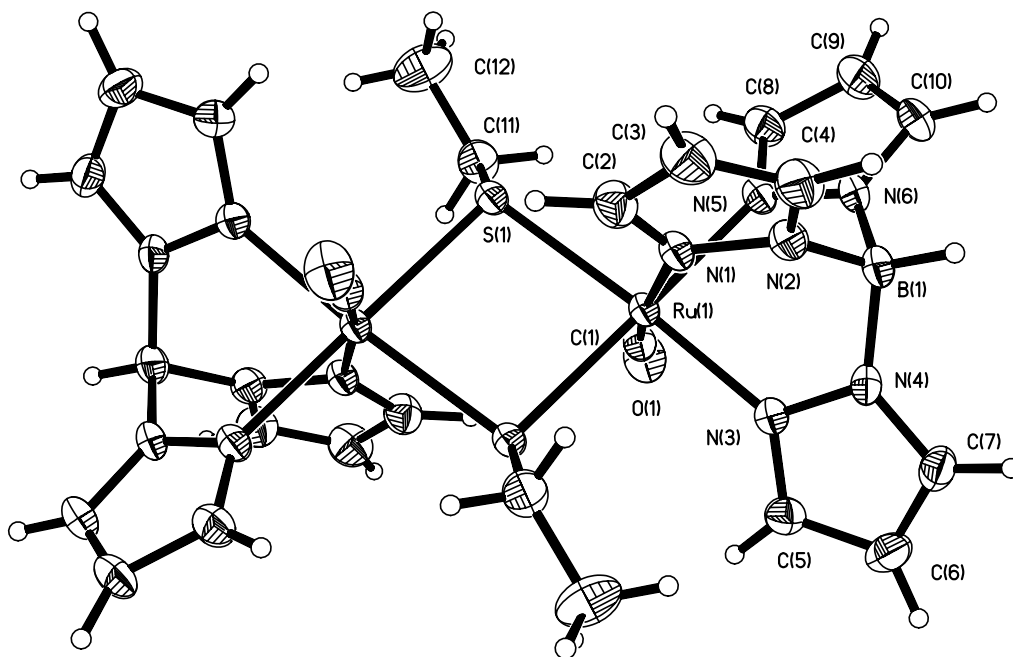


Figure S2. Perspective view of the molecular structure of $\{[HB(C_3N_2)_3]Ru(CO)(\mu-SCH_2CH_3)\}_2$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

Description of the X-ray Structural Analysis of $\{[\text{HB}(\text{C}_3\text{N}_2)_3]\text{Ru}(\text{CO})(\mu\text{-SCH}_2\text{CH}_3)\}_2$

A crystal of $\{[\text{HB}(\text{C}_3\text{N}_2)_3]\text{Ru}(\text{CO})(\mu\text{-SCH}_2\text{CH}_3)\}_2$ was washed with the perfluoropolyether PFO-XR75 (Lancaster) and sealed under nitrogen in a glass capillary. The sample was optically aligned on the four-circle of a Siemens P4 diffractometer equipped with a graphite monochromator, a Mo $K\alpha$ radiation source ($\lambda = 0.71073\text{\AA}$), and a SMART CCD detector held at 5.084 cm from the crystal. Four sets of 20 frames each were collected using the ω scan method and with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the monoclinic crystal lattice.

Data collection consisted of the measurement of a total of 1650 frames in five different runs covering a hemisphere of data. Frame scan parameters are summarized below:

Run	2θ	ω	ϕ	χ	Scan axis	Scan width ($^\circ$)	Frames (#)	Exposure time (sec.)
1	28	43.00	0.00	280.00	2	-0.3	100	30
2	28	43.00	90.00	280.00	2	-0.3	100	30
3	28	43.00	180.00	280.00	2	-0.3	100	30
4	28	43.00	270.00	280.00	2	-0.3	100	30
5	28	28.00	0.00	30.00	3	0.3	1250	30

The program SMART (version 5.6)¹ was used for diffractometer control, frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. All 1650 crystallographic raw data frames were read by program SAINT (version 5/6.0)¹ and integrated using 3D profiling algorithms. The

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resulting data were reduced to produce a total of 11341 reflections and their intensities and estimated standard deviations. An absorption correction was applied using the SADABS routine available in SAINT.¹ The data were corrected for Lorentz and polarization effects as well as any crystal decay. Data preparation was carried out by using the program XPREP,¹ which gave 3383 unique reflections ($R_{\text{int}} = 5.24\%$) with indices $-8 \leq h \leq 10$, $-21 \leq k \leq 21$, $-16 \leq l \leq 16$. The monoclinic space group was determined to be $P2_1/n$, a non-standard setting of $P2_1/c$ (No. 14).

The structure was solved by a combination of the Patterson method and difference Fourier analysis with the use of SHELXTL 6.1.² In the solid state this compound exists as a centrosymmetric dimer with a crystallographic center of inversion located at the intersection of the Ru...Ru and the S...S line segments. Idealized positions for the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 (aromatic and methylene protons; B-H) or 1.5 (methyl protons) times that of the adjacent non-hydrogen atom. The positions of the methyl hydrogen atoms were optimized by a rigid rotating group refinement with idealized tetrahedral angles. During the structural refinement it became apparent that the crystallographic asymmetric unit contained CH_2Cl_2 , which is disordered about a center of symmetry. The methylene chloride was treated as a diffuse electron density contribution with the aid of the SQUEEZE routine in the program PLATON.³ Although specific positions for the independent atoms of the CH_2Cl_2 molecule were not determined, the calculated density, absorption coefficient, and molecular weight reflect the presence of one-half of a molecule of CH_2Cl_2 in the asymmetric unit. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i |F_o^2 - F_c^2|^2$, with weighting $w_i^{-1} =$

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$[\sigma^2(F_o^2) + (0.0753 P)^2 + 0.0 P]$, where $P = (\text{Max}(F_o^2, 0) + 2 F_c^2)/3$, converged to give final discrepancy indices⁴ of $R_1 = 0.0449$, $wR_2 = 0.1171$ for 3118 with $I > 2 \sigma(I)$. The goodness of fit (GOF) value was 1.008.

A correction for secondary extinction was not applied. The maximum and minimum residual electron density peaks in the final difference Fourier map were 1.562 and $-0.971 \text{ e}/\text{\AA}^3$, respectively, were located in the vicinity of the Ru atom. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values found in the International Tables of X-ray Crystallography.⁵

References

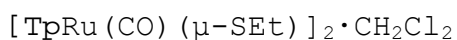
1. SMART, SAINT and XPREP programs are part of Bruker crystallographic software package for single crystal data collection, reduction and preparation.
2. Sheldrick, G. M., SHELXTL6.1 (2000), Crystallographic software package, Bruker AXS, Inc. Madison, Wisconsin, USA.
3. PLATON, written by Professor Anthony L. Spek, Bijvoet Centre for Biomolecular Research, Utrecht University. Current versions of PLATON for Windows are available from Professor Louis J. Farrugia, Department of Chemistry, University of Glasgow at www.chem.gla.ac.uk/~louis/software/.
4. $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$, $R_{\text{int}} = \sum|F_o^2 - F_o^2(\text{mean})|^2 / \sum[F_o^2]$, and $\text{GOF} = [\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters which were varied during the last refinement cycle.

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5. International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham:
Kynoch Press. (Present distributor, D. Reidel, Dordrecht.).

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Table 1. Crystal data and structure refinement for



Empirical formula	$\text{C}_{12.5}\text{H}_{16}\text{BClN}_6\text{ORuS}$	
Formula weight	445.70	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 7.9135(15)$ Å	$\alpha = 90^\circ$
	$b = 16.956(3)$ Å	$\beta = 92.377(3)^\circ$
	$c = 12.898(3)$ Å	$\gamma = 90^\circ$
Volume, Z	1729.3(6) Å ³ , 4	
Density (calculated)	1.712 g/cm ³	
Absorption coefficient	11.94 cm ⁻¹	
F(000)	892	
Crystal size	0.08 x 0.30 x 0.44 mm	
θ range for data collection	1.98 to 27.54° (completeness: 96.2%)	
Limiting indices	$-8 \leq h \leq 10$ $-21 \leq k \leq 21$ $-16 \leq l \leq 16$	
Reflections collected	11341	
Independent reflections	3833 ($R_{\text{int}} = 0.0524$)	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3833 / 0 / 200	
Goodness-of-fit on F^2	1.008	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0449$, $wR2 = 0.1170$	
R indices (all data)	$R1 = 0.0528$, $wR2 = 0.1223$	
Largest diff. peak and hole	1.562 and -0.972 eÅ ⁻³	

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Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for $[\text{TpRu}(\text{CO})(\mu\text{-SEt})]_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	10628(1)	1036(1)	4898(1)	32(1)
S(1)	8162(1)	217(1)	4586(1)	36(1)
O(1)	11781(5)	937(2)	2742(2)	62(1)
N(1)	9687(3)	1369(2)	6408(2)	38(1)
N(2)	10017(4)	2123(2)	6750(2)	42(1)
N(3)	12823(3)	1677(2)	5333(2)	39(1)
N(4)	12702(4)	2382(2)	5829(2)	42(1)
N(5)	9531(4)	2137(2)	4462(2)	39(1)
N(6)	9897(4)	2780(2)	5043(3)	44(1)
C(1)	11347(5)	933(2)	3588(3)	41(1)
C(2)	8653(5)	1056(2)	7078(3)	50(1)
C(3)	8282(6)	1602(3)	7855(3)	61(1)
C(4)	9165(5)	2261(3)	7615(3)	53(1)
C(5)	14466(4)	1546(3)	5211(3)	46(1)
C(6)	15427(5)	2173(3)	5612(3)	54(1)
C(7)	14268(5)	2676(2)	5997(3)	48(1)
C(8)	8546(5)	2382(3)	3657(3)	52(1)
C(9)	8266(6)	3184(3)	3719(4)	65(1)
C(10)	9149(5)	3420(3)	4604(4)	60(1)
C(11)	7610(5)	180(3)	3190(3)	54(1)
C(12)	5805(6)	-4(4)	2959(4)	82(2)
B(1)	10952(5)	2709(2)	6059(3)	45(1)

Table 3. Interatomic distances [Å] and bond angles [°] for
[TpRu(CO)(μ -SEt)]₂.

Ru(1)-C(1)	1.813(4)
Ru(1)-N(3)	2.106(3)
Ru(1)-N(5)	2.124(3)
Ru(1)-N(1)	2.189(3)
Ru(1)-S(1)#1	2.4129(9)
Ru(1)-S(1)	2.4148(9)
S(1)-C(11)	1.836(4)
O(1)-C(1)	1.157(5)
N(1)-C(2)	1.325(5)
N(1)-N(2)	1.374(4)
N(2)-C(4)	1.348(5)
N(2)-B(1)	1.544(6)
N(3)-C(5)	1.334(4)
N(3)-N(4)	1.361(4)
N(4)-C(7)	1.345(4)
N(4)-B(1)	1.532(5)
N(5)-C(8)	1.339(5)
N(5)-N(6)	1.347(4)
N(6)-C(10)	1.349(5)
N(6)-B(1)	1.530(5)
C(2)-C(3)	1.404(6)
C(3)-C(4)	1.360(7)
C(5)-C(6)	1.394(6)
C(6)-C(7)	1.361(6)
C(8)-C(9)	1.380(6)
C(9)-C(10)	1.374(7)
C(11)-C(12)	1.480(6)
C(1)-Ru(1)-N(3)	90.62(14)
C(1)-Ru(1)-N(5)	88.78(13)
N(3)-Ru(1)-N(5)	86.59(11)
C(1)-Ru(1)-N(1)	170.29(13)
N(3)-Ru(1)-N(1)	86.36(11)
N(5)-Ru(1)-N(1)	81.84(11)
C(1)-Ru(1)-S(1)#1	92.09(11)
N(3)-Ru(1)-S(1)#1	93.85(8)
N(5)-Ru(1)-S(1)#1	179.02(8)
N(1)-Ru(1)-S(1)#1	97.31(8)
C(1)-Ru(1)-S(1)	94.16(12)
N(3)-Ru(1)-S(1)	173.28(9)
N(5)-Ru(1)-S(1)	98.22(8)
N(1)-Ru(1)-S(1)	89.66(8)
S(1)#1-Ru(1)-S(1)	81.27(3)
C(11)-S(1)-Ru(1)#1	108.43(14)
C(11)-S(1)-Ru(1)	109.91(14)
Ru(1)#1-S(1)-Ru(1)	98.73(3)
C(2)-N(1)-N(2)	106.1(3)

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C(2)-N(1)-Ru(1)	136.0(3)
N(2)-N(1)-Ru(1)	117.3(2)
C(4)-N(2)-N(1)	109.4(3)
C(4)-N(2)-B(1)	129.4(3)
N(1)-N(2)-B(1)	120.2(3)
C(5)-N(3)-N(4)	106.8(3)
C(5)-N(3)-Ru(1)	132.8(3)
N(4)-N(3)-Ru(1)	120.3(2)
C(7)-N(4)-N(3)	108.6(3)
C(7)-N(4)-B(1)	132.0(3)
N(3)-N(4)-B(1)	119.4(3)
C(8)-N(5)-N(6)	106.5(3)
C(8)-N(5)-Ru(1)	134.1(3)
N(6)-N(5)-Ru(1)	119.2(2)
N(5)-N(6)-C(10)	109.8(3)
N(5)-N(6)-B(1)	120.6(3)
C(10)-N(6)-B(1)	129.6(3)
O(1)-C(1)-Ru(1)	174.1(3)
N(1)-C(2)-C(3)	110.8(4)
C(4)-C(3)-C(2)	104.7(4)
N(2)-C(4)-C(3)	109.0(4)
N(3)-C(5)-C(6)	110.4(4)
C(7)-C(6)-C(5)	104.3(3)
N(4)-C(7)-C(6)	109.9(4)
N(5)-C(8)-C(9)	110.5(4)
C(10)-C(9)-C(8)	105.0(4)
N(6)-C(10)-C(9)	108.2(4)
C(12)-C(11)-S(1)	113.1(3)
N(6)-B(1)-N(4)	109.1(3)
N(6)-B(1)-N(2)	106.7(3)
N(4)-B(1)-N(2)	109.8(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1

Table 4. Anisotropic displacement parameters [$\text{Å}^2 \times 10^3$]
 for $[\text{TpRu}(\text{CO})(\mu\text{-SEt})_2]$. The anisotropic
 displacement factor exponent takes the form:
 $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	34(1)	25(1)	38(1)	-2(1)	0(1)	2(1)
S(1)	36(1)	28(1)	43(1)	-3(1)	-2(1)	4(1)
O(1)	82(2)	57(2)	48(2)	0(1)	19(2)	-2(2)
N(1)	42(1)	28(2)	45(2)	-4(1)	2(1)	4(1)
N(2)	42(1)	39(2)	47(2)	-9(1)	3(1)	2(1)
N(3)	38(1)	32(2)	48(2)	-4(1)	0(1)	0(1)
N(4)	44(2)	27(2)	55(2)	-2(1)	-4(1)	-6(1)
N(5)	42(1)	29(2)	46(2)	1(1)	-1(1)	5(1)
N(6)	45(2)	23(2)	64(2)	2(1)	-2(1)	1(1)
C(1)	45(2)	32(2)	47(2)	1(1)	0(2)	-1(1)
C(2)	54(2)	46(2)	50(2)	-6(2)	9(2)	1(2)
C(3)	66(2)	64(3)	53(2)	-5(2)	14(2)	8(2)
C(4)	58(2)	54(3)	48(2)	-17(2)	6(2)	5(2)
C(5)	40(2)	46(2)	52(2)	1(2)	5(2)	4(2)
C(6)	38(2)	64(3)	60(2)	8(2)	-4(2)	-6(2)
C(7)	48(2)	42(2)	54(2)	3(2)	-3(2)	-13(2)
C(8)	55(2)	45(2)	54(2)	10(2)	-5(2)	6(2)
C(9)	67(3)	43(2)	84(3)	22(2)	-17(2)	9(2)
C(10)	59(2)	30(2)	89(3)	10(2)	-3(2)	8(2)
C(11)	62(2)	50(2)	49(2)	-1(2)	-12(2)	0(2)
C(12)	61(3)	121(5)	62(3)	-6(3)	-14(2)	-10(3)
B(1)	47(2)	28(2)	59(2)	-10(2)	-3(2)	0(2)

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Table 5. Hydrogen atom coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\text{TpRu}(\text{CO})(\mu\text{-SEt})]_2$.

	x	y	z	U(eq)
H(2)	8231	545	7039	60
H(3)	7586	1529	8411	73
H(4)	9179	2731	7988	64
H(5)	14907	1100	4902	55
H(6)	16595	2234	5615	65
H(7)	14521	3151	6327	58
H(8)	8110	2058	3130	62
H(9)	7620	3496	3261	78
H(10)	9218	3933	4858	71
H(11A)	7872	685	2882	65
H(11B)	8302	-217	2871	65
H(12A)	5667	-564	2888	123
H(12B)	5436	250	2325	123
H(12C)	5142	182	3516	123
H(1)	11059	3224	6400	54