Formation of a Bridging-Imido d^6-Rhodium Compound by Nitrene Capture. Insertion and Cycloaddition Reactions

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Supporting Information (pages S1-S8)

Experimental Section.

General Considerations. All reactions were carried out under argon using standard Schlenk techniques. Carbon monoxide (99.8%, Carburos Metalicos) and chloramine-T (Aldrich) were commercially available and were used without further purification. The complex $[(C_5Me_5)Rh(C_2H_4)_2]$[s1] (**1**) was prepared according to literature methods. Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen and nitrogen analyses were performed using a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded with a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at *ca*. 30 KV, NPOE (2-nitrophenyloctylether) was used as matrix. Mass spectra were also recorded with a Bruker MicroFlex spectrometer using DCTB (1,1-dicyano-4-^{t}butylphenyl-3-methylbutadiene) as matrix. ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV 400 and on a Bruker Av 300 spectrometers operating at 400.13 and 300.13 MHz for ^1H, respectively. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the signal of the deuterated solvent as reference.

Synthesis and characterization of the complexes.

[{(C_5Me_5)Rh(μ-N-*p*-$MeC_6H_4SO_2$)}$_2$] (2). The addition of solid chloroamine-T (194.0 mg, 0.85 mmol) to a dichloromethane (5 mL) solution of [(C_5Me_5)Rh(C_2H_4)$_2$] (250.0 mg, 0.85 mmol) produced an immediate change of the colour of the solution from yellow to navy blue along with the precipitation of a colourless solid (NaCl). After stirring for 1h, the suspension was filtered and the filtrate was concentrated to ca. 2 mL, layered with hexane and left at –35 ºC overnight. The microcrystalline navy blue solid deposited was filtered off, washed with cold hexane (2 x 5 mL) and vacuum-dried. Yield: 300.0 mg (87%). Anal. Calcd (%) for $C_{34}H_{44}N_2O_4Rh_2S_2$: C, 50.13; H, 5.44; N, 3.44; S, 7.87. Found: C, 50.05; H, 6.01; N, 3.12; S, 7.57. ^{1}H NMR (25 ºC, $CDCl_3$): δ = 7.70 (δ_A, 4H) and 7.12 (δ_B, J_{AB} = 8.0 Hz, 4H, *p*-MeC_6H_4), 2.36 (s, 6H, *p-Me*C_6H_4), 1.62 (s, 30H, C_5Me_5). ^{13}C{^{1}H} NMR (25 ºC, $CDCl_3$): δ = 144.6 (C^4), 140.0 (C^1), 128.4 (C^3) and 126.5 (C^2) (*p*-MeC_6H_4), 96.3 (d, J_{CRh}= 7.9 Hz, C_5Me_5), 21.4 (*p-Me*C_6H_4), 10.1 (C_5Me_5). MS (MALDI$^+$, DCTB): *m/z* 815 (MH^+, 100%).

[($C_5H_3Bu^t_2$)Rh(C_2H_4)$_2$] (3) was prepared as reported for **1** starting from [{($C_5H_3Bu^t_2$)$RhCl_2$}$_2$], followed by chromatographic purification (neutral alumina, pentane as eluent). Yield: 65%. Anal. Calcd for $C_{17}H_{29}Rh$: C, 60.71; H, 8.69; Found: C, 60.63; H, 8.39. ^{1}H NMR (25 ºC, $CDCl_3$): δ = 4.70 (s, 3H, $C_5H_3Bu^t_2$), 2.76 (m, 4H, C_2H_4), 1.22 (s, 18H, $C_5H_3Bu^t_2$), 0.93 (m, 4H, C_2H_4). ^{13}C{^{1}H} NMR (25 ºC, $CDCl_3$): δ = 119.8 (d, J_{CRh} = 4.3 Hz, C^1), 82.7 (d, J_{CRh} = 4.1 Hz, C^4) and 82.3 (d, J_{CRh} = 4.1 Hz, C^2) ($C_5H_3Bu^t_2$), 36.4 (d, J_{CRh} = 13.5 Hz, C_2H_4), 32.4 (C*Me*$_3$), 31.5 (*C*Me_3). MS (FAB$^+$, NPOE): *m/z* 336 (M^+, 24%), 308 ([M-C_2H_4]$^+$, 100%).

[{($C_5H_3Bu^t_2$)Rh(μ-N-*p*-$MeC_6H_4SO_2$)}$_2$] (4) was prepared as described above for **2** starting from [($C_5H_3Bu^t_2$)Rh(C_2H_4)$_2$] (3) (42.5 mg, 0.13 mmol) and chloramine-T (28.8 mg, 0.13 mmol). Yield: 35.5 mg (62%). Anal. Calcd (%) for $C_{40}H_{56}N_2O_4Rh_2S_2$: C, 53.45; H, 6.28; N, 3.12; S, 7.14. Found: C, 53.23; H, 6.36; N, 3.13; S, 7.33. ^{1}H NMR (25 ºC, $CDCl_3$): δ = 7.70 (δ_A, 4H) and 7.15 (δ_B, J_{AB} = 7.9 Hz, 4H, *p*-MeC_6H_4), 5.43 (s, 2H) and 5.03 (s, 4H) ($C_5H_3Bu^t_2$), 2.36 (s, 6H, *p-Me*C_6H_4), 1.10 (s, 36H, $C_5H_3Bu^t_2$). ^{13}C{^{1}H} NMR (25 ºC, $CDCl_3$): δ = 144.0 (C^4), 140.3 (C^1), 128.7 (C^3) and 126.8 (C^2) (*p*-MeC_6H_4), 117.1 (d, J_{CRh} = 4.3 Hz, C^1), 80.7 (d, J_{CRh} = 7.4 Hz, C^4) and 79.5 (d, J_{CRh} = 5.2 Hz, C^2) ($C_5H_3Bu^t_2$), 30.3 (C*Me*$_3$), 29.2 (*C*Me_3), 21.4 (*p-Me*C_6H_4).

[(C_5Me_5)Rh(μ-{(*p*-$MeC_6H_4SO_2$)N-CO-N(*p*-$MeC_6H_4SO_2$)}Rh(CO)(C_5Me_5)] (5). Carbon monoxide was bubbled through a solution of [{(C_5Me_5)Rh(μ-N-*p*-$MeC_6H_4SO_2$)}$_2$] (**2**) (50.0 mg, 0.06 mmol) in dichloromethane (4 mL) for 10 min giving a dark-green solution which was concentrated to ca. 1 ml, carefully layered with hexane (5 mL) and keep at 0 ºC for 2 days. The

deposited green microcrystals were decanted, washed with hexane (2 x 5 mL) and vacuum dried (32.5 mg, 61% yield). Anal. Calcd (%) for $C_{36}H_{44}N_2O_6Rh_2S_2$: C, 49.66; H, 5.09; N, 3.21; S, 7.37: Found: C, 49.46; H, 4.95; N, 3.15; S, 7.15. IR (nujol, cm^{-1}): 1962, 1699, 1669. ^1H NMR (25 ºC, CD_2Cl_2): δ = 7.91 (δ_A, 2H) and 7.27 (δ_B, J_{AB} = 8.2 Hz, 2H, (p-MeC_6H_4)^A), 7.85 (δ_A, 2H) and 7.32 (δ_B, J_{AB} = 8.2 Hz, 2H, (p-MeC_6H_4)^B), 2.43 (s, 3H, (p-MeC_6H_4)^B), 2.41 (s, 3H, (p-MeC_6H_4)^A), 1.79 (s, 15H) and 1.56 (s, 15H), (C_5Me_5). $^{13}C\{^1H\}$ NMR (25 ºC, CD_2Cl_2): δ = 196.8 (d, J_{CRh} = 87.8 Hz, Rh-*C*O), 159.4 (d, J_{CRh} = 3.2 Hz, N*C*ON), 143.2 (C^4), 142.0 (C^1), 129.5 (C^3) and 128.6 (C^2), (p-MeC_6H_4)^A, 142.2 (C^4), 137.8 (C^1), 129.0 (C^3) and 125.8 (C^2) (p-MeC_6H_4)^B, 101.1 (d, J_{CRh} = 4.8 Hz) and 92.4 (d, J_{CRh} = 8.3 Hz) (C_5Me_5), 21.2 (p-*Me*C_6H_4), 10.2 and 9.6 (C_5Me_5). MS (MALDI$^+$, DCTB): *m/z* 842 (M-CO$^+$, 37%).

[(C_5Me_5)Rh(CO)(p-$MeC_6H_4SO_2$)N-CO-N(-p-$MeC_6H_4SO_2$)] (6). Carbon monoxide was bubbled through a dichloromethane (5 mL) solution of [{(C_5Me_5)Rh(μ-$NSO_2C_6H_4Me$-p)}$_2$] (**2**) (82.3 mg, 0.20 mmol). The resulting green solution, containing **5**, was exposed to CO (1 atm) for a further 1.5 h to render an orange solution. Thereafter, the solution was concentrated to 2 mL, layered with hexane (5 mL) and maintained under a CO atmosphere (1 atm) for 24 h. The orange crystals deposited (**6**) where filtered off, washed with hexane (2 x 3 mL), and vaccum-dried. Yield: 50.5 mg (79%). Evaporation of the filtrate to dryness afforded a yellow residue identified as [(C_5Me_5)Rh(CO)$_2$]. **Complex 6:** Anal. Calcd (%) for $C_{26}H_{29}N_2O_6RhS_2$: C, 49.37; H, 4.62; N, 4.43; S, 10.14. Found: C, 49.69; H, 4.61; N, 4.60; S, 10.15. IR (CH_2Cl_2, 298 K): 2088, 1708, 1688. ^1H NMR (25 ºC, CD_2Cl_2): δ = 7.74 (δ_A, 4H) and 7.24 (δ_B, J_{AB} = 8.4 Hz, 4H, p-MeC_6H_4), 2.41 (s, 6H, p-MeC_6H_4), 2.02 (s, 15H, C_5Me_5), $^{13}C\{^1H\}$ NMR (25 ºC, CD_2Cl_2): δ = 193.2 (d, J_{CRh} = 83.9 Hz, Rh-*C*O), 159.1 (d, J_{CRh} = 3.2 Hz, N*C*ON), 142.9 (C^4), 139.0 (C^1), 129.0 (C^3) and 127.3 (C^2), (p-MeC_6H_4), 105.3 (br, C_5Me_5), 21.2 (p-*Me*C_6H_4), 9.8 (C_5Me_5).

[(C_5Me_5)Rh(CO)$_2$]: IR (hexane, cm^{-1}): 2026, 1963. ^1H NMR (25 ºC, C_6D_6): δ = 1.73 (C_5Me_5). $^{13}C\{^1H\}$ NMR (25 ºC, C_6D_6): δ = 195.1 (d, J_{CRh} = 42 Hz, Rh-*C*O), 100.7 (d, J_{CRh} = 3.8 Hz, C_5Me_5), 10.5 (C_5Me_5).

[(C_5Me_5)Rh{(p-$MeC_6H_4SO_2$)N_4(C_6F_5)}] (7). Neat $C_6F_5N_3$ (22.3 μL, 0.18 mmol) was added to a dark blue solution of [{(C_5Me_5)Rh(μ-N-p-$MeC_6H_4SO_2$))}$_2$] (**2**) (73.3 mg, 0.090 mmol) in toluene (10 mL). After heating for 3h at 60 ºC, the resulting orange-red solution was filtered and the filtrate concentrated to ca. 1 mL. Addition of hexane (3 mL) produced the precipitation of the product, which was filtered under argon, washed with hexane (2 x 5 mL) and vacuum dried. Yield: 83.2 mg (75%). Anal. Calcd (%) for $C_{23}H_{22}F_5N_4O_2RhS$: C, 44.82; H, 3.60; N, 9.09; S, 5.20. Found: C, 45.05; H, 3.56; N, 8.95; S, 5.46. IR (nujol, cm^{-1}): 1521 ($\nu_{N=N}$). ^1H NMR (25 ºC, C_6D_6): δ = 8.14 (δ_A,

2H) and 6.71 (δ_B, J_{AB} = 8.4 Hz, 2H; *p*-MeC_6H_4), 1.79 (s, 3H, *p-Me*C_6H_4), 1.24 (s, 15H, C_5Me_5). ^{19}F NMR (25 ºC, C_6D_6): δ -148.81 (m, 2F, C^2), -158.25 (t, 1F, J_{FF}= 22.1 Hz, C^4), -163.75 (m, 2F, C^3) (C_6F_5). $^{13}C\{^1H\}$ NMR (25 ºC, $CDCl_3$): δ = 143.7 (dm, $^1J_{CF}$= 248.2 Hz, C^2), 139.6 (dm, J_{CF}= 250.9 Hz, C^4), 137.7 (dm, J_{CF}= 250.9 Hz, C^3F), (C_6F_5); 143.2 (C^4), 138.1 (C^1), 129.3 (C^2) and 129.2 (C^3) (*p*-MeC_6H_4), 96.6 (d, J_{CRh}= 8.0 Hz, C_5Me_5), 21.1 (*p-Me*C_6H_4), 9.3 (C_5Me_5).

X-ray diffraction studies on complexes 2, 4, 5, 6, and **7**·0.5$CHCl_3$.

X-ray data were collected with a Bruker Smart Apex CCD diffractometer, with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) using ω scans (0.3º). Data were corrected for absorption using a multi-scan method applied with SADABS program.[S2] Selected crystallographic data can be found in Table S1. The structures were solved by direct methods and refined by full-matrix least-squares on F^2, with the program SHELX97[S3] in the WINGX[S4] package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions. All of them were refined riding on the corresponding atom with an isotropic displacement parameter related to that of the bonded atom. The highest electronic residuals were observed in close proximity of the metal centres and make no chemical sense.

Table S1. Selected crystallographic data of **2, 4, 5, 6,** and **7**·0.5$CHCl_3$.

	2	**4**	**5**	**6**	**7**·0.5$CHCl_3$
formula	$C_{34}H_{44}N_2O_4Rh_2S_2$	$C_{40}H_{56}N_2O_4Rh_2S_2$	$C_{36}H_{44}N_2O_6Rh_2S_2$	$C_{26}H_{29}N_2O_6RhS_2$	$C_{23}H_{22}F_5N_4O_2RhS$ ·0.5$CHCl_3$
formula weight	814.65	898.81	870.67	632.54	676.10
color	dark blue	green	dark red	orange	red
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	P2/n	$P2_1/c$	$P2_1/m$	$P2_1/n$
a[Å]	14.1348(14)	13.2409(10)	10.1760(9)	7.8460(8)	14.9461(7)
b[Å]	14.2221(14)	10.2362(7)	15.8390(14)	21.966(2)	17.8646(8)
c[Å]	17.6383(17)	14.8786(11)	22.203(2)	8.2972(9)	19.7834(9)
β[°]	113.287(2)	97.5420(10)	96.785(2)	114.359(2)	97.2630(10)
V[$Å^3$]	3256.9(6)	1999.1(3)	3553.5(5)	1302.7(2)	5239.9(4)
Z	4	2	4	2	8
F(000)	1664	928	1776	648	2712
ρ_{calcd}[g cm^{-3}]	1.661	1.493	1.627	1.613	1.714
μ (mm^{-1})	1.183	0.971	1.094	0.861	0.950
crystal size[mm]	0.18 × 0.15 × 0.07	0.21 × 0.08 × 0.04	0.12 × 0.07 × 0.05	0.32 × 0.05 × 0.04	0.24 × 0.18 × 0.17
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
θ limits [°]	1.57 - 27.00	1.94 - 26.99	1.58 - 25.20	1.85 - 27.00	1.54 - 26.00
collected reflns.	20461	12390	26978	11758	56854
uniq. reflns. (R_{int})	7086 (0.0335)	4347 (0.0363)	6397 (0.0853)	2912 (0.0393)	10308 (0.0289)
reflns. with I>2σ(I)	6152	3688	4935	2673	9439
param./restraints	409/0	233/0	445/0	181/0	702/73
R_1 (on F, I>2σ(I))	0.0342	0.0348	0.0665	0.0388	0.0496
wR_2 (on F^2, all data)	0.0781	0.0758	0.1292	0.0954	0.1275
max./min. $\Delta\rho$ [e $Å^{-3}$]	0.489/-0.510	0.589/-0.565	2.200/-1.344	0.862/-0.382	1.612/-1.949

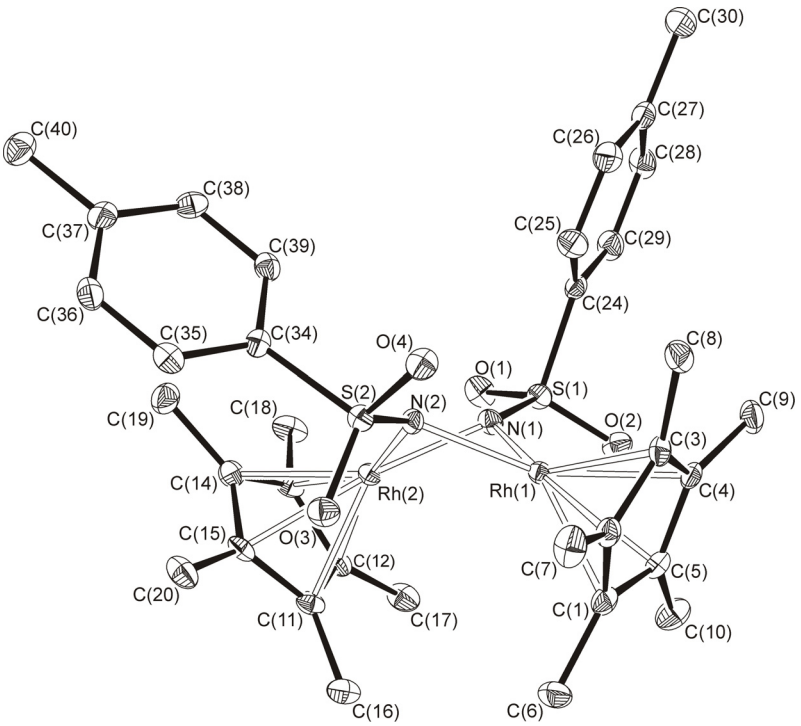

Figure S3. Molecular structure (ORTEP at 50 % level) of complex **2**.

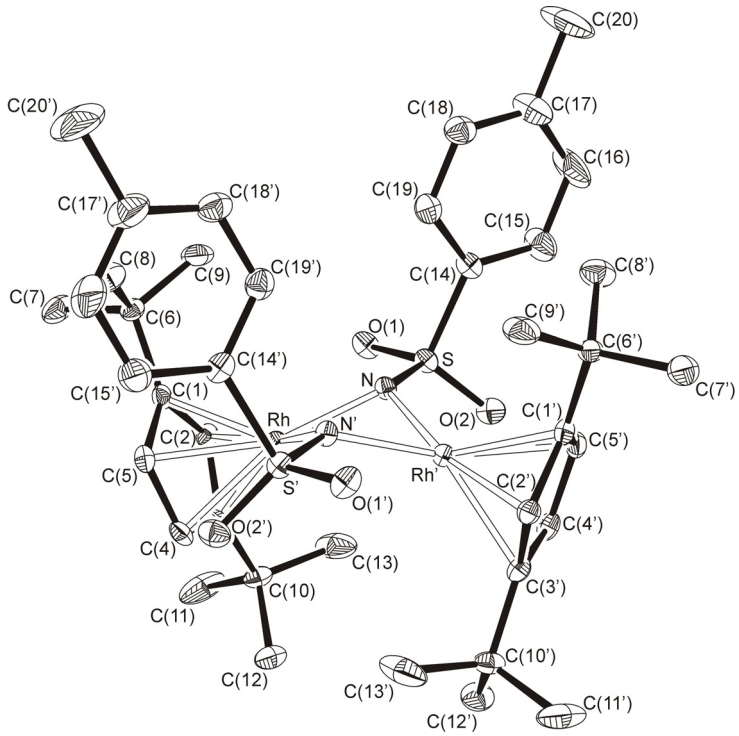

Figure S4. Molecular structure (ORTEP at 50 % level) of complex **4**.

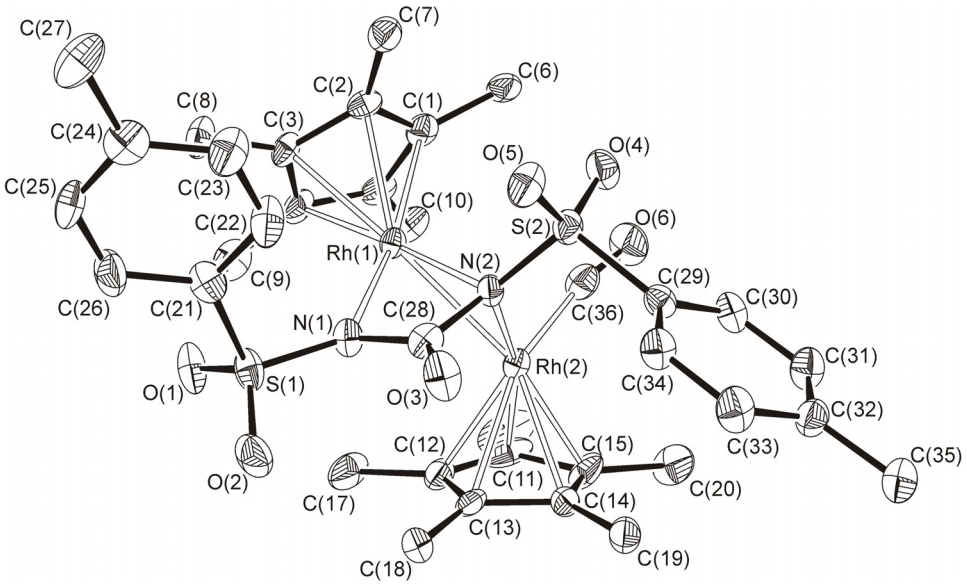

Figure S5. Molecular structure (ORTEP at 50 % level) of complex **5**.

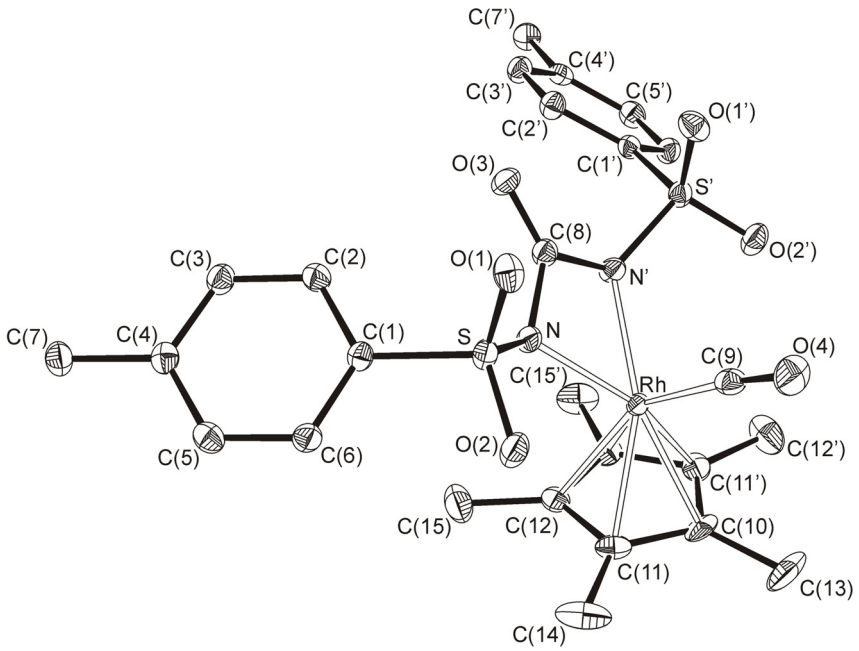

Figure S6. Molecular structure (ORTEP at 50 % level) of complex **6**.

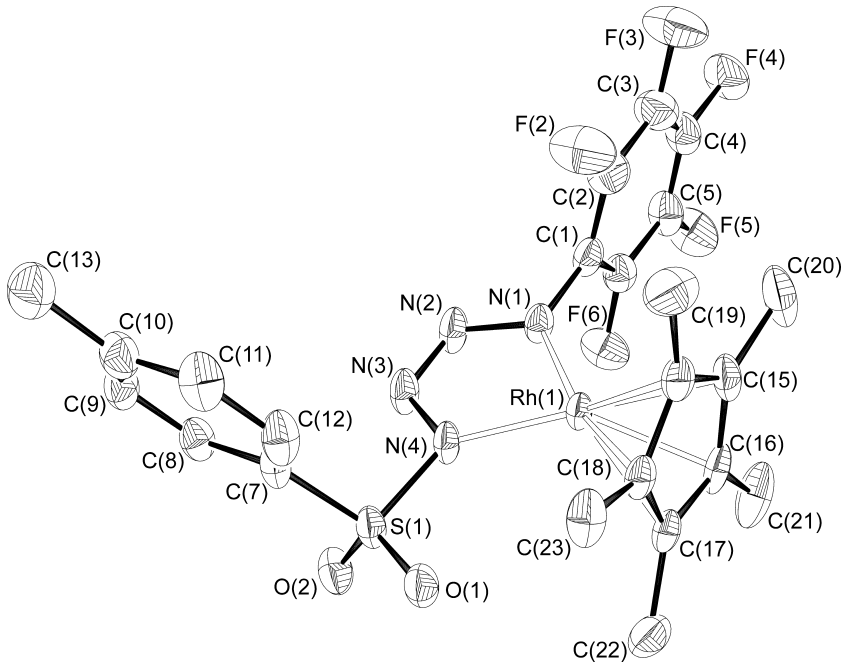

Figure S6. Molecular structure (ORTEP at 50 % level) of complex **7**.

References

[S1] K. Moseley, J. W. Kang, P. M. Maitlis, *J. Chem. Soc. (A)* **1970**, 2875.

[S2] G. M. Sheldrick, *SADABS*, Bruker AXS: Madison, WI, **1997**.

[S3] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, **1997**.

[S4] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.