Coordination Chemistry of Rh(III) Porphyrins: Complexes with Hydrazine, Disulfide, and Diselenide Bridging Ligands

James E. Redman,[†] Neil Feeder,[†] Simon J. Teat,[‡] and Jeremy K. M. Sanders*[,†]

Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K., and CLRC Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, U.K.

Received October 13, 2000

Rh(III) porphyrin complexes with bridging hydrazine and substituted hydrazine ligands were characterized in solution by ^{1}H NMR spectroscopy and in the solid state by X-ray diffraction. Addition of further ligand to these species afforded 1:1 complexes in which methylhydrazine and *N*,*N*-dimethylhydrazine preferentially bound to the Rh center through the substituted nitrogen atom, as evidenced by ^{1}H NMR chemical shifts. An alkylated Rh(III) porphyrin was isolated as a decomposition product of the reaction of *N*,*N*-dimethylhydrazine with Rh(III) porphyrin in the presence of light and oxygen. Me_2Se_2 and Me_2S_2 formed bridging and nonbridging complexes with Rh(III) porphyrin, analogous to that observed with *N*,*N*′-dimethylhydrazine.

Introduction

The crystal structure of a nitrogenase enzyme cofactor[1] revealed an Fe−Mo sulfide cluster believed to be responsible for the biological fixation of nitrogen. These findings renewed interest in the coordination chemistry of dinitrogen with transition metals with a view to both understanding the natural system and developing artificial nitrogen fixation processes. Of particular importance is the reduction of coordinated nitrogen to hydrazine and ammonia or its incorporation into organic molecules under mild conditions. Recent advances in this field have included the formation of ammonia by reaction of a tungsten−dinitrogen complex with an acidic Ru−η^2-H_2 complex[2] and reaction of a Zr_2 (μ-η^2:η^2-N_2) species with H_2 to form an N−H bond.[3] The complexes of hydrazines with metalloporphyrins have generated interest as models for intermediates in the reduction of dinitrogen. Collman et al. have reported the preparation and redox chemistry of covalently linked Ru(II) porphyrin dimers in which hydrazine was bound between the already cofacial porphyrins.[4−6] We have previously described hydrazine binding to steroid-capped Zn(II) porphyrins,[7] and more recently, others have reported syntheses of Ru(IV) and Ti(IV) porphyrin complexes with hydrazido ligands.[8,9] Continuing our studies of rhodium porphyrins,[10,11] in this paper, we describe the preparation of Rh(III) porphyrin complexes with hydrazine ligands and demonstrate the formation of analogous species with disulfide and diselenide ligands in solution.

Experimental Section

Instrumentation. NMR spectra were recorded on Bruker DRX 500 (500.1 MHz for ^{1}H, 125.7 MHz for ^{13}C), AM 400 or DRX 400 (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C), and DPX 250 or AC 250 (250.1 MHz for ^{1}H, 62.9 MHz for ^{13}C) instruments. Chemical shifts are quoted in parts per million with respect to tetramethylsilane (TMS). Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer at 4 cm^{-1} resolution or better. UV−visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

X-ray Crystallography. Diffraction data were collected in Cambridge on a Rigaku R-Axis IIc or Nonius Kappa CCD device, or for small crystals, were collected at the Daresbury SRS (UK), Station 9.8, using a Bruker AXS SMART CCD area detector.[12−14] Structures were solved with either SHELXS-97 or SIR92.[15−17] Refinement was carried out with SHELXL-97.[18] Extensive disorder was often observed in the solubilizing hexyl chains, typical of this kind of structure.[19] The carbon

* Corresponding author e-mail: jkms@cam.ac.uk.
† Cambridge Centre for Molecular Recognition.
‡ CLRC Daresbury Laboratory.

(1) Kim, J.; Rees, D. C. *Nature* **1992**, *360*, 563.
(2) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540.
(3) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
(4) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guilard, R.; Reed, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2794.
(5) Collman, J. P.; Kim, K.; Leidner, C. R. *Inorg. Chem.* **1987**, *26*, 1152.
(6) Collman, J. P.; Hutchison, J. E.; Ennis, M. S.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1992**, *114*, 8074.
(7) Bonar-Law, R. P.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3085.
(8) Sun, X.-R.; Huang, J.-S.; Cheung, K.-K.; Che, C.-M. *Inorg. Chem.* **2000**, *39*, 820.
(9) Thorman, J. L.; Woo, L. K. *Inorg. Chem.* **2000**, *39*, 1301.
(10) Kim, H.-J.; Redman, J. E.; Nakash, M.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *Inorg. Chem.* **1999**, *38*, 5178.
(11) Redman, J. E.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *Inorg. Chem.* **2001**, *40*, 2486.
(12) Cernik, R. J.; Clegg, W.; Catlow, C. R. A.; Bushnell-Wye, G.; Flaherty, J. V.; Greaves, G. N.; Burrows, I.; Taylor, D. J.; Teat, S. J.; Hamichi, M. *J. Synchrotron Radiat.* **1997**, *4*, 279.
(13) Clegg, W. *J. Chem. Soc., Dalton Trans.* **2000**, 3223.
(14) *SMART (control) and SAINT (integration) software*, version 4; Bruker AXS Inc.: Madison, WI, 1994.
(15) Sheldrick, G. M. *SHELXS-97*: *Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
(16) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.
(17) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(18) Sheldrick, G. M. *SHELXL-97*: *Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

10.1021/ic0011314 CCC: $20.00
Published on Web 05/24/2001

Table 1. Crystallographic Data for **2**, **4**, **5**, **7**, and **9**

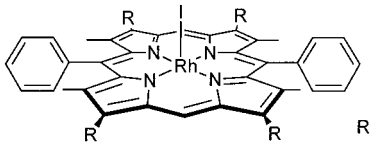
	2	**4**	**5**	**7**	**9**
empirical formula	$C_{120}H_{156}I_2N_{10}Rh_2$	$C_{60}H_{79}IN_5Rh$	$C_{123}H_{162}Cl_2I_2N_{10}Rh_2$	$C_{123}H_{162}Cl_2I_2N_{10}Rh_2$	$C_{122}H_{160}Cl_2I_2N_{10}Rh_2$
fw	2198.17	1100.09	2311.15	2311.15	2297.12
cryst size, mm	0.09 × 0.04 × 0.02	0.07 × 0.06 × 0.02	0.16 × 0.14 × 0.03	0.20 × 0.04 × 0.04	0.12 × 0.06 × 0.06
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	16.2361(13)	16.3158(13)	15.1170(4)	15.231(2)	15.1665(9)
b, Å	18.6695(15)	26.431(2)	18.7980(8)	18.438(3)	18.7297(11)
c, Å	20.6876(16)	12.7523(10)	21.9870(9)	22.377(3)	21.7848(12)
α, deg	72.554(2)	90	68.4040(14)	65.943(5)	67.709(5)
β, deg	87.348(2)	100.830(2)	81.457(2)	83.689(5)	81.345(5)
γ, deg	67.114(2)	90	79.604(2)	81.358(5)	79.304(5)
V, Å^3	5493.8(8)	5401.5(8)	5691.0(4)	5664.8(14)	5604.5(6)
Z	2	4	2	2	2
ρ_{calc}, mg/m^3	1.329	1.353	1.349	1.355	1.361
R	0.0895	0.0632	0.0863	0.1544	0.0702
wR2	0.2170	0.1177	0.1988	0.3393	0.1891
GOF on F^2	1.065	1.073	1.032	1.143	0.997

atoms in these disordered groups were refined with isotropic temperature factors and restrained to give chains with a reasonable geometry. Even with synchrotron radiation, crystals were found to be weakly diffracting, resulting in a relatively high R1 value.

^{1}H NMR Titrations. $CDCl_3$ for use in titrations was stored over anhydrous K_2CO_3 in a refrigerator. Typically, a solution of Rh(III) porphyrin (**1**)·MeOH (4 mg) in $CDCl_3$ (600 μL) was titrated with 5-μL aliquots of a solution of ligand in $CDCl_3$ at a concentration of 72 mM. ^{1}H spectra (400 MHz) were acquired at room temperature. Me_2Se_2 was filtered through neutral alumina before use.

UV−Visible Titrations. A 3.0-mL aliquot of a 4 μM solution of **1**·MeOH in CH_2Cl_2/MeOH (200 μL MeOH/100 mL of solvent) was titrated at 25 °C with 10-μL aliquots of a 75 μM solution of ligand in the same solvent mixture. The cuvette was magnetically stirred for ∼30 s prior to recording each spectrum. Spectra were processed by factor analysis followed by least-squares fitting using the program Specfit.[20]

Materials. 1 was prepared as previously described[10] and recrystallized from $CHCl_3$ layered with MeOH. Other chemicals were obtained from Aldrich and used without further purification. Merck 60 mesh silica gel was used for column chromatography.



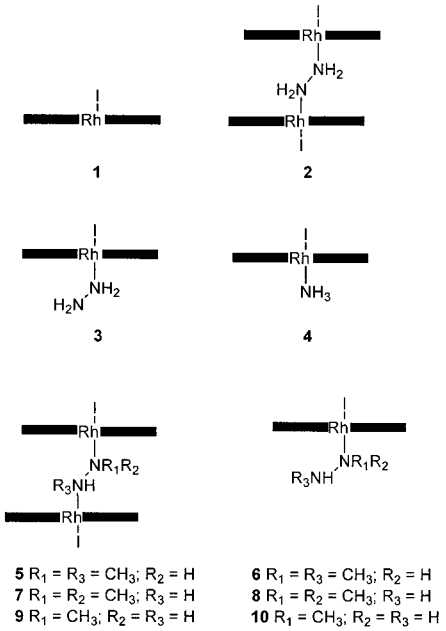
R = *n* - hexyl

1

Synthesis. 1$_2$·NH$_2$NH$_2$ (2). Hydrazine monohydrate (0.5 μL, 10 μmol) in water (10 mL) was added to a mixture of a solution of **1** (10 mg, 9.2 μmol) in CH_2Cl_2 (1 mL) and water (5 mL). After 150 min at room temperature, an additional portion of CH_2Cl_2 (20 mL) was added, and the organic layer was separated, washed with water (2 × 30 mL), and dried ($MgSO_4$). Evaporation of the solvent afforded the product as an orange solid (5 mg, 49%).

For structure determination, crystals of **2** were obtained from a solution of **2** and **3** (prepared by adding > 0.5 equiv of N_2H_4·H_2O to **1**) in toluene layered with MeOH (see Table 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (s, 4H, meso), 7.84 (m, 8H, Ar), 7.55 (m, 8H, Ar), 7.25 (m, Ar), 3.72 (m, 16H, hex H^1), 2.24 (s, 24H, CH_3), 2.04 (m, 16H, hex H^2), 1.84 (m, 16H, hex H^3), 1.63 (m, 16H, hex H^4), 1.52 (m, 16H, hex H^5), 1.05 (t, J = 7 Hz, 24H, hex H^6), −11.03 (s, 4H, NH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.5, 141.6, 138.6, 138.0, 137.8, 133.0, 132.9, 128.5, 127.6, 127.3, 118.3, 96.8, 33.4, 31.9, 30.5, 27.0, 22.9, 15.1, 14.2. UV−vis (CH_2Cl_2) λ_{max}, nm: 360, 408, 528, 558. IR (CCl_4) ν_{max} (cm^{-1}): 3287 (w), 3231 (w), 3147 (w), 2957 (s), 2930 (s), 2858 (m), 1466 (m).



1·NH$_3$ Complex (4). A solution of **1** (5 mg, 4.6 μmol) in CH_2Cl_2 (1 mL) was treated with vapor from aqueous NH_3 solution for 30 min at room temperature. The solvent was evaporated by blowing with N_2, and the product was obtained quantitatively after being dried in vacuo. Crystals for structure determination were obtained from a toluene solution layered with MeOH.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 2H, meso), 8.14 (d, J = 7 Hz, 2H, Ar), 7.98 (d, J = 7 Hz, 2H, Ar), 7.78−7.68 (m, 6H, Ar), 4.00 (m, 4H, hex H^1), 3.89 (m, 4H, hex H^1), 2.45 (s, 12H, CH_3), 2.22 (m, 8H, hex H^2), 1.80 (m, 8H, hex H^3), 1.55 (m, 8H, hex H^4), 1.43 (m, 8H, hex H^5), 0.95 (t, J = 7 Hz, 12H, hex H^6), −5.77 (s, 3H, NH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.1, 142.8, 140.5, 140.1, 138.6, 134.0, 132.8, 128.3, 127.8, 127.2, 119.3, 98.8, 33.4, 32.0, 30.3, 27.1, 22.8, 15.6, 14.2. UV−vis (CH_2Cl_2) λ_{max} (nm): 360, 420, 532, 562. MALDI MS *m*/*z*: [M − NH_3]$^+$ 1084. IR (CCl_4) ν_{max} (cm^{-1}): 3381 (w), 2957 (s), 2930 (s), 2858 (m). Anal. Calcd for $C_{60}H_{79}IN_5Rh$: C, 65.51; H, 7.24; N, 6.37. Found: C, 65.70; H, 7.43; N, 6.03.

1$_2$·NHMeNHMe (5). A solution of 1·NHMeNHMe (**6**) (10 mg, 8.7 μmol) in CH_2Cl_2/hexane (1:1) was passed through a silica column. The solvent was evaporated to afford the product as an orange solid (7.1 mg, 73%). Crystals for structure determination were obtained from a CH_2Cl_2 solution layered with MeOH.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 4H, meso), 7.79 (m, 12H, Ar), 7.53 (m, 8H, Ar), 4.17 (m, 4H, hex H^1), 4.05 (m, 4H, hex H^1),

(19) Nakash, M.; Clyde-Watson, Z.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *Chem.—Eur. J.* **2000**, *6*, 2112.
(20) *Specfit*, version 2.09X; Spectrum Software Associates: Chapel Hill, NC.

3.79 (m, 8H, hex H^1), 2.32 (s, 12H, CH_3), 2.29 (s, 12H, CH_3), 1.96 (m, 4H, hex H^2), 1.85 (m, 12H, hex H^2), 1.65 (m, 16H, hex H^3), 1.47−1.33 (m, 32H, hex $H^{4,5}$), 0.93, 0.90 (2 × t, J = 7 Hz, 24H, hex H^6), −7.32 (d, J = 6 Hz, 6H, NHCH_3), −9.40 (t, J = 6 Hz, 2H, NHCH_3).

1·NHMeNHMe (6). To a solution of **1**·MeOH (12.2 mg, 11 μmol) in CH_2Cl_2 (20 mL) was added *N*,*N*′-dimethylhydrazine dihydrochloride (17.3 mg, 0.13 mmol) in water (20 mL). NaOH (10%, 2 drops) was added, and the mixture was shaken. The organic phase was separated, dried ($MgSO_4$), and evaporated to an orange solid (10.6 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 2H, meso), 8.10 (m, 2H, Ar), 8.04 (m, 2H, Ar), 7.76 (m, 6H, Ar), 4.03 (m, 4H, hex H^1), 3.91 (m, 4H, hex H^1), 2 × 2.48 (s, 12H, CH_3), 2.21 (m, 8H, hex H^2), 1.77 (m, 8H, hex H^3), 1.52 (m, 8H, hex H^4), 1.41 (m, 8H, hex H^5), 2 × 0.92 (t, J = 7 Hz, hex H^6), −0.66 (s, 3H, NHCH_3), −3.27 (d, J = 6 Hz, 3H, RhNHCH_3), −4.09 (s, 1H, NHCH_3), −4.90 (m, 1H, RhNHCH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 2 × 144.3, 142.7, 140.5, 140.4, 140.1, 140.0, 138.8, 138.7, 133.8, 133.0, 128.3, 127.7, 127.3, 119.5, 98.9, 34.3, 33.8, 2 × 33.3, 32.0, 2 × 30.1, 2 × 27.0, 22.7, 15.5, 14.1.

1_2·NH_2NMe_2 (7). **7** was prepared by titration of a solution of **1**·MeOH (4.0 mg, 3.6 μmol) with *N*,*N*-dimethylhydrazine in $CDCl_3$. Material for crystal growth was prepared by passing a solution of **1** (5.2 mg, 4.8 μmol) and *N*,*N*-dimethylhydrazine (1 μL, 13 μmol) in CH_2Cl_2 (0.5 mL) and hexane (0.5 mL) through a silica column. Porphyrin was washed from the column with CH_2Cl_2/hexane (1:1), and the solvent was evaporated. X-ray quality crystals were obtained from a CH_2Cl_2 solution layered with MeOH.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 2H, meso), 0.37 (s, 2H, meso), 7.80 (m, 12H, Ar), 7.62 (m, 6H, Ar), 7.37 (d, J = 7 Hz, 2H, Ar), 4.04 (m, 8H, hex H^1), 3.76 (m, 8H, hex H^1), 2.38 (s, 12H, CH_3), 2.29 (s, 12H, CH_3), 1.85 (m, 16H, hex H^2), 1.63 (m, 16H, hex H^3), 1.50−1.30 (m, 32H, hex $H^{4,5}$), 0.93 (t, J = 7 Hz, 12H, hex H^6), 0.88 (t, J = 7 Hz, 12H, hex H^6), −7.83 (s, 6H, NCH_3), −10.24 (s, 2H, NH_2).

1_2·$NHMeNH_2$ (9). **9** was prepared by titration of a solution of **1**·MeOH (4.2 mg, 3.8 μmol) with methylhydrazine in $CDCl_3$. After the titration, the sample was eluted through a silica column with hexane/CH_2Cl_2 (1:1) and evaporated to an orange solid. This was dissolved in CH_2Cl_2 and layered with MeOH to obtain crystals for structure determination.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (s, 2H, meso), 9.43 (s, 2H, meso), 7.93 (d, J = 7 Hz, 2H, Ar), 7.82 (m, 8H, Ar), 7.52 (m, 8H, Ar), 7.33 (d, J = 4 Hz, 2H, Ar), 4.03 (m, 4H, hex H^1), 3.89 (m, 4H, hex H^1), 3.75 (m, 4H, hex H^1), 3.66 (m, 4H, hex H^1), 2.33 (s, 6H, CH_3), 2 × 2.27 (2 × s, 18H, CH_3), 2.17−1.34 (m, 64H, hex H^{2-5}), 0.96 (m, 24H, hex H^6), −7.79 (d, J = 6 Hz, 3H, NHCH_3), −10.00 (m, 2H, NHMeNHH), −10.34 (m, 1H, NHH).

Results and Discussion

1 was prepared as a methanol complex according to the literature.[10] A solution of **1**·MeOH in $CDCl_3$ was titrated with hydrazine monohydrate, and the product distribution was monitored by ^{1}H NMR spectroscopy. Hydrazine displaced the coordinated methanol and initially formed a 2:1 complex (**2**) with a bridging hydrazine ligand as evidenced by a highly shielded resonance at −11.03 ppm and an upfield shifted porphyrin meso resonance at 9.37 ppm. Collman et al. observed a similarly upfield shifted resonance at −10.15 ppm, corresponding to hydrazine bound within a Ru(II) cofacial diporphyrin.[6] Addition of >0.5 equiv of hydrazine resulted in the breakup of the dimeric complex to afford the 1:1 complex **3**, which displayed a pair of shielded NH_2 resonances at −3.77 and −3.28 ppm and a porphyrin meso resonance at 10.25 ppm. **2** and **3** were in slow exchange on the NMR chemical shift time scale, although equilibration occurred too rapidly to readily monitor the kinetics of this process by ^{1}H NMR. The more upfield NH_2 resonance, assigned to RhNH_2NH_2, remained sharp throughout the titration, whereas the peak at −3.28 ppm, assigned to RhNH_2NH_2, progressively broadened. Broadening can be attributed to exchange of the latter protons catalyzed by traces of acidic impurity. In support of this hypothesis, exposure of the sample to trifluoroacetic acid vapor further broadened the RhNH_2NH_2 resonance without affecting the width of the Rh$NH_2$$NH_2$ peak.

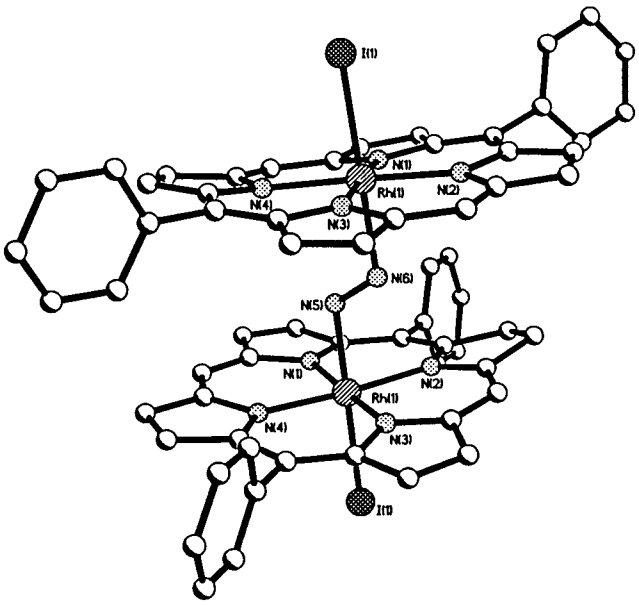


Figure 1. Molecular structure of **2**. Hydrogen atoms and porphyrin β substituents have been omitted for clarity.

Passage of a solution of **2** and **3** through a silica gel column eluted with CH_2Cl_2/hexane (1:1) retained hydrazine on the silica and converted **3** to **2**. In this way, a mixture with initial meso resonances in the intensity ratio of 1:0.77 (**3**:**2**) was converted to a mixture in which this ratio was 1:9.6. Starting from 10 mg of **1**·MeOH, a total of 8.0 mg of material was recovered after this treatment, confirming that there is a true conversion of **3** to **2** on the silica gel and that this filtration does not simply remove **3** to leave a mixture enriched in **2**. An alternative route to **2** was extraction of an aqueous solution of hydrazine with a solution of **1** in CH_2Cl_2 followed by a standard aqueous workup. The infrared spectrum of **2** in CCl_4 solution showed a band at 3231 cm^{-1} and a further pair of very weak bands in the same spectral region, which may be assigned to the NH stretches of the hydrazine.[21]

Crystallization of a mixture of **3** and **2** from a toluene solution layered with methanol resulted in preferential crystallization of **2**, most likely because of the poor solubility of this complex in methanol. A single-crystal X-ray diffraction study revealed that in the solid state the hydrazine adopts a trans geometry with a Rh−N−N−Rh torsion angle of 178.5(1)° (Figure 1). The N−N bond length of 1.47(1) Å is in the range typically reported for bridging hydrazine complexes.[22] The two inequivalent Rh−N_{axial} bond lengths are 2.030(9) and 2.089(9) Å. The porphyrins are oriented with almost parallel planes but with the axes joining the opposite meso positions twisted slightly, apparently to avoid steric clash of the peripheral substituents. The deviation of the porphyrins from planarity is irregular and not easily classified into one of the commonly observed distortion modes.[23]

For comparison with **2** and **3**, the complex of **1** with ammonia, **4**, was prepared by exposure of a CH_2Cl_2 solution of **1** to

(21) Sacconi, L.; Sabatini, A. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1389.
(22) Heaton, B. T.; Jacob, C.; Page, P. *Coord. Chem. Rev.* **1996**, *154*, 193.
(23) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding* **1987**, *64*, 1.

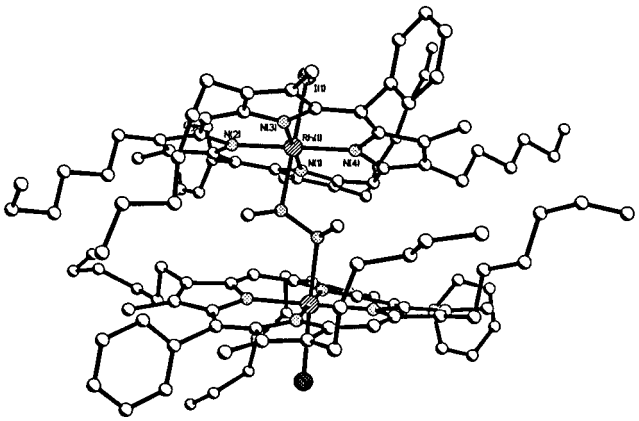


Figure 2. Molecular structure of **5**. Hydrogen atoms have been omitted.

Table 2. Selected Bond Lengths (Å), Angles (deg), and Torsions for **2**, **4**, and **5**

	2	**4**	**5**
$Rh-N_{axial}$	2.030(9), 2.089(9)	2.113(5)	2.195(7), 2.199(7)
$Rh-I_{axial}$	2.622(1), 2.620(1)	2.6447(6)	2.6261(8), 2.6261(9)
$I_{axial}-Rh-N_{axial}$	177.7(3), 179.5(3)	178.0(1)	176.4(2), 175.9(2)
$N_{axial}-N_{axial}$	1.47(1)		1.479(9)
$Rh-N_{axial}-N_{axial}$	120.1(6), 115.8(6)		118.2(5), 117.3(5)
$Rh-N_{axial}-N_{axial}-Rh$	178.5(5)		151.4(3)
$C-N_{axial}-N_{axial}-C$			58.2(9)
$Rh-N_{axial}-C$			114.5(5), 114.6(5)

ammonia vapor. The ^{1}H NMR spectrum of **4** displays a singlet at −5.77 ppm, arising from the ammonia ligand. We have been unable to observe any coupling between the NH_3 protons and ^{103}Rh. The X-ray structure of **4** revealed a $Rh-N_{axial}$ bond length of 2.113(5) Å, comparable with the corresponding bond lengths of **2** (see Table 2).

Treatment of **1** in dichloromethane with an aqueous solution of *N*,*N*′-dimethylhydrazine dihydrochloride basified by addition of NaOH afforded the 1:1 complex **6**. Both the ^{13}C and ^{1}H NMR spectra of this compound are complicated by the formation of a chiral center at the bound nitrogen atom of the dimethylhydrazine. This removes mirror symmetry from the porphyrin, leaving only average C_2 symmetry, assuming free rotation about the $Rh-N_{axial}$ bond. Splittings are observed in the hexyl and β-methyl resonances but not the meso and aryl resonances. Coupling is observed between the proton of the coordinated nitrogen atom at −4.90 ppm and its methyl group at −3.27 ppm with $J = 6$ Hz. The value of $^3J_{HNCH}$ in *N*,*N*′-dimethylhydrazine has been reported as 6.1 Hz.[24] The other methyl group of the ligand appears as a singlet at −0.66 ppm while the NH resonance at −4.09 ppm is broad, presumably because of proton exchange. Passage of this sample through silica gel and recrystallization from a chloroform/methanol mixture afforded the 2:1 complex **5**. Although this could exist as a mixture of diastereomers, ^{1}H NMR spectroscopy suggested that only one was present or that interconversion was rapid on the NMR time scale. A single meso resonance and doubled hexyl and β-methyl resonances were observed, consistent with the presence of a chiral center at the nitrogen atom of the bound ligand but with rapid rotation about the $Rh-N_{axial}$ bond. The methyl groups of the ligand at −7.32 ppm are split into a doublet with $^3J_{HNCH} = 6$ Hz, and a corresponding splitting is observed in the NH resonance at −9.40 ppm. In the solid-state structure (Figure 2), the ligand is ordered, and the chirality of each of the nitrogen atoms in a molecule is the same, but overall, the crystal is centrosymmetric with a molecule of each enantiomer in the unit cell. The porphyrin planes are not parallel but are tilted by 28.31(5)° to accommodate the methyl groups of the ligand. The axes joining the opposite substituted meso positions of each porphyrin are rotated by approximately 90° with respect to each other to avoid steric clash. The $Rh-N_{axial}$ bond lengths of 2.195(7) and 2.199(7) Å are comparable to the value of 2.216(8) Å reported for the Rh−N distance of the $[RhCl_4(PPh_3)(NHMeNHMe)]^-$ anion.[25]

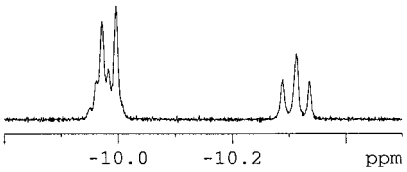


Figure 3. Upfield region of the 500 MHz ^{1}H NMR spectrum of **9** showing the NH resonances.

Titrations of **1**·MeOH in $CDCl_3$ with methylhydrazine and *N*,*N*-dimethylhydrazine were carried out. On addition of <0.5 equiv of these substituted hydrazines, the expected bridging complexes **7** and **9** were observed, as evidenced by highly shielded NH and methyl resonances. The resonances of methylhydrazine in **9** all appear as multiplets (Figure 3). The methyl resonance is assigned to a doublet at −7.79 ppm with $^3J_{HNCH} = 6$ Hz. $^3J_{HNCH}$ for free methylhydrazine has been reported as 6.25 Hz.[26] A COSY spectrum revealed a cross-peak between this resonance and a multiplet at −10.00 ppm that integrated to two protons. This peak is assigned to the overlapping resonances of the N*H*CH_3 proton and a single proton of the diastereotopic NH_2 group. The resonance of the other proton of this group resembles a triplet at −10.34 ppm. In contrast to **9**, the ^{1}H NMR spectrum of **7** is simple with singlets at −7.83 and −10.24 ppm assigned to the $N(CH_3)_2$ and NH_2 resonances, respectively. Addition of >0.5 equiv of the hydrazines dissociated the dimers to afford the 1:1 complexes **8** and **10**. Here, the situation is complicated by the possibility of isomeric forms in which the hydrazine coordinates through different nitrogen atoms. Although theoretical and NMR studies[27] have supported the belief that the substituted nitrogen of alkyl hydrazines is the more basic, in reported crystal structures of methylhydrazine and *N*,*N*-dimethylhydrazine, these ligands bound through the unsubstituted and less sterically hindered nitrogen atom.[28−33] The ability of the Rh(III) porphyrin to act as a shift reagent for bound ligands has now permitted the elucidation of the binding mode of these substituted hydrazines. We propose that the *N*,*N*-dimethylhydrazine ligand of **8** is bound through the substituted nitrogen atom on the basis of the chemical shifts of the methyl groups (−3.31 ppm) and by comparison with the spectrum of

(24) Yunda, N. G.; Lagodzinskaya, G. V.; Fel'dman, E. B.; Manelis, G. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1977**, *26*, 1181.

(25) Hursthouse, M. B.; Newton, J.; Page, R. P.; Villax, I. *Polyhedron* **1988**, *7*, 2087.

(26) Yunda, N. G.; Lagodzinskaya, G. V.; Manelis, G. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1975**, *24*, 2330.

(27) Bagno, A.; Menna, E.; Mezzina, E.; Scorrano, G.; Spinelli, D. *J. Phys. Chem. A* **1998**, *102*, 2888.

(28) Le Floc'h, C.; Henderson, R. A.; Hitchcock, P. B.; Hughes, D. L.; Janas, Z.; Richards, R. L.; Sobota, P.; Szafert, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2755.

(29) Ashworth, T. V.; Nolte, M. J.; Singleton, E. *J. Organomet. Chem.* **1977**, *139*, C73.

(30) Goedkin, V. L.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1975**, 258.

(31) Ashworth, T. V.; Nolte, M. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1040.

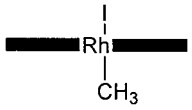
(32) Davies, C. J.; Dodd, I. M.; Harding, M. M.; Heaton, B. T.; Jacob, C.; Ratnam, J. *J. Chem. Soc., Dalton Trans.* **1994**, 787.

(33) Sellman, D.; Waeber, M. *Z. Naturforsch., B*: *Chem. Sci.* **1986**, *41*, 877.

6. The situation for **10** is not so clear-cut, although the observation of a doublet at −3.24 ppm with $J = 6$ Hz, assigned to the hydrazine methyl group, suggests that the hydrazine is bound through the substituted nitrogen atom in the major species in solution. However, a minor singlet at −0.79 ppm can be tentatively assigned to the methyl group of the isomeric complex in which the unsubstituted nitrogen is bound to the rhodium center. In support of this assignment was the observation of a cross-peak in the NOESY spectrum, acquired at 40 °C, between the peaks at −0.79 and −3.24 ppm. At room temperature, this cross-peak was extremely weak, consistent with an increasing rate of exchange of the methylhydrazine between the two binding modes as the temperature was increased. The NH protons of the minor species cannot be located with confidence, although the peak at −3.91 ppm assigned to the N*H*CH_3 resonance of the major isomer appears to be overlapping with another minor resonance.

Passage of samples of **8** and **10** through silica gel, eluted with dichloromethane/hexane (1:1), converted them into **7** and **9,** respectively. The solid-state structures of **7** and **9** were found to resemble that of **5**, except the ligands were disordered. As in **5**, the porphyrins are canted to accommodate the methyl groups. The angles between the best fit planes of **7** and **9** are 25.49(9) and 25.94(3)°, respectively.

Initial attempts to obtain crystals of **7** by diffusion of methanol into a solution of **8** and excess *N*,*N*-dimethylhydrazine afforded a mixture of crystals from which could be identified the organometallic derivative **11** by X-ray diffraction and ^{1}H NMR, in comparison with an authentic sample.[10] By integration of the



11

meso resonances in the ^{1}H NMR spectrum, **11** was estimated to comprise 6% of the porphyrinic material in this sample, with the remainder largely attributed to **7**. Further experiments, in which samples of **8** and excess *N*,*N*-dimethylhydrazine in $CDCl_3$ were exposed to combinations of air and light, revealed that a combination of both accelerates the formation of **11** and other unidentified products. Similarly, others have reported the formation of metal alkyls from decomposition of alkyl hydrazine complexes.[34−38] The IR spectrum of **7** showed a sharp but weak peak at 3216 cm^{-1}, whereas **9** gave a group of peaks at 3224 cm^{-1}, which are attributed to NH stretches by analogy with **2**.

As Me_2S_2 and Me_2Se_2 are also known to act as bridging ligands,[39−43] we predicted that they would form complexes with **1** analogous to **5**. An ^{1}H NMR titration of **1** in $CDCl_3$ with Me_2S_2 led to broadening of the porphyrin resonances and an upfield shift of the meso resonance to 9.8 ppm. Evidence for a bridged dimer was the observation of a broad peak at −5.6 ppm assigned to the methyl groups of the bridging ligand. On addition of >0.5 equiv of Me_2S_2, this peak progressively disappeared, to be replaced by peaks at 0.1 and −2.7 ppm assigned to the inequivalent methyl groups of a 1:1 complex in which a single sulfur atom binds to the rhodium center. This was accompanied by a sharpening and downfield shift of the meso resonance to 10.22 ppm. Likewise, a titration of **1** in $CDCl_3$ with Me_2Se_2 afforded a bridged dimer with a meso resonance at 9.62 ppm and ligand−methyl resonance at −5.21 ppm. The 1:1 complex displayed a meso resonance at 10.21 ppm and methyl groups at 0.58 and −2.30 ppm. In this case, peaks were sharper, and the meso resonances were in slow exchange on the 400 MHz ^{1}H NMR chemical shift time scale, indicating that the diselenide ligand has a lower exchange rate than the disulfide ligand. Additional support for these complexes was obtained from UV−visible titrations of **1** with Me_2S_2 and Me_2Se_2 in dichloromethane with methanol added as a competitive ligand. On addition of the chalcogenide, the Soret band of **1** at 412 nm was replaced by a red-shifted Soret band, observed at 422 nm in the case of Me_2S_2 and 428 nm for Me_2Se_2. In the former instance, we have been able to account for the observed spectral changes during the course of the titration using a model consisting solely of **1**, Me_2S_2, and **1**·Me_2S_2 with a binding constant of $\log(K) = 5.7$. The concentration of 2:1 complex is likely to be negligible at the porphyrin concentration employed for the titration experiment. However, the data for Me_2Se_2 cannot be satisfactorily modeled without inclusion of the species $\mathbf{1}_2$·Me_2Se_2 with a broad Soret band centered at 426 nm. In this case, we calculate $\log(K) = 6.6$ for the binding of a single porphyrin to Me_2Se_2, and $\log(K) = 5.4$ for the binding of a second porphyrin unit, implying weakly anticooperative behavior.

In summary, we have prepared complexes of Rh(III) porphyrins with bridging hydrazine and substituted hydrazine ligands and characterized these in solution by ^{1}H NMR spectroscopy and in the solid state by X-ray diffraction. Addition of further hydrazine to these species afforded 1:1 complexes. On the basis of ^{1}H NMR chemical shift evidence, we propose that methylhydrazine and *N*,*N*-dimethylhydrazine preferentially bind to the Rh center through the substituted nitrogen atom. A methylated Rh(III) porphyrin was obtained as a decomposition product of the reaction of *N*,*N*-dimethylhydrazine with Rh(III) porphyrin in a process accelerated by oxygen and light. Me_2Se_2 and Me_2S_2 behaved analogously to *N*,*N*′-dimethylhydrazine and formed bridging and nonbridging complexes with Rh(III) porphyrin.

Acknowledgment. We thank EPSRC and Avecia for financial support and Dr. N. Bampos for helpful discussions.

Supporting Information Available: ^{1}H NMR spectra of **1**−**10** and titrations of **1** with Me_2S_2 and Me_2Se_2. Crystallographic data of **2**, **4**, **5**, **7**, and **9** in CIF format. Equations of least-squares planes and deviations from them. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0011314

(34) Samsel, E. G.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2450.
(35) Goedken, V. L.; Peng, S.-M.; Park, Y. *J. Am. Chem. Soc.* **1974**, *96*, 284.
(36) Dey, K.; De, R. L. *J. Inorg. Nucl. Chem.* **1977**, *39*, 153.
(37) Kunze, K. L.; Ortiz de Montellano, P. R. *J. Am. Chem. Soc.* **1983**, *105*, 1380.
(38) Braunstein, P. *J. Chem. Soc., Chem. Commun.* **1973**, 851.
(39) Boorman, P. M.; Merrit, C. L.; Nandana, W. A. S.; Richardson, J. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1251.
(40) Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *Isr. J. Chem.* **1977**, *15*, 153.
(41) Lewkebandara, T. S.; McKarns, P. J.; Haggerty, B. S.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Polyhedron* **1998**, *17*, 1.
(42) Abel, E. W.; Khan, A. R.; Kite, K.; Hursthouse, M. B.; Malik, K. M. A.; Mazid, M. A. *J. Organomet. Chem.* **1982**, *235*, 121.
(43) Abel, E. W.; Khan, A. R.; Kite, K.; Orrell, K. G.; Sik, V.; Cameron, T. S.; Cordes, R. *J. Chem. Soc., Chem. Commun.* **1979**, 713.